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#### Cover

The picture shows the high-resolution structure image of zirconia (ZrO2) projected along the a-axis of a cubic lattice (a=5.1Å). As indicated by arrowheads in the micrograph, both zirconium (Zr) and oxygen (O) atom positions are imaged as strong and weak dark dots, respectively. This is the first electron microscope data in which individual oxygen positions in inorganic compounds are directly observed as weak dark dots. The microgram was obtained by the ultra-high-resolution, high-voltage electron microscope (Model: H-1500) has been developed in 1990 as NIRIM's second high-voltage electron microscope. It achieved a resolution of 1.0Å, which is the world's best at present. In order to obtain such high resolution, maximum operating voltage of 1300kV and also maximum applicable one of 1500kV are employed. Very low spherical aberration coefficient of an objective lens (Cs = 1.85mm at 1300kV) was achieved by computeraided designing of electron-magnetic lens systems. Owing to the success of the new machine, it has now become possible to image not only metal atoms but also light atoms such as oxygen in many inorganic materials, by means of high-resolution electron microscopy.

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# Papers, Letters and Notes



High resolution electron microscope photograph of the modulation doped structure of Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>y</sub> ( $T_c$ =80K) in the [100] direction. Figures at right side indicate number of copper layers, symbol B indicates bismuth rich region.

# Compositional Dependence of Bioactivity of Glasses in the System CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>: Its *in Vitro* Evaluation

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The essential condition for glasses and glass-ceramics to bond to living bone is the formation of an apatite laver on their surfaces in the body. The apatite layer can be reproduced on their surfaces even in an acellular simulated body fluid which has ion concentrations almost equal to those of the human blood plasma. In the present study, in order to investigate the compositional dependence of bioactivity of glasses fundamentally, the apatite formation on the surfaces of glasses in the system CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> was examined in the simulated body fluid. Thin-film X-ray diffraction, Fourier transform infrared reflection spectroscopy and scanning electron microscopic observation were used for detecting the apatite formation. It was found that CaO-SiO2 glasses free from  $P_2O_5$  as well as those containing small amounts of  $P_2O_5$ form the apatite layer on their surfaces, whereas CaO- $P_2O_5$  glasses free from SiO<sub>2</sub> as well as those containing SiO<sub>2</sub> do not form it. This indicates that bioactive glasses and glass-ceramics are obtained in compositions based on CaO-SiO<sub>2</sub> rather than CaO-P<sub>2</sub>O<sub>5</sub>, contrary to the general view. These results were interpreted in terms of ions dissolved from glasses.

[Accepted July 12, 1990; Received September 26, 1990]

**Key-words:** CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> glass, bioactivity, apatite, simulated body fluid, surface structure

# 1. Introduction

Since the discovery of Bioglass by Hench et al. in 1970,<sup>1)</sup> various kinds of glasses and glass-ceramics have been found to bond to living bone.<sup>24)</sup> Among such bioactive glasses and glass-ceramics, Bioglass in the system Na<sub>2</sub>O-CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>,<sup>5)</sup> Ceravital glass-ceramic containing apatite,<sup>6)</sup> A-W glass-ceramic containing apatite and wollastonite,<sup>7)</sup> Bioverit glass-ceramic containing apatite and phlogopite<sup>8)</sup> etc. are already clinically used as bone substitutes for artificial middle ear bones, alveolar ridge reconstruction implants, artificial vertebrae, intervertebral spacers, iliac bone spacers, tooth roots etc.

It has been revealed as to the bone-bonding mechanism of these bioactive glasses and glass-ceramics by Hench et al.,<sup>9,10)</sup> Gross et al., <sup>11,12)</sup> the present authors<sup>13,14)</sup> and Karlsson et al.<sup>15,16)</sup> that they bond to living bone through an apatite layer which is formed on their surfaces in the body, and that the formation of the surface apatite layer is the prerequisite for glasses and glass-ceramics to bond to living bone. It has not been revealed, however, what kind of glasses or glassceramics form the surface apatite layer in the body.

Hench et al. showed that apatite formation on the surface

of glasses in the system Na<sub>2</sub>O-CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> is restricted to a certain compositional region.<sup>17,18</sup> The present authors later showed that Na<sub>2</sub>O-free MgO-CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> glasses<sup>19,20</sup> and glass-ceramics<sup>21,22</sup> also form the surface apatite layer, and furthermore suggested on the basis of mechanism of apatite formations on their surfaces that P<sub>2</sub>O<sub>5</sub>-free CaO-SiO<sub>2</sub> glasses will also form the surface apatite layer. On the other hand, some workers still believe that glasses and glassceramics must contain both the CaO and P<sub>2</sub>O<sub>5</sub>, which constitute the apatite, for showing the bioactivity.<sup>23,24</sup>

In the present study, in order to investigate compositional dependence of bioactivity of glasses fundamentally, apatite formation on the surfaces of glasses in the simple ternary system CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> was examined in an acellular simulated body fluid which has almost equal ion concentrations to those of the human blood plasma.<sup>25)</sup> This fluid had been previously confirmed to be able to reproduce the apatite formation on the surfaces of bioactive glasses and glass-ceramics.<sup>26)</sup> All the bioactive glasses and glass-ceramics hind of fundamental study might be essential for developing new kinds of bioactive glasses and glass-ceramics.

# 2. Experiment

#### 2.1. Preparation of Glass

The compositional region for glass formation in the system CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> has not yet been reported. Powder mixtures (about 20g) of various compositions in this system were prepared using reagent grade chemicals of CaCO<sub>3</sub>, SiO<sub>2</sub>, CaHPO<sub>4</sub>·2H<sub>2</sub>O and H<sub>3</sub>PO<sub>4</sub>. They were put into a 50ml platinum crucible, and melted at 1600°C for 1 hour in a MoSi<sub>2</sub> furnace. The melts were poured onto a stainless steel plate to be formed into a plate about 1mm thick, and allowed to cool in a SiC furnace from an appropriate temperature. The cooled substances were examined by visual observation and X-ray diffraction to determine whether they contained crystalline phase or not.

### 2.2. Soaking in Simulated Body Fluid

The obtained glasses by the method described above were cut into rectangular specimens  $15\times10\times1mm$ , polished with 3-4µm diamond paste, and washed with pure acetone and an ion-exchanged water in an ultrasonic cleaner. They were immersed in 35ml of an acellular simulated body fluid, which had almost equal ion concentrations to those of the human blood plasma as shown in **Table 1**.<sup>25)</sup> The fluid was prepared by dissolving reagent grade chemicals of NaCl, NaHCO<sub>3</sub>, KCl, K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O, MgCl<sub>2</sub>·6H<sub>2</sub>O, CaCl<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub> into an ion-exchanged water. It was buffered at pH 7.25 with 50mM trishydroxymethyl-aminomethane

Table 1. Ion concentrations of simulated body fluid and human blood plasma.

	Ion concentration (mM)								
	Simulated fluid	Blood plasma							
Na <sup>+</sup>	142.0	142.0							
κ <sup>+</sup>	5.0	5.0							
Mg <sup>2+</sup>	1.5	1.5							
Ca <sup>2+</sup>	2.5	2.5							
CI <sup>-</sup>	147.8	103.0							
HCO3	4.2	27.0							
HPO42-	1.0	1.0							
50.2-	0.5	0.5							



Fig. 1. Glass-forming tendency of CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> melts. O: formed into clear glass, ●: formed into immiscrible opaque glass, ∆: partially devitrified, \*: incompletely melted.

((CH<sub>2</sub>OH)<sub>3</sub>CNH<sub>2</sub>) and 45mM hydrochloric acid (HCl), and its temperature was kept at 36.5°C.

#### 2.3. Analysis of Surface Structure

After the specimens were soaked in the simulated body fluid for 7, 20 and 30 days, they were taken out from the fluid, and gently washed with the acetone. Their surfaces were subjected to thin-film X-ray diffraction, Fourier transform infrared reflection spectroscopy and scanning electron microscopic observation. In the X-ray diffraction experiment, a Rigaku 2651Al thin-film attachment was used and the surface of the specimen was fixed at 1° against the incident beam. In the infrared spectroscopy, a Japan Spectroscopic FT-IR5M spectrometer was used and reflection angle was 75.° These two techniques allowed detection of a layer about 1µm thick at the surface. In the scanning electron microscopic observation, platinum film was coated on the surface of the specimen and a Hitachi-S450 electron microscope was used.

# 3. Results

Figure 1 shows glass-forming tendency of melts of various compositions in the system CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> under the melting and cooling conditions described in section 2.1. It can be seen from Fig.1 that glass can be obtained in two compositional regions, i.e. one is the region near CaO  $\cdot$  SiO<sub>2</sub> composition and another is that containing P<sub>2</sub>O<sub>5</sub> more than 40mol%. Some glasses in the region near the CaO  $\cdot$  SiO<sub>2</sub> showed glassy two-phase separation.

Thin-film X-ray diffraction patterns and Fourier transform infrared reflection spectra of the surfaces of some of the obtained glasses are shown in Figure 2 for reference. Their compositions are given in Table 2.

Figures 3 and 4 show thin-film X-ray diffraction patterns and infrared reflection spectra, respectively, of the surfaces of the same glasses after soaked in the simulated body fluid for 7 days. Assignment of main peaks based on previously published data<sup>22)</sup> is also given in Figs.3 and 4. It can be seen from Figs.3 and 4 that Ca50Si50, Ca50Si45P5 and Ca60Si30P10 glasses form an apatite phase on their surfaces in the simulated body fluid in 7 days, whereas Ca35Si65, Ca50Si5P45 and Ca50P50 glasses do not form it. The apatite phase is characterized with broad X-ray diffraction peaks and a infrared reflection peak at 1400cm.<sup>-1</sup> This indicates that the apatite phase is a carbonate-containing hydroxyapatite of small crystallites and/or defective structure, similar to the apatite in the natural bone. Intensity of both the X-ray diffraction and the infrared reflection peaks which are ascribed to the apatite are larger for Ca50Si45P5 and Ca60Si30P10 glasses than for Ca50Si50 glass. This indicates that the rate of apatite formation is higher for the



Fig. 2. Thin-film X-ray diffraction patterns and Fourier transform infrared reflection spectra of the surfaces of some of CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> glasses before soaking in the simulated body fluid.

Table 2. Composition of some examined glasses.

	Compo	(mol%				
Name	CaO	CaO SiO <sub>2</sub>				
Ca50P50	50	0	50			
Ca50Si5P45	50	5	45			
Ca60Si30P10	60	30	10			
Ca50Si45P5	50	45	5			
Ca50Si50	50	50	0			
Ca35Si65	35	65	0			

formers than the latter.

**Figures 5** and **6** show thin-film X-ray diffraction patterns and infrared reflection spectra, respectively, of the same glasses after soaked for 20 days. These patterns and spectra are essentially same as those in Figs.3 and 4.

Figures 7 and 8 show thin-film X-ray diffraction patterns and infrared reflection spectra, respectively, of the same



Fig. 3. Thin-film X-ray diffraction patterns of the surfaces of some of CaO-Si<sub>2</sub>- $P_2O_5$  glasses soaked in the simulated body fluid for 7 days.



Fig. 4. Fourier transform infrared reflection spectra of the surfaces of some of CaO-SiO<sub>2</sub>- $P_2O_5$  glasses soaked in the simulated body fluid for 7 days.

surfaces of the glasses after soaked for 30 days. It can be seen from Figs.7 and 8 that Ca35Si65 glass also forms the apatite phase on its surface after soaking for 30 days, whereas Ca50Si5P45 and Ca50P50 glasses do not form the apatite even after soaking for 30 days.

Figure 9 shows scanning electron micrographs of the surfaces of the same glasses soaked for 30 days. It can be



Fig. 5. Thin-film X-ray diffraction patterns of the surfaces of some of CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> glasses soaked in the simulated body fluid for 20 days.



Fig. 6. Fourier transform infrared reflection spectra of the surfaces of CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> glasses soaked in the simulated body fluid for 20 days.

seen from Fig.9 that leaf-like particles are deposited on the surfaces of Ca35Si65, Ca50Si50, Ca50Si45P5 and Ca60Si30P10 glasses, but not on the surfaces of Ca50Si5P45 and Ca50P50 glasses. The morphology of the leaf-like particles is very similar to that of the apatite formed on the surface of glass-ceramic A-W<sup>22)</sup> and Ceravital-type glass-ceramic.<sup>27)</sup>



Fig. 7. Thin-film X-ray diffraction patterns of the surfaces of some of CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> glasses soaked in the simulated body fluid for  $_{3O}$  days



Fig. 8. Fourier transform infrared reflection spectra of the surfaces of some of CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> glasses soaked in the simulated body fluid for 30 days.

The results described above as well as those for glasses of other compositions are summarized in **Fig.10**. It can be seen from Fig.10 that CaO-SiO<sub>2</sub> glasses free from  $P_2O_5$  as well as those containing small amounts of  $P_2O_5$  form the apatite layer on their surfaces in the simulated body fluid, whereas CaO-P<sub>2</sub>O<sub>5</sub> glasses free from SiO<sub>2</sub> as well as those containing SiO<sub>2</sub> do not form it. CaO-P<sub>2</sub>O<sub>5</sub> glasses containing fairly large amounts of SiO<sub>2</sub> were severely dissolved into the simulated body fluid.

# 4. Discussion

According to the previous investigations by Hench et al.<sup>9,10)</sup> and the present authors, <sup>13,14,22,27)</sup> the essential condition for glasses and glass-ceramics to bond to living bone is formation of the apatite layer on their surfaces in the body. This apatite layer can be reproduced on their surfaces in the simulated body fluid given in Table 1.<sup>26)</sup> In view of these findings, it can be concluded from the results given in Fig.10 that bioactive glasses and glass-ceramics are obtained in compositions based on CaO-SiO<sub>2</sub> rather than CaO-P<sub>2</sub>O<sub>5</sub>. This is in contrast with the conventional view that glasses and glass-ceramics must contain both the CaO and P<sub>2</sub>O<sub>5</sub>, which constitute the apatite, for showing bioactivity.

These results might be interpreted as follows. According



Fig. 9. SEM photographs of the surfaces of some of CaO-SiO<sub>2</sub>- $P_2O_5$  glasses soaked in the simulated body fluid for 30 days.



Fig. 10. Compositional dependence of apatite formation on the surface of CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> glasses as a function of soaking period in the simulated body fluid.

◊: apatite formation, ♦: no apatite formation, ★: severe dissolution.

to the previous investigation by the present authors, 13,14) glass-ceramic A-W forms an apatite layer on its surface by a chemical reaction of Ca(II) and Si(IV) ions dissolved from the wollastonite and glassy matrix of the glass-ceramic with P(V) ion present in the surrounding body fluid. In this reaction, Ca(II) ion increases the degree of supersaturation of the surrounding body fluid with respect to the apatite, which is already supersaturated even in the normal condition, and Si(IV) ion provides favorable sites for nucleation of the apatite on the surface of the glass-ceramic. Apatite formation on the surfaces of P2O5-free CaO-SiO2 glasses in the body environment might be similarly interpreted. Phosphate ion required for formation of the apatite is supplied only from the fluid. Higher rate of apatite formation for Ca50Si50 glass than Ca35Si65 glass might be attributed to higher rate of dissolution of Ca(II) and Si(V) ions for the former. In the case of CaO-SiO<sub>2</sub> glasses containing small amounts of P2O5, phosphate ion might be also dissolved to increase the degree of the supersaturation of the surrounding fluid with respect to the apatite, and hence increase the rate of apatite formation. Higher rate of apatite formation for Ca50Si45P5 and Ca60Si30P10 glasses than Ca50Si50 glass might be thus interpreted. In the case of CaO-P2O5 glasses containing a certain amount or no SiO<sub>2</sub>, a large amount of phosphate ions might be dissolved to decrease pH of the surrounding fluid, thereby suppressing the apatite formation. The relation between the surface apatite formation and the

dissolved ions might be discussed in more details elsewhere.

It has already been confirmed by *in vivo* experiments that  $P_2O_5$ -free Ca50Si50 glass bonds to living bone, forming a Ca, P-rich layer on its surface,<sup>28)</sup> whereas SiO<sub>2</sub>-free Ca50P50 glass does not.<sup>29)</sup> This is consistent with the present results.

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# Crystallization of (FeO, Fe<sub>2</sub>O<sub>3</sub>)-CaO-SiO<sub>2</sub> Glasses and Magnetic Properties of their Crystallized Products

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The crystallization process of an Fe<sub>2</sub>O<sub>3</sub> 40, CaO · SiO<sub>2</sub> 60wt% glass was investigated as well as magnetic properties of the crystallized products, in order to reveal principles for obtaining ferrimagnetic and bioactive glass-ceramics useful as thermoseeds for hyperthermia of cancer. When the glass was heat-treated up to temperatures of 700 to 950°C, magnetite particles were homogeneously precipitated in a CaO · SiO<sub>2</sub>-based glassy and/or crystalline matrix. The diameter and content of the magnetite increased from 6 to 30 nm and 10 to 36wt%, respectively, with increasing temperature of the heat treatment from 700 to 950°C. Above 1000°C, a part of the magnetite was converted into hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>). The glass showed maxima in saturation magnetization and coercive force, 32 emu/g and 500 Oe, respectively, when heat-treated up to 950°C. The variation of the magnetization with heat treatment temperature could be well quantitatively interpreted in terms of the content of the magnetite, whereas that of the coercive forces could be explained only qualitatively in terms of the particle size of the magnetite. The coercive forces of the magnetite-containing glass-ceramics were much higher than those of the magnetite powders of the corresponding particle sizes which were prepared from aqueous solutions. [Received July 16, 1990; Accepted September 26, 1990]

**Key-words:** Crystallization, Fe<sub>2</sub>O<sub>3</sub>-CaO-SiO<sub>2</sub> glass, Ferrimagnetic glass-ceramics, Magnetite, Hyperthermia.

# 1. Introduction

It was previously shown by the present authors on the basis of investigations of bone-bonding mechanism of high strength bioactive glass-ceramic A-W<sup>1,2)</sup> that  $P_2O_5$ -free CaO-SiO<sub>2</sub> glasses also bond to living bone forming an apatite layer on their surfaces in body environment<sup>3,4)</sup>. It can be expected from these findings that bioactive and ferrimagnetic glass-ceramics precipitating magnetite (Fe<sub>3</sub>O<sub>4</sub>) in CaO-SiO<sub>2</sub> glassy matrices are obtained by crystallization of CaO-SiO<sub>2</sub> glasses containing appreciable amounts of Fe<sup>2+</sup> and Fe3+ ions. Such glass-ceramics can be expected to be useful as thermoseeds for hyperthermia of cancers, especially such as bone tumor, since this type of glass-ceramic will bond to living bone as well as with each other <sup>5)</sup> to be fixed, when implanted around bone tumor in granular forms, and then the tumor will be locally heated up to temperatures above 43°C useful for cancer treatment by magnetic hysteresis loss, when placed under an alternating magnetic field. In the present study, in order to reveal principles for obtaining such bioactive and ferrimagnetic glass-ceramics, crystallization processes of (FeO, Fe<sub>2</sub>O<sub>3</sub>)-CaO  $\cdot$  SiO<sub>2</sub> glasses were investigated as well as magnetic properties of their crystallized products.

Generally, tumor is more easily heated than the surrounding normal tissues, since blood vessels and nervous systems are poorly developed in the tumor, and cancer cells are easily killed by heat treatment, since oxygen supply by the blood vessel is not sufficient in the tumor. Hence, hyperthermia is expected to be a most useful treatment of cancer which has no side effect.<sup>6)</sup> Effective technique for local heating of cancer, however, has not been developed, especially for cancers, such as bone tumor, located at deep parts of body. Luderer et al. previously showed by animal experiments using glass-ceramic containing lithium ferrite (LiFe<sub>5</sub>O<sub>8</sub>) and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) in an Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> glassy matrix that a ferrimagnetic glass-ceramic can be useful as a thermoseed for hyperthermia of cancer.<sup>7)</sup> Their glass-ceramic was, however, not bioactive. Precipitation of magnetite from glasses had been studied by several workers.<sup>8-10)</sup> Crystallization of (FeO, Fe<sub>2</sub>O<sub>3</sub>)-CaO-SiO<sub>2</sub> glasses, however, has not been investigated.

# 2. Experiment

#### 2.1. Preparation of Glass

Powder mixtures about 30g in amount of various compositions in the system  $Fe_2O_3$ - $CaO \cdot SiO_2$  were prepared by reagent grade chemicals of  $Fe_2O_3$ ,  $CaCO_3$  and  $SiO_2$ . They were put into a platinum crucible and melted at 1550°C for 1h in a MoSi<sub>2</sub> electric furnace. The melts were poured onto a stainless steel plate at room temperature and pressed into a plate 1 to 2 mm thick. The cooled substances were examined by powder X-ray diffraction to determine whether they contained crystalline phase or not.

#### 2.2. Crystallization of Glass

The glass plates obtained by the method described above were placed on a platinum sheet and heated at a rate of 5°C/min in a SiC electric furnace for crystallization. They were taken out from the furnace at various temperatures below 1100°C and allowed to cool in a laboratory atmosphere. The specimens heated up to temperatures above 850°C showed a change in color from black to red only at the surface. These specimens were used in the following experiments after their surface layers (about 50µm thick) were removed.

#### 2.3. Powder X-ray Diffraction

The heat-treated specimens were subjected to powder

X-ray diffraction using Ni-filtered CuK $\alpha$  rays. The kinds of the crystalline phases precipitated in the specimens were determined by referring to Data of Joint Committee on Powder Diffraction Standards.

The magnetite contents precipitated in the specimens were determined from the ratio of the intensity of 311 reflection of the magnetite to that of 111 reflection of calcium fluoride (CaF2), which was added as the internal standard by 1g to 5g of the specimen. For the specimens precipitating both the magnetite and the hematite, the intensity of 311 reflection of the magnetite was obtained by subtracting the intensity of 110 reflection of the hematite from the intensity of the reflection at the corresponding diffraction angle, since both the reflections overlapped. In this calculation, the intensity of 110 reflection of the hematite was assumed to be half that of 104 reflection.<sup>11)</sup> The calibration curve for determination of the magnetite content was made using standard powder mixtures of the parent glass and the magnetite prepared by aqueous chemical reaction. The calcium fluoride was also added to the standard mixtures in a weight ratio of 1:5. The area of the observed reflection peak was taken as the intensity of the reflection.

The contents of the  $\beta$ -wollastonite (CaO · SiO<sub>2</sub>) and the hematite precipitated in the specimens were only relatively determined from the ratios of the intensities of 400 reflection of the wollastonite and 104 reflection of the hematite, respectively, to 111 reflection of the calcium fluoride.

The lattice constant, *a*, of the cubic magnetite precipitated in the specimen was obtained by plotting values calculated from interplanar spacing *d* values for 111, 311, 400, 422, 511, 440, 533 and 731 reflection against  $\cos^2\theta$  and extrapolating linearly to  $\cos^2 I=0$ .

Crystallite size and strain of the magnetite precipitated in the specimens were determined from broadening of reflection peaks of the magnetite using the following equation.<sup>12</sup>

$$(B^2 - b^2)\cos^2\theta = 4\epsilon^2\sin^2\theta + 0.81 \lambda^2/t^2 \dots (1)$$

where B, b,  $\theta$ ,  $\lambda$  and t are the measured full width at half maximum intensity, the width due to the instrument, the strain, the wave length of X-ray and the crystallite size, respectively.

#### 2.4. Mössbauer Spectroscopy

The heat-treated specimens as well as the parent glass were subjected to Mössbauer spectroscopy at 300, 77 and 4.2K, in order to investigate the state of iron ions in them. Cobalt<sup>57</sup> in 10mCi diffused into a copper matrix was used as a radioactive source.<sup>13)</sup> The  $\gamma$  rays were detected in a proportional counter filled with a gas mixture of Kr and CO<sub>2</sub>. The data was accumulated in a 512-channel analyzer operating in the time-sequence-stage mode. The velocity calibration was obtained from the six-line hyperfien spectra of an iron foil.

### 2.5. Transmission Electron Microscopic (TEM) Observation

The heat-treated specimens were crushed and sonically suspended in methanol. A few drops of the suspended solution were placed on an amorphous carbon film held by a copper microgrid mesh, and then observed under a transmission electron microscope (JEOL, JEM-2000FM).

#### 2.6. Measurement of Magnetic Property

Magnetizations (M) of the heat-treated specimens as well as the parent glass were measured as a function of the magnetic field (H) up to 10 kOe at room temperature using a vibrating sample magnetometer (TOEI, VSM-2).

# 3. Results

# **3.1.Glass Formation**

Among the examined melts in the  $Fe_2O_3$ -CaO  $\cdot$  SiO<sub>2</sub> system, only those less than 40wt% in  $Fe_2O_3$  content formed glass containing no crystalline phase under the conditions described in section 2-1. In the following experiments, the glass containing the largest amount of  $Fe_2O_3$ , i.e. of the nominal composition  $Fe_2O_3$  40, CaO  $\cdot$  SiO<sub>2</sub> 60wt%, was used.

#### 3.2. X-ray Diffraction

Powder X-ray diffraction of the heat-treated specimens showed that the glass began to precipitate the magnetite around 600°C and its content increases with increasing temperature reaching 36wt% at 950°C as shown in **Fig.1**. Above 950°C, the magnetite decreased with increasing temperature, while the hematite increased. The  $\beta$ -wollastonite began to precipitate around 700°C and maintained the content at a constant above 800°C.

The lattice constant, *a*, of the magnetite precipitated in the specimens was 8.39 to 8.40 irrespective of the heat treatment temperature, which almost coincided with the lattice constant 8.397 reported for the magnetite having the composition  $Fe_3O_4$ .<sup>14</sup>

The crystallite sizes of the magnetite determined from equation (1) are shown in **Fig.2** as a function of heat-treated temperature. It increased with increasing temperature from about 6 nm at 700°C, through 35 nm at 950°C to 110 nm at 1100°C. The strains (da/a) of the magnetite determined from equation (1) were about  $3 \times 10^{-3}$  irrespective of the heat treatment temperature.



Fig. 1. Contents of crystalline phases as a function of heat treatment temperature.

## 3.3. Mössbauer Spectra

The Mössbauer spectra of the glass as-formed and heattreated up to 700° and 950°C are shown in **Figs.3** to **5**, respectively. Assignment of each peak based on the data reported for iron ion-containing glasses<sup>15</sup> and magnetite<sup>16</sup> is also shown in Figs.3 to 5. Isomer shift, quadruple splitting and hyperfien field of each spectrum are shown in



Fig. 2. Crystallite size of magnetite as a function of heat treatment temperature.



Fig. 4. Mössbauer spectra at 300 and 77K of the glass heat-treated up to 700°C.

Table 1 Mössbauer parameters for the glass as-formed and heattreated up to 700°C, and atomic fraction of  $Fe^{2*}$  and  $Fe^{3*}$  ions in tetrahedral and octahedral sites.

Specimen	Peak	Isomer	Quadrupole	Assignment	Atomic
		Shift	Splitting		fractio
As-formed					
at 300 K	I	0.38	0.83	Fe <sup>3+</sup> oct	0.55
	II	0,34	1.44	Fe <sup>3+</sup> tet	0.34
	III	0.88	2.46	Fe <sup>2+</sup>	0.11
at 77 K	I	0.39	0.85	Fe <sup>3+</sup> oct	0.53
	II	0.35	1.44	Fe <sup>3+</sup> tet	0.31
	III	0.92	2.46	Fe <sup>2+</sup>	0.16
Heat-treated					
up to 700°C					
at 300 K	I	0.37	0,57	Fe <sup>3+</sup> oct	0.54
	II	0.34	1.24	Fe <sup>3+</sup> tet	0.36
	III	0.73	2.58	Fe <sup>2+</sup>	0.10

**Table 1** and **2**, as well as atomic fraction of each iron ion in different sites, which was estimated from intensity of the respective spectrum. It can be seen from Fig.3 that iron ions are present in the form of  $Fe^{2+}$  and  $Fe^{3+}$  in the as formed



Fig. 3. Mössbauer spectra at 300, 77 and 4.2K of the glass asformed.



Fig. 5. Mössbauer spectra at 300 and 77K of the glass heat-treated up to 950°C. M: Magnetite.

Table 2 Mössbauer parameters for the glass heat-treated up to  $950^{\circ}$ C and atomic fraction of Fe<sup>2+</sup> and Fe<sup>3+</sup> ions in different sites.

Temperature	Peak	Isomer Shift (mm/sec)	Hyperfine field (KOe)	Assignment	Atomic fraction
at 300 K	I	-	-	para	0.02
	II	0.72	462	Fe <sup>2+</sup> +Fe <sup>3+</sup> oct(M)	0.52
	III	0.26	487	Fe <sup>3+</sup> tet(M)	0.46
at 77 K	I	1.02	469	Fe <sup>2+</sup> (M)	0.23
	II	0.43	511	Fe <sup>3+</sup> (M)	0.77

(M): Magnetite



Fig. 6. TEM photographs of the glass heat-treated up to 700° and 950°C.

glass, and Fe<sup>3+</sup> ions exist in both the tetrahedral and octahedral sites. The atomic fraction of the Fe<sup>2+</sup>, Fe<sup>3+</sup><sub>tet</sub> and Fe<sup>3+</sup><sub>oct</sub> ions were 0.11-0.16, 0.31-0.34 and 0.53-0.55, respectively. The iron ions showed paramagnetic spectra at 300 and 77K, but weak Zeeman splitting due to magnetic interaction at 4.2K. Those in the specimen heat-treated up to 700°C also showed paramagnetic spectra at 300K but Zeeman splitting at 77K. Most of the iron ions in the specimen heat-treated up to 950°C showed Zeeman splitting characteristics to the magnetite even at 300K. Only 0.02 atomic fraction of iron ions gave the paramagnetic spectra.

#### 3.4. TEM Observation

Transmission electron micrographs of the specimen heattreated up to 700° and 950°C are shown in **Fig.6**. The dark particles on the photographs were identified as the magnetite. Electronlucent matrix was identified as glassy phase and the  $\beta$ -wollastonite for the specimens heat-treated up to 700° and 950°C, respectively. It can be seen from Fig.6 that the magnetite particles take a spherical form and are homogeneously dispersed in the matrices. The particle sizes of the magnetite were about 6 and 35 nm for the specimens heat-treated up to 700° and 950°C, respectively. These values almost coincided with the crystallite sizes obtained from the X-ray diffraction.

#### 3.5. Magnetic Property

A part of magnetization curves under magnetic field up to 10 kOe of the specimens heat-treated up to 700°, 800° and 950°C are shown in **Fig.7**. Saturation magnetization  $M_s$ , that is defined as the magnetization at 10 kOe, and



Fig. 7. A part of M-H curves under magnetic field up to 10 kOe of the glass heat-treated up to 700°, 800° and 950°C.



Fig. 8. Saturation magnetization  $M_s$  and coercive force  $H_c$  of the glass as a function of heat treatment temperature.

coercive force  $H_c$  of the heat-treated specimens are shown in **Fig.8** as a function of heat-treatment temperature. Those for the specimens heat-treated up to temperatures below 800°C were also included in Fig.8, although their magnetizations were not saturated even at 10 kOe. It can be seen in Fig.8 that the magnetization at 10 kOe increases with increasing heat treatment temperature from 2 emu/g at 600°C to 32 emu/g at 950°C, and then decreases. The coercive force increased with increasing heat treatment temperature from 20 Oe at 700°C to 500 Oe at 950°C, and then decreased.

**Figure 9** shows M-H curves measured under magnetic field up to 300 Oe, for the specimens heat-treated up to 700°, 800°, 850° and 950°C. It can be seen from Fig.9 that the magnetic hysteresis loops under 300 Oe are much different from those under 10 kOe.

# 4. Discussion

#### 4.1. Glass Structure

The melt of the nominal composition  $Fe_2O_3$  40,  $CaO \cdot SiO_2$  60wt% quenched on the stainless steel plate was



Fig. 9. M-H curves under magnetic field up to 300 Oe of the glass heat-treated up to 700°, 800°, 850° and 950°C.



Fig. 10. Saturation magnetization M<sub>3</sub> of the crystallized products of the glass as a function of magnetite content .

identified as an amorphous state by the X-ray diffraction. It is, however considered to contain a certain amount of cluster in which magnetic interaction is caused between iron ions, since Mössbauer spectrum at 4K showed Zeeman 'splitting. Coexistence of the Fe<sup>2+</sup> with the Fe<sup>3+</sup> ions in the glass is attributed to the partial reduction of the Fe<sup>3+</sup> ions during the melting procedure at 1550°C.

#### 4.2. Microstructure of Crystallized Product

X-ray diffraction and transmission electron microscopic observation showed that crystallized products of the glass take a structure in which spherical particles of the magnetite are homogeneously dispersed in a glassy matrix or a matrix consisting of glassy phase and  $\beta$ -wollastonite. The composition of the magnetite is speculated to be almost Fe<sub>3</sub>O<sub>4</sub> from the lattice constant determined by X-ray diffraction, but a little rich in Fe<sup>3+</sup> from Mössbauer spectra of the specimen heat-treated up to 950°C (see Table 2). Composition of the  $\beta$ -wollastonite of the matrix might be essentially CaO · SiO<sub>2</sub>, since both the Fe<sup>2+</sup> and Fe<sup>3+</sup> ions hardly enter into the lattice of the wollastonite. The composition of the glassy phase of the matrix is varied with the heat treatment temperature. That of the glassy phase in the specimen heattreated up to 950°C is speculated to be essentially  $CaO \cdot SiO_2$ , since most of iron ions enter into the lattice of the magnetite and only 0.02 atomic fraction are present in paramagnetic state (see Table 2). In this specimen, the magnetite takes 35 nm in size and 36wt% in content.

### 4.3. Magnetic Properties of Crystallized Product

The saturation magnetization of the crystallized products of the glass, which are shown in Fig.8, are plotted against their magnetite content in Fig. 10. It can be seen from **Fig.10** that the saturation magnetization of the crystallized products depends almost linearly on the content of the magnetite. The saturation magnetization of the crystallized products extrapolated to 100wt% of the magnetite is about 90emu/g. This value almost coincides with the magnetization, 92emu/g, reported for the magnetite of the composition Fe<sub>3</sub>O<sub>4</sub>.<sup>17)</sup> This means that the magnetize precipitated in the glass has almost same magnetization as that of the magnetize of the composition Fe<sub>3</sub>O<sub>4</sub> and that the saturation magnetization of the crystallized products is almost determined by the content of the magnetite.

The coercive forces of the crystallized products of the glass are plotted against crystallite size of the magnetite in them in Fig.11. Those reported for magnetite powders prepared from aqueous solutions<sup>18)</sup> are also shown for comparison in Fig.11. It can be seen from Fig.11 that dependence of the coercive force of the crystallized products on the crystallite size of the magnetite is similar to that of the magnetite powders, but that the values of the coercive force of the former are much higher than those of the latter. The dependence of the coercive forces of the crystallized products on the crystallite size might be interpreted in terms of magnetic domain structure, as in the case of the magnetite powders<sup>19)</sup>: i.e. at crystallite sizes smaller than 40 nm, the degree of ordering of the magnetic moment in the individual particles increases with increasing crystallite size, forming a well-ordered single domain at 40 nm, and at those larger than 40 nm, the number of the magnetic domain in the individual particles increases with increasing crystallite size, to decrease the coercive force.

The higher values of the coercive force of the crystallized product than those of the magnetite powders might be attributed to a larger stress applied to the magnetite particles and/or smaller magnetic interaction among the magnetite particles for the former. When the crystallized product was cooled to room temperature, some stress might be applied to the magnetite particles, because of the difference in the thermal expansion coefficient between the magnetite and the



Fig. 11. Coercive force H<sub>c</sub> of the crystallized products as a function of crystallite size of the magnetite, in comparison with those of magnetite powders prepared from aqueous solutions.



Fig. 12. Area of magnetic hysteresis loop under magnetic field up to 10 kOe and 300 Oe, for the glass heat-treated up to various temperatures.

matrix phase. Such internal stress might inhibit rotation of magnetic moment, increasing the coercive force.<sup>20)</sup> In the crystallized products, each magnetite particle is isolated by a non-ferromagnetic matrix, hence the magnetic interaction among the magnetite particles, which decreases the coercive force,<sup>21)</sup> might not be so large as in the magnetite powders. The coercive force, 500 Oe, of the specimen heat-treated up to 950°C, which contains almost single domain particles of magnetite, is very near to the coercive force, 550 Oe, calculated for the isolated single domain magnetite using the equation 0.96 K/M<sub>s</sub>, where K is constant of anisotropy, and  $- 13 \times 10^4$  erg/cm3 for the magnetite.20)

#### 4.4. Heat-generating Property of Crystallized Products

Generally, ferrimagnetic materials generate heat in an amount proportional to the area of the magnetic hysteresis loop and the frequency of the applied alternating magnetic field. Fig.12 shows the area of the magnetic hysteresis loop observed under the magnetic fields up to 10 kOe and 300 Oe, respectively, for the crystallized products, as a function of the heat treatment temperature. It can be seen from Fig.12 that the amount of heat generation is appreciably decreased with decreasing magnetic field, and that the specimen heat-treated up to 950°C shows the maximum heat generation under 10 kOe, whereas the specimen heated up to 850°C does so under 300 Oe. This indicates that when a magnetic field as large as 10 kOe is available, the 950° C-heated specimen of the maximum coercive force is best as the thermoseed, whereas when only a magnetic field as low as 300 Oe is available, the 850° C-heated specimen of a lower coercive force is better than the 950° C-heated specimen. An alternating magnetic field as high as 10 kOe is not always available.

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# Preparation and Properties of Pillared Clays with Controlled Pore Structures (Part 1) – Effects of Organic Cation Additives –

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In the preparation of SiO<sub>2</sub>-TiO<sub>2</sub> sol pillared clays from the organic cation, octadecyltrimethylammonium, was added to a montmorillonite suspension, together with SiO<sub>2</sub>-TiO<sub>2</sub> mixed sol solutions. The order of the addition was important; if the organic cation was added first, the effect of the addition was very small. On the other hand, if the SiO<sub>2</sub>-TiO<sub>2</sub> sol solutions were added first, followed by the addition of the organic cation, a pillared clay with mesopores was obtained on calcination, whose surface area increased with an increase in the amount of the organic cation additive. In the latter case, the organic cations probably occupied a part of the interlayer spaces of montmorillonite together with the sol particles, and burning off the organic cations left behind mesopores in the interlayer spaces.

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**Key-words:** Pillared clay, Porous material, SiO-TiO<sub>2</sub> sol, Montmorillonite, Alkylamine

# 1. Introduction

Pillared clays consisting of silicate layers of clay minerals as a host structure and ceramic fine particles as cross-linking agents between the layers are a new type of microporous materials, the pore sizes at which can be controlled by adjusting the particle sizes of the inserted ceramic pillars.<sup>1)</sup>

These porous materials with high specific surface area and superior in their heat and corrosion resistant properties can be promising candidates for the use as catalysts or catalyst supports, or as adsorbents. However, in order to give highly shape-selective norpertris for reaction or adsorption, it is necessary to control the pore structures more strictly in the micro- and mesopore region.

The synthesis of pillared clay is basically an ion exchange reaction: the exchangeable cations between the clay layers are ion-exchanged with polynuclear metal hydroxide such as  $[Al_{13}O_4(OH)_{24}]^{7+,23}$   $[Zr_4(OH)_{14}]^{2+4,5)}$  [Fe<sub>3</sub>O(OCOCH<sub>3</sub>)<sub>6</sub>]<sup>+,6,7)</sup> etc., and the hydroxdes are converted into the respective oxides between the layers by calcination. The resulting micropores are of 7 to 10Å in diameter, which is almost corresponding to the increase in the interlayer distance.

It has been reported by Yamanaka, et al.<sup>6-10</sup> that not only these metal hydroxides, but also larger oxide particles such as silica sols can be introduced between the layers by ionexchange, as long as the particles are positively changed. The basal spacing of the clay pillared with sol particles increased to more than 40Å, and it was expected that the pillared clays having mesopores would be produced, however, nitrogen gas atsorption measurements revealed that only pores smaller than 10Å in diameter were formed.

It is very likely that sol particles smaller than the distance between layers were closely packed in the interlayer space, and that micro pores were formed between sol particles or in the intenstices existing between the sol particles and the silicate layer surface. However, if the packing density of sol particles between layers can be controlled, it may be possible to make pores of mespore sizes between the layers.

In this study, we have tried to control the packing density of sol particles in the interlayer spaces of clay by adding organic cations in the cross-linking reactions, in an attempt to introduce mesopores into the interlayer spaces of clay and to control the pore structures.

# 2. Experiment

#### 2.1. Preparation of Samples

The clay used for synthesizing pillared clay was Namontmorillonite (Kunipia F) manufactured by Kunimine Industry Co., Ltd. The chemical composition was  $(Na_{0.35}K_{0.01}Ca_{0.02})$  (Si<sub>3.89</sub>Al<sub>0.11</sub>) (Al<sub>1.60</sub>Mg<sub>0.32</sub>Fe<sub>0.08</sub>)O<sub>1</sub>.  $_0(OH)_2$ nH<sub>2</sub>O with a cation exchange capacity of 100 med/100 g.

SiO<sub>2</sub>-TiO<sub>2</sub> mixed sol solutions used for cross-linking were prepared by mixing the two and solutions in a molar ratio of SiO<sub>2</sub>/TiO<sub>2</sub> =10/1.<sup>9)</sup> Tetraethylsilicate, Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, 2N hydrochloric acid, and ethanol were mixed in a ratio of 41.6g:10ml:12ml and hydrolyzed to obtain the SiO<sub>2</sub> sol solution. Titanium tetraisopropoxide Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> and 2N hydrochloric acid were mixed in a ratio of 1g:10ml and hydrolyzed; white precipitate thus obtained was stirred until they were peptized to a TiO<sub>2</sub> sol solution.<sup>8)</sup> A cation surfactant octadecyltrimethylamonium (OTMA) chloride (Nissan Cation AB, manufactured by Nihon Yusi Co., Ltd.) was used as the organic cation agent.

Pillared clays were synthesized by the following two methods:

Process I: OTMA in various ratios was added to a 0.8wt% montmorillonite suspension and stirred;  $SiO_2$ -TiO<sub>2</sub> sols were then added.

Process II: SiO<sub>2</sub>-TiO<sub>2</sub> sols were added to a 0.8wt% montmorillonite suspension and stirred; OTMA was then added. Each mixture was stirred for 1.5h at room temperature, and centrifuged and washed several times.

#### 2.2. Analysis and Characterization

The paste samples obtained after washing were partially collected and coated on glass plates to attain preferential orientation on the basal plane. The samples on the glass plates were dried at 60°C in air, and then calcined at 500°C before x-ray powder diffraction patterns (XDR) were measured. An automatic surface-area measurement apparatus (Autosop G) manufactured by Cantachrome Co., Ltd. was used for the measurement of nitrogen adsorption-desorption isotherms at liquid nitrogen temperatures. The specific surface area of each sample was calculated from the isotherms, and the pore size distribution was calculated by the BJH method.<sup>11)</sup>

The organic components of the samples were deternined by C, H, N analysis. The inorganic components were determined by atomic absorption analysis on the sampler calcined at 900°C, which was melted with LiBO<sub>2</sub> in a graphite crucible and dissolved in a nitrate solution.<sup>15)</sup>

# 3. Results

#### 3.1. Composition of Porous Materials

The molar ratios of starting materials used for synthesis via Processes I and II are shown in **Table 1** along with the

 Table 1. Compositions of SiO<sub>2</sub>-TiO<sub>2</sub> pillared montmorillonite

 prepared by adding OTMA in Processes I and II.

	Co	mposi	tion mixed1)			Compo	sition found <sup>1)</sup>					
					Proce	ess I		Process	11			
	SiO <sub>2</sub>	TiO <sub>2</sub>	ОТМА	SiO <sub>2</sub>	TiO <sub>2</sub>	OTMA	SiO <sub>2</sub>	TiO <sub>2</sub>	ОТМА			
#1(I), #1(II)	4	0.4	2.88	0.48	0.08	2.79	3.65	0.30	2.88			
#2(1), #2(11)	4	0.4	1.44	1.27	0.14	1.41	4.05	0.34	1.41			
#3(1), #3(11)	4	0.4	0.72	1.97	0.34	0.72	3.47	0.36	0.66			
#4(I), #4(II)	4	0.4	0.36	3.34	0.44	0.26	3.56	0.40	0.26			

1) Compositions are given in molar ratios to one equivalent of CEC of clay.



Fig. 1. X-ray powder diffraction profiles of the products prepared by Process I: (a) after air-drying at 60°C and (b) after calcining at 500°C. The OTMA/clay mixed ratios (mol/CEC) are designated in parentheses.

composition of SiO<sub>2</sub>-TiO<sub>2</sub> sols and the content of OTMA contained in the products. SiO<sub>2</sub>-TiO<sub>2</sub> sols in the ratio 4SiO<sub>2</sub>:0.4TiO<sub>2</sub> were added to one cation-exchange equivalent of montmorillonite in all cases. If it is assumed that the composition of clay host layers is retained after the reaction, the SiO<sub>2</sub> content from the clay itself can be estimated from the Al<sub>2</sub>O<sub>3</sub> content analyzed. The amount of SiO<sub>2</sub> sol incorporated in the layer can be obtained by deducting the SiO<sub>2</sub> content of the clay from the total content of the product. As shown in Table 1, the amount organic cations incorporated into the clay decreased nearly in proportion to the amounts initially added when OTMA was added first (Process I), indicating that the non-reacted sol particles were washed away by water. On the other hand, when the sol was added first (Process II), almost the entire amount of organic cations as well as the sol remained in the clay independent of the amount of organic cations added.

#### 3.2. Interlayer Distance

The XRD patterns of samples synthesized via the two different processes are shown in Figs.1 and 2. Except for the samples with small amounts of additive cations, the average basal spacing measured from the lowest angle diffraction peak of the Process I samples was approximately 22Å, in good agreement with that of the samples treated with OTMA alone. However, when the amount of additives was less than 0.36 moles per equivalent of CEC, the basal spacing was much greater, approaching 40Å of the sample cross-linked with sols alone. When these samples were calcined at 500°C, the XRD patterns became broader as shown in the figure, and the basal spacing was reduced to about 15Å. In the case of the samples with less OTMA, the spacing of ~40Å was retained at 500°C with no appreciable changes even after calcination although the XRD pattern was broader.

As shown in Fig.2 when OTMA was added after the addition of  $SiO_2$ -TiO<sub>2</sub> sols (Process II), the basal spacings of the products were all greater than 40 regardless of the amount of additive, and tended to be slightly larger as the amount of additives increased. The diffraction patterns



Fig. 2. X-ray powder diffraction profiles of the products prepared by Process II: (a) after air-drying at 60°C and (b) after calcining at 500°C. The OTMA/clay mixed ratios (mol/CEC) are designated in parentheses.

were quite similar to that of the sample containing no OTMA, and the diffraction patterns became broader when calcined at 500°C.

### 3.3. Nitrogen Adsorption Isotherm

The samples were calcined at 500°C for 3hrs prior to the measurement of nitrogen adsorption isotherms. Figure 3 shows the nitrogen adsorption isotherms of the samples pillared with  $SiO_2$ -TiO<sub>2</sub> sols with no addition of OTMA. Although the basal spacing is larger than 40Å, the isotherm is Langmuir type-like and the hysteresis is small. Figure 4 compares the typical adsorption and desorption isotherms of samples synthesized by Processes I and II. It is clear from



Fig. 3. Nitrogen gas adsorption-desorption isotherms for SiO<sub>2</sub>-TiO<sub>2</sub> pillared montmorillonite without adding OTMA: O, adsorption;
 , desorption.



Fig. 4. Nitrogen gas adsorption-desorption isotherms for SiO<sub>2</sub>-TiO<sub>2</sub> pillared samples, (a), #2(I) and (b), #1(II) by the Processes I and II respectively: O, adsorption: ●, desorption.



Fig. 5. Surface areas and pore volumes of the calcined products by Process I as a function of the OTMA/clay mixed ratio (mol/CEC), R.

the figure that the adsorption curves are changed to the BET type by the addition of OTMA and that the hysteresis is enlarged.

Figure 5 (Process I) and Fig.6 (Process II) show the BET specific surface areas and pore volumes obtained by varying the added amount of OTMA; the pone volumes were estimated from the saturated adsorption volumes. It is clear from Fig.5 that upon addition of OTMA, the specific surface area tended to decrease in the Process I synthesis and that the increase in the pore volume is small. In addition, both the specific surface area and pore volume became almost constant independent of the amounts of OTMA added. However, in Process II syntheses, when OTMA was added later, the specific surface area and porous volume increased almost in proportion to the amount of OTMA added. Figure 7 shows the pore size distribution of Process II samples obtained by the BJH method<sup>11)</sup> using the adsorption isotherms. It is also clear that the pore volume was increased by the increase in pores volume of mesopore range of 10 to 20Å in diameter.

# 4. Discussion

The pillaring with sol particles is also considered to be initiated by an ion exchange reaction. Thus, negatively charged  $SiO_2$  sol particles are not used for direct ion exchange with interlayer cations of clay. However, the ion



Fig. 6. Surface areas and pore volumes of the calcined products by Process II as a function of the OTMA/clay mixed ratio (mol/CEC), R.



Fig. 7. Pore size distribution of the products by Process II followed by calcination at 500°C: the OTMA/clay mixed ratio (mol/CEC) were (●). 2.88, (○), 1.44. (▲). 0.72 and (□). 0.

exchange is possible, if the surface of the SiO<sub>2</sub> sol particles is modified by adding TiO<sub>2</sub> sols and are positively charged due to a rise of isoelectric points.<sup>9,10</sup> It is conceivable that when organic cations are added, a competitive ion exchange occurs between the sol particles and the organic cations. In view of the experimental results, the ion selectivity of clay may be considerably higher for organic cations than for SiO<sub>2</sub>-TiO<sub>2</sub> sols. When organic cations are added first, the OTMA occupying an interlayer space retains an interlayer distance at 20Å, (the interlayer separation is approximately 10Å), subsequently added sol particles are presumably unable to enter the occupied interlayer.

When OTMA is added after the exchange with the sol is done, the higher affinity for OTMA results in its being incorporated into the interlayer space in proportion to the amount added. As shown in **Table 1**, the amounts of sols incorporated into the clay were nearly constant for all samples even if the added amounts of OTMS were increased. However, the basal spacing of the products tended to increase with the amount of OTMA. This suggested that most sol particles remained in the interlayer space with rearrangements as shown in **Fig.8**, and that the OTMA ions were being incorporated in the interstices of the sol particles.

Thus, the incorporation of OTMA in the interlayer space is not made by ion exchange with sol particles, but presumably by ion exchange with protons on the sol surface, which give the positive charge to the sol particles. Mesopores are conceivably formed where interlayer OTMA is burned off when this sample is calcined (Fig.8).

Suzuki, et al.,<sup>13)</sup> used large, soluble molecules such as polyvinylalcohol (PVA) in the synthesis of pillared clay with aluminum hydroxide, etc., and investigated the additive effects. They reported that although an interlayer space of montmorillonite was enlarged by intercalation of PVA, the aluminam hydroxy cations were further exchanged with the interlayer cations, and that a porous material with a high specific surface area possessing mesopores 25Å in diameter was obtained by calcination.

The pores in the aluminum oxide pillared clay, obtained in the absence of PVA were approximately 7 to  $8\text{\AA}$  in diameter.<sup>14</sup> It is quite interesting to note that the porous structures formed are considerably different depending on the organic additive, even though the same aluminum hydroxide ion is used as a precursor for cross-linking.

Polymer molecules are adsorbed not only in the inter-



Fig. 8. Schematic structural model for the formation of mesopores in the interlayer spaces of montmorillonite by Process II: (i) ionexchange with sol particles, (ii) uptake of OTMA along with the rearrangement of the interlayer sol particles, (iii) removal of OTMA by calcination and formation of mesopores.

layer space to change the arrangement of interlayer ion hydroxides but also on an external surface of the clay particles to cause the delamination of the silicate layers as pointed out by Pinnavaia, et al.<sup>15)</sup> Suzuki, et al.,<sup>16)</sup> prepared pillared hectorite in a similar manner, and reported that both the interlayer distance and the amount of pillar material increased three times when PVA was used. These findings are in accordance with the fact that the pore size distribution has a sharp peak at around 20Å.

Torii<sup>17)</sup> recently reported that in the preparation of pillared clay from synthetic hectorite, the hysroxide layers originally existing between the silicate layers were rearranged by the addition of organic cations so as to give high specifie surface area. Although the effects of the organic additives used in those studies were rather different from those presented here, the results suggested that the porous structure of pillared clay is largely different depending on the organic additive.

OTMA used in this study was mostly trapped by the clay regardless of its added amount. Since the water-solubility of OTMA is considerably high, the OTMA should not have been trapped by the samples after water washing. However, it appears that a micromixture of OTMA with the clay or the SiO<sub>2</sub>-TiO<sub>2</sub> sol possibly formed a sparingly soluble composite of clay or sol, and the OTMA partially remained in the clay interlayer due to an ion exchange, with the rest conceivably existing on the external surface of the clay as uncharged species.

The relatively high BET specific surface area which was obtained in the Process I sample synthesized with almost no interlayer sols may be explained by the delamination effects of the silicate layers which were noted when the OTMA in this grain boundary was burned off.

# 5. Conclusion

When oxide sols are added prior to the addition of bulky organic cations in synthesizing pillared clay, organic cations are incorporated in the clay interlayer together with sol particles. Thus, it was clarified in this study that mesopores can be controlled when these incorporated organic cations acting as a kind of template are burned off. Furthermore, the order of the addition of organic cations and sols is important in the above procedure.

When organic cations with high affinity are added to the clay first, the same effects cannot be expected. It is presumably possible to control pore sizes of not only mesopores but also micro pores and their distribution by changing an arrangement and combination of the kinds of cross-linking oxides and organic cations.

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# Coating of β-Tricalcium Phosphate on Yttria-Partially Stabilized Zirconia Using Magnesium Metaphosphate as an Interlayer

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It was studied for developing high-strength bioceramic materials to coat yttria partially stabilized zirconia (Y-PSZ) with  $\beta$ -tricalcium phosphate ( $\beta$ -TCP). A Y-PSZ substrate was first coated with a slurry of magnesium meta-phosphate as an interlayer and heated at 1120° to 1240°C. The product was then coated with a slurry of  $\beta$ -TCP and heated at 110° to 1120°C. The result was that coating bonded well to the substrate and  $\beta$ -TCP phase was observed in the coating layers of all samples. A tetragonal-to-monoclinic destabilization of the Y-PSZ was observed in the reaction layer.

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**Key-words:** Bioceramic material, Tricalcium phosphate, Coating, Composite ceramics, Yttria-partially stabilized zirconia

# 1. Introduction

Ceramics of  $\beta$ -tricalcium phosphate ( $\beta$ -TCP) are expected to be useful as the bioactivre materials. However, it was difficult to achieve adequate mechanical strengths for use as alterative materials for the hard issues of living bodies.<sup>1,2)</sup>

Studies to create composites of  $\beta$ -TCP with kinds of metals or ceramics have been made in order to develop new materials having high-strength and bio-affinity.<sup>3-5)</sup> The composite materials shown in these reports were those of bulk-state, which were sintered  $\beta$ -TCP with high-strength ceramics as additives. The materials mentioned above did not have sufficient strength to be used for artificial joints and other areas that are subject to complex and impactive forces. It cannot be expected that drastic improvements of biomaterials in mechanical strength will be brought by these synthesis methods.

In order to make the bioceramic materials much stronger, it is reasonable way to supply bio-affinity for the high-strength materials as the substrate by coating with  $\beta$ -TCP. In this study, the authors attempted to coat partially stabilized zirconia of high strength and toughness with  $\beta$ -TCP using magnesium metaphosphate as an intermediate reaction layer.

# 2. Experimental Procedure

Partially stabilized zirconia powder (Tosoh; TZ-3YB abbreviated as Z3Y) and stabilized zirconia powder (Tosoh; TZ-8Y abbreviated as Z8Y) were uniaxially press-molded ( $1t/cm^2$ ) to prepare disks of 20mm diameter and 3mm thickness. The molded disks were heated to 500°C at the rate of 200°C/hr and kept at 500°C for 1hr. They were further heated to 1450°C at the same rate and kept at 1450°C for 2hrs to sinter. The sintered products were used as the substrate.

Magnesium metaphosphate  $(Mg(PO_3)_2 \text{ abbreviated as} MP)$  was synthesized using magnesia (Iwatani; MTK-30) and phosphoric acid (Wako Pure Chemical Industries, Led., guaranteed reagent). A specified composition ratio of magnesia was dissolved in hot phosphoric acid and viscous solution was obtained. In order to complete the reaction, the solution was heated at 700°C for 8hrs. The reaction product was ground to powder in ethylene grycol (Wako Pure Chemical Industries, Ltd., extra pure reagent) with a zirconia pot-mill.

 $\beta$ -TCP was synthesized by the dry process<sup>6)</sup> and used for coating procedure. Zirconia substrate were coated by the following method. The slurry of MP or  $\beta$ -TCP powder, to which carboxymethylcellulose (CMC, Daiichi Kogyo; Serogen) was added as the binder, was applied to the sintered disks of Z3Y and Z8Y with a brush. After drying, these disks were heated to 500°C at the rate of 20°C/min and kept at 500°C for 30min. Then MP coating was performed by heating at four different temperatures (1120,° 1160,° 1200° and 1240°C) for 40min and  $\beta$ -TCP coating was also performed by heating at four different temperatures (1100,° 1150,° 1180° and 1220°C) for 40min.

The crystal phase of the coated samples were identified by the powder X-ray diffraction method (Rigaku Co., Ltd.: CN2028 Model and Geiger flex) with CuK $\alpha$  radiations (30kV, 20mA). Their microstructures of the coated samples were observed with a scanning electron microscope (SEM) (Hitachi, Ltd.: S-530 and S-2300) after the cross section of the samples were polished. Then an elemental analysis was carried out on the coating interface with an energy-dispersive X-ray spectrometer (EDX Horiba, Ltd.: EMAX-200).

# 3. Results and Discussion

#### 3.1. β-TCP Direct Coating

In directly coating of β-TCP at 1100°C, the coating layer

was easily peeled off by fingernails and the surface of Z3Y substrate seemed not to react with  $\beta$ -TXP.

The surface of ceramics can be coated by some methods, plasma spraying, CVD, etc.<sup>7)</sup> Higashikata et al. reported that in coating the surface of some metals with hydroxyapatite (HAp) by plasma spraying, the coated HAp was decomposed into Ca<sub>4</sub>(PO<sub>4</sub>)<sub>2</sub>O,  $\alpha$ -TCP and CaO under some spraying conditions<sup>8)</sup> Considering this results, we thought that since  $\beta$ -TCP is more unstable in high temperature than HAp, it is difficult to decide the conditions of plasma spraying with  $\beta$ -TCP. In addition, it is difficult to decide the condition and the starting materials, which product  $\beta$ -TCP on substrate by CVD method.

AS mentioned above, there was no reactivity between zirconia and  $\beta$ -TCP. In order to bind  $\beta$ -TCP and zirconia chemically, we suggested making an intermediate reaction layer as a binder. We used MP to make an intermediate reaction layer by following reasons: (1) phosphoric acid and phosphate are often used as binders for alumina, magnesia, and zirconia refractories;<sup>9,10)</sup> (2) Toriyama et al. reported that solid solution of  $\beta$ -TCP and MgO is more stable at high temperature than  $\beta$ -TCP;<sup>11)</sup> (3) the melting point of MP (1165°C) is relatively low in the chemical compounds of the MgO-P<sub>2</sub>O<sub>5</sub> system.<sup>12)</sup>

## 3.2. Formation of a Magnesium Metaphosphate Interlayer on Yttria Partially Stabilized Zirconia Substrate

The feature of the ample, the Z3Y sintered disk that was coated with MP and then heat-treated (abbreviated as 3Y-MPZ), will be mentioned. The coating layer of 3Y-MPZ did not melt at 1120°C, and it was likely that MP powder was adhering on the surface of Z3Y substrate weakly, because the coating layer easily peeled off with fingernails. As for the products heat-treated at the temperatures 1160°C and above, the coating layers was being adhered strongly, because of the melting of MP powder and the solidifying of the melt in a cooling process on the substrate.

Powder X-ray diffraction patterns of 3Y-MPZ disk sur-



Fig. 1. SEM photograph of cross-section of 3mol% Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> disk coated with magnesium metaphosphate at 1200°C. Mg and Zr distributions across the interface are given.

face comprised the diffraction lines of Mg(PO\_3)<sub>2</sub>, tetragonal ZrO<sub>2</sub> and two reaction phases of cubic ZrPO<sub>7</sub> and  $\alpha$ -Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>.

From SEM photographs of cross sections of 3Y-MPZ disks, the original shape of MP particles remained in the coating layer when treated at 1120°C and no reaction layer was observed. The SEM photograph of the 3Y-MPZ heat-treated at 1200°C is shown in **Fig.1**. The coating layer was about 10µm thickness. The reaction layer between Z3Y substrate and MP coating layer was observed. From EDX analysis it was found that this layer contained magnesium of higher concentration and zirconium of lower concentration, than MP coating layer. Considering the results of powder X-ray analysis, the reaction layer presumably consists of cubic ZrP<sub>2</sub>O<sub>7</sub> phase.

#### 3.3. B-TCP Coating on Intermediate Reaction Layer

Powder X-ray patterns of the surface of samples, the 2Y-MPZ disks which were coated with  $\beta$ -TCP and then heat-treated (abbreviated as 3Y-TCPZ), showed no significant differences depending on MP coating temperature. Thus the detected phases of the 3Y-TCPZ disk coated with MP at 1200°C were only shown in **Table 1**. Although the  $\beta$ -TCP phase was observed in the samples of all temperature heat-treated, diffraction lines assigned to  $\beta$ -TCP were observed in higher angle side than those of JCPDS card.<sup>13</sup> This phenomenon was attributable to dissolution of magnesium in the  $\beta$ -TCP layer. Tetragonal ZrO<sub>2</sub> phase was observed, while mono-clinic ZrO<sub>2</sub> phase also recognized. Ca<sub>4</sub>Mg<sub>5</sub>(PO<sub>4</sub>)<sub>6</sub> phase<sup>14</sup> was observed in the disk heat-treated at the temperature below 1140°C.

Several diffraction lines, including the relatively strong line in the vicinity to  $2\theta(CuK)=26^\circ$ , were not assigned to the phases mentioned previously. Assuming these lines to be YPO4 (Xenotime),<sup>15)</sup> the following experiment was carried out. The sintered disk of Z8Y coated with B-TCP was prepared under the same condition as 3Y-TCPZ (abbreviated as 8Y-TCPZ), then the B-TCP coating layers of 3Y- and 8Y-TCPZ were dissolved in 6mol/l acetic acid. Powder X-ray diffraction patterns of these products were shown in Fig.2. Though diffraction lines of B-TCP were not observed in both patterns, the line in the vicinity to  $2\theta(CuK)=26^{\circ}$  was observed strongly. It is known that YPO<sub>4</sub> is insoluble in acids,<sup>16)</sup> and the lines in the vicinity to  $2\theta(CuK)=20^{\circ}$  and 26° were attributed to diffraction lines from (101) and (200) plane, respectively, which were stronger in 8Y-TCPZ of higher concentration of yttrium than 3Y-TCPZ, so that these lines were assigned to YPO<sub>4</sub> phase.

The destabilization of stabilized or partially stabilized zirconia, as mentioned above, has been widely investigated from refractories. Oki *et al.* reported that zirconia refractories (CaO stabilized zirconia) were destabilized and damaged by Si and SiO<sub>2</sub> included in molten steel and slag.<sup>17-19</sup>

Coating temp.(°C)	Detected phases
1100	B-TCP, ZrO2(tetra), ZrO2(mono), YPO4, Ca4Mg5(PO4)6
1140	B-TCP, ZrO2(tetra), ZrO2(mono), YPO4, Ca4Mg5(PO4)
1180	B-TCP, ZrO <sub>2</sub> (tetra), ZrO <sub>2</sub> (mono), YPO <sub>4</sub>
1220	B-TCP, ZrO <sub>2</sub> (tetra), ZrO <sub>2</sub> (mono), YPO <sub>4</sub>

It was reported that  $Y_2O_3$ -stabilized zirconia (YSZ) with which coated metallic gas turbine blade was destabilized by  $V_2O_5$  in fuel to produce  $YVO_4$ .<sup>20-23</sup> From these results, the formation of YPO4 in TCPZ was proceeded by following process; coating MPZ with  $\beta$ -TCP brought the elution of yttria as a stabilizer from substrate to react with coating material to  $YPO_4$ , accompanied with phase trans-formation of tetragonal zirconia to monoclinic.

The SEM photographs of the 3Y-TCPZ heat-treated at 1100° and 1220°C are shown in **Fig.3**. In both cases the coating layers were well bonded to the substrates and were about 10–20m in thickness. From EDX analysis it was found that calcium and magnesium were distributed homogeneously in the coating layer. Permeated by the coating layer, the zirconia particles in the reaction layer shown in Fig.3 were likely to float from the substrate. This phenomenon, which was remarkable at 1220°C, was caused by fol-

lowing process; first, cracks occurred by the volume expansion through the phase transition of tetragonal zirconia to monoclinic, then the melted coating layer permeated the cracks. The reaction layer, at which the coating layer and the substrate gear each other, made the coating layer adhered stongly on the substrate.

# 4. Conclusion

Y-PSZ substrate was coated with B-TCP using magnesium metaphosphate as an interlayer. The results are as follows;

- 1) It was possible to retain the B-TCP phase.
- It was possible to let the coating layer adhere on the substrate.



Fig. 2. Powder X-ray diffraction patterns of  $\beta$ -TCP coated zirconia disk surface after  $\beta$ -TCP dissolution by 6 mol/l CH<sub>3</sub>COOH: (a) 3 mol% Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>, (b) 8 mol% Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>. Before  $\beta$ -TCP coating, magnesium metaphosphate was coated at 1200°C on the zirconia disks as an interlayer.  $\bigstar$ : ZrO<sub>2</sub> (tetragonal),  $\bigstar$ : ZrO<sub>2</sub> (monoclinic),  $\bigcirc$ : ZrO<sub>2</sub> (cubic),  $\times$ : YPO4.



(a)

(b)

Fig. 3. SEM photographs of cross-section of  $3mol\% Y_2O_3$ -ZrO<sub>2</sub> disk coated with  $\beta$ -TCP at (a)  $1100^{\circ}$ C and (b)  $1220^{\circ}$ C. Before  $\beta$ -TCP coating, magnesium metaphosphate was coated at  $1200^{\circ}$ C on the zirconia disks as an interlayer. Ca and Mg distributions across the interface are given.

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3) Destabilization of Y-PSZ was observed in the reaction layer.

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# Fabrication, Properties, and HIP Treatment of (Y, Ce)-TZP Ceramics Obtained from Fine Powders Prepared by a Hydrolysis Technique

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Fine powders with the compositions of 4mol% YO<sub>15</sub> -4mol%CeO<sub>2</sub>-ZrO<sub>2</sub> (4Y, 4Ce), 2.5mol% YO<sub>1.5</sub> -4mol% CeO<sub>2</sub> -ZrO<sub>2</sub> and 2.5mol% YO<sub>1.5</sub> -5.5mol% CeO<sub>2</sub> -ZrO<sub>2</sub> were prepared by the hydrolysis method. Using the powders thus obtained, vttria- and ceria-doped tetragonal zirconia ceramics ((Y, Ce)-TZP) were fabricated by a normal sintering and a hot isostatic pressing (post-sintering hot isostatic pressing). Their bending strengths, microstructures, and tetragonal-to-monoclinic phase transformations during low-temperature aging were studied. Mean values of the bending strength of (Y, Ce)-TZP fabricated by a normal sintering at 1500°C for 2h were 840MPa for (4Y, 4 Ce)-TZP, 860MPa for (2.5Y, 5.5Ce) -TZP and 1000MPa for (2.5Y, 4Ce)-TZP. The grain size of (Y, Ce)-TZP was larger than that of 3Y-TZP. (4Y, 4 Ce)-TZP and (2.5Y, 5.5Ce)-TZP showed improved thermal stability as compared with 3Y-TZP. The bending strength of (4Y, 4Ce)-TZP increased from 840MPa to 1100MPa by post-sintering HIP at 1500°C and 147MPa for 0.5h.

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**Key-words:** (Y, Ce)–TZP, Hot isostatic pressing, Hydrolysis, Bending strength, Microstructure, Transformation

# 1. Introduction

A sintered body (Y-TZP) consisting of tetragonal zirconia using yttria as a stabilizer is widely being used as a specifically strong and tough ceramic material.<sup>1)</sup> Such strength and toughness are derived from the tetragonal phase being meta-stable at high temperature. However, this Y-TZP possesses disadvantages in that its strength declines when retained at 200° ~ 300°C in the atmosphere.<sup>2,3)</sup> This was attributed to micro-cracks caused by the shift of a tetragonal phase on the surface of a sample over to the monoclinic system being more stable at room temperature.<sup>4,5)</sup>

Efforts have been made to improve the above deterioration. For example, one of the methods is to control the particle size of Y-TZP below a fixed level, since the stability of the tetragonal system highly depends on the particle size of the sintered body.<sup>3,6</sup> Stabilizers are also being studied, so that the stability of the tetragonal system may increase,<sup>71</sup> whereas reports have been made on the systems such as  $CeO_2$ -ZrO<sub>2</sub> and  $CeO_2$ -Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>, for which  $CeO_2$  has been used as a stabilizer. However, since the property of a zirconia sintered body highly depends on its particle size and micro-structure, it becomes significantly different according to the decision on the chemical composition, material powder, firing methods, etc. The zirconia material powder was manufactured by co-precipitation and several other methods,<sup>11)</sup> but fine powder obtainable by hydrolysis,<sup>12,13)</sup> heating an aqueous solution of zirconium oxychloride, has resulted in superior sintering properties.<sup>14)</sup>

In this current study, an aqueous solution of  $ZrOCl_2$ mixed with a pH control solution and  $H_2O_2$  solution was hydrolyzed in order to obtain zirconia sols, which were used for the preparation of fine powders containing yttria and cerium as stabilizers. The hydrolyzed fine powers purposely obtained for the development of zirconia ceramics possessing higher thermal stability and higher strength were used for the preparation of (Y, Ce)–TZP by atmospheric sintering and HIP processing (post-sintering HIP) for further investigations of the strength of sintered bodies, fine structure, thermal stability and the HIP conditions.

## 2. Experimental Methods

#### 2.1. Preparation of Samples

Figure 1 shows the preparation processes for the sample powders. An aqueous solution of zirconium oxychloride (ZrOCl<sub>2</sub>:8H<sub>2</sub>O) was mixed with ammonium water (28wt%) and H<sub>2</sub>O<sub>2</sub> solution (30wt%) in a ratio given in **Table 1**, and hydrolyzed while being retained at boiling point in a glass-lined container equipped with a reflux condenser. To a monoclinic ZrO<sub>2</sub> sol solution thus obtained, an aqueous solution mixed with the fixed amounts of yttrium chloride



Fig. 1. Schematic diagram for the powder preparation.

Table 1. Preparation conditions of hydrolyzed zirconia sols.

S	tarti	ng solution	1	Boiling time
Zr0C1	2	H 2 0 2	NH4 OH	(h)
(mol/l)	(1)	(ml)	(m1)	
0.2	45	500	750	48

Table 2. Composition of specimens and specific surface area of powders.

	and the second se	and the second se			
Material	Specimen	Composition (mol%)	Specific surface		
			area of	powder	(m²/g)
Y-TZP	2.5Y	2.5Y <sub>2</sub> 0 3 97.5Zr0 2		24	
	3¥	3Y <sub>2</sub> 0 3 97Zr0 2		25	
	(4Y,4Ce)	4Y0 1. 5 4Ce0 2 92Zr0 2		27	
(Y,Ce)-TZP	(2.5Y,4Ce)	2.5Y0 1.5 4CeO2 93.5Z	r0 z	25	
	(2.5Y,5.5Ce)	2.5Y0 1 5.5CeO2 92Z	r0 2	26	

 $(YCl_3 \cdot 6H_2O)$  and cerium chloride  $(CeCl_3 \cdot 7H_2O)$  was allowed to be precipitated in an ammonium water by dropwise while being stirred. The precipitates thus obtained were washed with water, dried and calcined at  $800^{\circ} \sim$  $1150^{\circ}C$ . The specific surface area of zirconia powder prepared by calcining at  $1050^{\circ}C$  and wet-milling for 48hr is shown in **Table 2**. The zirconia powder thus obtained was preliminarily molded under pressure of 19.6MPa, before it was molded under the static water pressure of 196MPa and sintered at  $1400 \sim 1600^{\circ}C$  for 2hr in the atmosphere.

#### 2.2. HIP Treatment

After zirconia powder in a composition shown in Table 2 (4Y, 4Ce) had been preliminarily molded under the pressure of 19.6MPa, it was molded with the static water pressure of 196MPa to obtain a pre-sintered compact after atmospheric firing at 1350 ~ 1500°C for 2hr. After this pre-sintered compact was placed in a small-sized experimental apparatus for HIP equipped with a graphite heater, the temperature was elevated from room temperature up to 1200°C at a rate of 30°C/min and from 1200°C up to 1400°C or the maintenance temperature of 1500°C at a rate of 10°C/min for HIP treatment while being retained under the pressure of 147MPa for 30min. Ar gas of high purity was used as the hydraulic media. **Figure 2** shows the schedule of HIP treatment.

#### 2.3. Analytical Procedure

As for the precision of a molded product, the volume and weight were obtained from a sample whose dimension was measured by a micrometer and slide caliper, while the mass density of a sintered product was measured by the Archimedean method. A sample specimen measuring 3×4×40mm finished by a #140 diamond grindstone was used for the test of mechanical strength, which was determined by three-point bending at 30mm in span and 0.5mm/min in cross-head speed in accordance with JISR1610 using an Instron, Model 1123. Ten specimens were obtained from a compact sintered body under constant pressure, with 5 specimen being from each product treated by HIP. A test specimen of 1.2×10×5mm was used for the test of elasticity to be obtained by a load-strain pattern using an Instron, Model 1123.

The fracture surfaces and micro-structure of a sintered body were observed by SEM (Hitachi, S450). A test specimen finished by a #140 diamond grindstone and retained at  $250^{\circ}$ C in the atmosphere for a fixed length of time before the thermal stability of a sintered product was evaluated by identifying the surface phase and quantitatively determining the monoclinic phase by X-ray diffraction using the method of Garvie et al.<sup>15)</sup>

# 3. Results and Discussion

# 3.1. Powder Preparation and Compact Sintered with Normal Pressure

The crystal diameter of monoclinic ZrO<sub>2</sub> generated under hydrolytic conditions for the current experiments was approximately 40 ~ 50Å in the preliminary particles and approximately 300 ~ 1000Å in the secondary particles. Salt solutions of Yttria and ceria were added to hydrolytic solution generated from the monoclinic ZrO<sub>2</sub> particles, and the precipitates obtained from an ammonium solution were washed with water and dried to obtain the powder, whose relationship of calcination temperature and specific surface area is shown in **Fig.3**.

The specific surface area of the powder prior to calcina-



Fig. 2. HIP treating schedule.



Fig. 3. Variation of specific surface area with calcining temperature for the powders (4Y, 4Ce) prepared by hydrolysis of ZrOCl<sub>2</sub> solution.



**Fig. 4.** Bending strength and bulk density of (a) (4Y, 4Ce)–TZP, (b) (2.5Y, 4Ce)–TZP and (c) (2.5Y, 5.5Ce)–TZP sintered at various temperatures for 2h in air.

tion was as large as  $180m^2/g$  and the specific surface are linearly decreased with rising calcination temperature. However, the decrease of the specific surface area in proportion to the calcination temperature became slightly smaller around  $1100^{\circ}$ C. The density and bending strength of (Y, Ce)–TZP sintered at 1450°C and 1500°C are shown in **Fig.4**, however, there occurred almost no difference due to sintering temperatures of 1450°C and 1500°C. The true densities of (Y, Ce)–TZP obtained from the lattice constants were 6.12g/cm<sup>3</sup> in (2.5Y, 5.5Ce). The density obtained from (4Y, 4Ce) was higher at either 1450°C or 1500°C than that of the two compacts of other compositions sintered containing less  $Y_2O_3$  contents.

Although Ce-TZP was known to be hardly sinterable as compared with Y-TZP, (Y, Ce)–TZP tended to be lower in its sintered levels when the  $Y_2O_3$  content was decreased or the CeO<sub>2</sub> content was increased. No existence of monoclinic were recognized from the results of X-ray diffraction of the sample surface in any of the three kinds of (Y, Ce)–TZP sintered at 1450°C and 1500°C.

The bending strength of a sintered body tended to be slightly higher at  $1500^{\circ}$ C than at  $1450^{\circ}$ C. The mean bending strength of the compacts sintered at  $1500^{\circ}$ C were 840MPa in (4Y, 4Ce), 1000MPa in (2.5Y, 4Ce) and 860MPa in (2.5Y, 5.5Ce). As compared with the hydrolyzed fine powder for 3Y-TZP whose mean bending strength was 1050MPa when synthesized through the same process, (4Y, 4Ce) and (2.5Y, 5.5Ce) were slightly lower in their strength.

However, (2.5Y, 4Ce) containing the least content of stabilizers showed the strength to be as high as for 3Y-TZP. As for the bending strength of (Y, Ce)–TZP, it has been reported that it was 300MPa in (2Y, 12Ce)–TZP when sintered under normal pressure.<sup>16</sup> It has also been reported that the strength of Ce-TZP not containing  $Y_2O_3$  was 500 ~ 800MPa in a compact sintered under normal pressure.<sup>81</sup> These Ce-TZP and (Y, Ce)–TZP were superior in their thermal stability but equally lower in the strength of the sintered compacts.

However, strength as high as 500 ~ 700MPa was obtained in (Gd, Ce)–TZP containing CeO<sub>2</sub> of 3~8mol% and GdO<sub>1.5</sub> of 3mol%.<sup>7)</sup> When compared with the above findings, it was found that the flexural strength of (Y, Ce)–TZP

Table 3. Elastic modulus of 3Y-TZP and (4Y, 4Ce)-TZP.

Specimen	Elastic modulus
	(GPa)
3¥	217
(4Y.4Ce)	195







Fig. 5. SEM photographs of the fracture surface of (a) (4Y, 4Ce)– TZP, (b) (2.5Y, 4Ce)–TZP and (c) (2.5Y, 5.5Ce)–TZP sintered at 1500°C for 2h.

composed for the current experiment using hydrolyzed fine powders was relatively higher ranging from 800 to 1000MPa. As for the elasticity modulus of the sintered compacts shown in **Table 3**, (Y, Ce)–TZP was slightly lower than Y-TZP. The micro-structure of the fracture surfaces of a compact sintered at 1500°C is shown in **Fig.5**. A sintered compact composed of tetragonal zirconia showed a specific iso-particulate structure. The mean particle size of (Y, Ce)–





Fig. 6. SEM photographs of as-sintered surface of (2.5Y, 4Ce)-TZP sintered at (a) 1400° and (b) 1600°C.



**Fig. 7.** Results of thermal aging at 250°C in air for Y-TZP and (Y, Ce)–TZP.

TZP consisting of relatively uniform particles was larger than that of 3Y-TZP sintered at the same temperature.

The particle sizes of (2.5Y, 4Ce) and (2.5Y, 5.5Ce) were slightly larger than that of (4Y, 4Ce). Since the bulk density of the sintered compacts were slightly lower, a large number of micropores were recognized in the sintered bodies. The microstructure of the surface of compacts sintered at 1400°C and 1600°C is shown in **Fig.6**. As shown in the figure, the particulate growth of (Y, Ce)–TZP was larger than that of Y-TZP and has notably increased at 1600°C. It was found from the above results that the Y<sub>2</sub>O<sub>3</sub> content was less in (Y, Ce)–TZP, while the particulate growth tended to be significant when the CeO2 content was high.

#### 3.2. Thermal Stability

The atmospheric changes of the monoclinic quantity during the retained curing at 250°C is shown in **Fig.7**. The mean particle size of a compact sintered at 1500°C was  $0.5\mu$ m in 3Y-TZP, while it was  $0.6\mu$ m for (4Y, 4Ce) and  $0.8\mu$ m for (2.5Y, 4Ce) and (2.5Y, 5.5Ce) in (Y, Ce)–TZP. While an increase was noted in the monoclinic system of 3Y-TZP, no changes were recognized in the crystal phases of (4Y, 4Ce) and (2.5Y, 5.5Ce) even when retained for 1500hrs, although (2.5Y, 4Ce) content slightly increased in (Y, Ce)–TZP. Thus, (Y, Ce)–TZP was predominant over 3Y-TZP with respect to thermal stability despite the larger particle size.

In view of the results of 3Y-TZP sintered at 1500°C and 1550°C, an increase of the monoclinic system was smaller in 3Y-1500 containing fewer particle sizes, when sintered at lower temperature. It was conceivably possible to level the thermal stability of (Y, Ce)-TZP as well when it is sintered at lower temperature. Since TZP containing CeO<sub>2</sub> tends to be hardly sinterable, it may be effective in respect of (Y, Ce)-TZP sinterable at lower temperatures to use easily sinterable hydrolyzed fine powders.

## 3.3. HIP Treatment

Figure 8 shows the changes in the density of a sintered compact before and after HIP treatment. No sufficient density was obtained by HIP treatment in the presintered compacts whose density was less than  $5.75g/cm^3$  (the relative



Fig. 8. Density of (4Y, 4Ce)-TZP before and after HIP.



Fig. 9. Bending strength of (4Y, 4Ce)-TZP presintered at various temperatures for 2h in air, then hot isostatically pressed at 1500°C and 147MPa for 0.5h.

density was 94% when the true density of (4Y, 4Ce)–TZP obtained from the lattice constant<sup>17,18</sup>) was calculated as 6.12g/cm<sup>3</sup>). This was attributed to open pores being retained in the pre-sintered bodies. The density up to an almost theoretical level was achieved by HIP treatment in the pre-sitered compact whose density was above 5.75g/cm<sup>3</sup>. This was more or less in agreement with the relative density (above 95%) required for HIP treatment in alumina, ferrite, etc.

Figure 9 shows the relationship between the flexural strength and preliminary sintering temperatures, whilst under HIP treatment temperature of 1500°C. It was clear from this figure that the highest strength was obtained when the preliminary sintering temperature was 1450°C at 1100MPa.

**Figure 10** shows the bending strengths at 1400°C and 1500°C for HIP treatment when the preliminary sintering temperature was fixed to 1400°C. There was less scattering in the strength at 1500°C for HIP treatment than at 1400°C. However, it was presumably favorable to obtain smaller particle sizes of the sintered compact by performing HIP at lower temperatures when the thermal stability of TZP was taken into consideration.

Figure 11 shows the microstructure of a HIP-treated compact. The particle size of a compact treated with HIP at 1500°C was about  $1.5 \sim 2$  times more compact than compared to treatment at 1400°C, equally with a microstructure being composed of uniform particle sizes. Figure 12 shows the surface of typical fracture of a HIP-treated compact. This fracture was similar to that of glasses in that it formed vaguely observed images of flat mirror in a peripheral area of its starting point as well as of mist in its outer area and hackle in its further outer area. Figure 12(a) shows the defects in the neighborhood of the surface or those deriving from a damage on the surface, but those derived from rough and abnormal particles were also observed as shown in Fig.12(b). Figure 12(d) is an EMPA photograph in the neighborhood of abnormal particles.

The abnormal particles shown in this figure were distinguished from others in view of the distributional condition of Ce. Since less Zr was distributed and more Ce was found in these abnormal particles, it was surmised that they were zirconia particles with ubiquitous Ce elements generated



Fig. 10. Bending strength and bulk density of (4Y, 4Ce)-TZP presintered at 1400°C for 2h in air, then hot isostatically pressed at various temperatures for 0.5h.

from the precipitates of the synthesized materials. As shown in Fig.12(a), the fracture of HIP-treated compacts mostly originated in the defects or damages in the surface neighborhoods.

While a sintered body of (Y, Ce)-TZP fired in the atmosphere and was slightly yellowish white with transparency, a HIP-treated, sintered body was blackish brown in colour affected by the atmosphere. The color depended on the temperatures for HIP treatment was more darker when treated at 1500°C than when treated at 1400°C. (Y, Ce)-TZP which was blackish brown when treated by HIP for the current experiment turned white when treated with heat above 1000°C in the atmosphere. A trace amount of carbon was contained in a compact sintered in the atmosphere of (CO + Ar) when (Y, Ce)-TZP turned blackish brown in color after HIP treatment for the current experiment using a graphite heater. CeO<sub>2</sub> contained in TZP as a stabilizer was partially reduced in the atmosphere of (CO + Ar) and changed from CeO<sub>2</sub> to Ce<sub>2</sub>O<sub>3</sub>. This was conceivably an important factor.

Since the conditions for preliminary sintering and HIP treatment were studied in Y-TZP from various angles, the strength even exceeding 1500MPa has been achieved.<sup>19,20)</sup> As for TZP containing  $CeO_2$ , the strength improvement from 500MPa to 550MPa by HIP treatment in 12 Ce-TZP has been reported,<sup>16)</sup> but no marked increase was seen in Y-TZP. In the current experiment, the mean bending strength of (4Y, 4Ce) increased from 840MPa to 1100MPa when treated by HIP and thus the strength improved by about more than 20%.



Fig. 11. SEM photographs of the fracture surface of (4Y, 4Ce)-TZP presintered at 1400°C for 2h in air, then hot isostatically pressed at (a) 1400°C and (b) 1500°C.



**Fig. 12.** SEM photographs of fracture origins of (4Y, 4Ce)-TZP fabricated by a hot isostatic pressing. (a) The neighborhood of fracture origin (defect),

- (b) The neighborhood of fracture origin (coarse grain),
- (c) A magnification view of (b),
- (d) Ce X-ray image of (c).

# 4. Summary

Zirconia fine powders containing yttria and ceria as stabilizers, synthesized by the hydrolysis technique, were used for the preparation of (Y, Ce)-TZP by sintering with normal pressure and HIP treatment in an attempt to study the strength, thermal stability and microstructure of a sintered compact and the conditions for HIP treatment. The following were the results thus obtained.

- The bending strengths of a compact sintered with normal pressure at 1500°C were 840MPa and 860MPa in (4Y, 4Ce) and (2.5Y, 5.5Ce), respectively, but even as high as 1000MPa in (2.5Y, 4Ce) which was well comparable with that of 3Y-TZP.
- 2) No tetragonal to monoclinic phase transformations were recognized in (4Y, 4Ce) and (2.5Y, 5.5Ce) sintered at 1500°C while being retained in the atmosphere at 250°C

for 1500hrs with greater thermal stability than that of 3Y-TZP.

- 3) The strength of (4Y, 4Ce) was improved, standing about 20% higher than that of a compact sintered with normal pressure when treated by HIP at both 1400°C and 1500°C.
- The fracture of HIP-treated compacts mostly originated in the defects and damages in the neighborhood of the surface of the compact.

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# Pyroelectric Properties of c-Axis Oriented [(1-x)PbTiO<sub>3</sub> + xMgO] Thin Films Prepared by rf-Magnetron Sputtering Method

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Pyroelectric properties of c-axisoriented thin films with compositions of  $[(1-x) PbTiO_3 + xMgO]$ , where x=0.015 ~ 0.090, prepared by rf-magnetron sputtering method were investigated. With increasing Mg content and film thickness, the relative dielectric constant & increased and the dielectric loss tand deceased. The effects of film thickness on them were also seen. Results of measuring the pyroelectric coefficient P showed that the direction of natural polarization is in the upward direction perpendicular to the [100]-oriented Pt thin film on a (100) MgO single crystal substrate. The Curie point Tc lowered linearly with increasing Mg content. The lowering rate was about 11.8°C/mol%(MgO), i.e. in good agreement with that for PMT single crystals. It was found that these films have large P value independent of temperature ranging from room temperature to about 300°C after undergoing a heating and cooling process beyond Tc. F.M. and F.M.D\* exhibited the highest values for an x=0.045 PMT thin film of 2µm thickness reaching 1.5ö10<sup>-10</sup>Ccm/J and 2.1×10<sup>-8</sup>Ccm/J, respectively. The above-mentioned values were about 2.5 and 2.6 times larger than those of the PMT single crystals, respectively. Both the above values were about 1.5 times larger, compared to those of Pb<sub>1-x</sub>L<sub>ax</sub> Ti<sub>1-x/4</sub>O<sub>3</sub> [PLT] thin films. [Received May 28, 1990; Accepted September 26, 1990]

**Key-words:** Pyroelectric property, Degree of c-axis orientation, Relative dielectric constant, Dielectric loss, Natural polarization, Figure of merit

# 1. Introduction

PbTiO<sub>3</sub><sup>1)</sup> at the degree of c-axis orientation of  $\alpha$ =0.8 and the thin film solid  $\alpha$ =0.9 solution Pb<sub>1-x</sub>La<sub>x</sub>Ti<sub>1-x/4</sub>O<sub>3</sub><sup>-2.3)</sup> with x=0.10 (hereinafter referred to as "PLT"), with La being substituted for a part of Pb of the former material, has been identified as a prospective pyroelectric material, whose figures of merit, F.M. and F.M.D\*, are approximately 2.7 and 3 times that of PbTiO<sub>3</sub> ceramics<sup>4)</sup> respectively.

Takayama, et al., <sup>1-3.5)</sup> having employed the phenomena of shrinkage of the a-axis and expansion of the c-axis due to compressional stress during the formation process of these films, reported the occurrence of a so-called a "natural polarization" where respective polarizations fall equally in the perpendicular direction against the substrate during the preparation as well as the various properties of the pyroelectric thin films involving this phenomenon, and on the merit of this natural polarization. They proposed in this report that these films should be applicable as sensor elements without requiring the polarization treatment which are generally called for when using ceramic materials.<sup>4)</sup>

On the other hand, it is generally known that when PbTiO<sub>3</sub> ceramics<sup>4)</sup> not in a state of the natural polarization are heated up to the temperatures above the Curie points Tc and then cooled to the room temperature, they lose their ability to function as sensor elements, being depolarized into the state of multidomain. No studies have been made, however, on the possible changes that may occur when naturally polarized ferroelectric thin films undergo the thermal history described above. In this study, the authors have attempted to develop further the merits of the natural polarization reported by Takayama, et al.<sup>1-3,5)</sup> By this, the authors thought it possible to materialize a truly dependable infrared sensor coupled with a high performence. In the previous report,<sup>6,8)</sup> the authors described the significant effect that a solid solution of Mg ions had on the acceleration of crystal growth and crystal perfection, as well as on the improvement in resistance and pyroelectric properties. With a view to realizing miniaturization of sensor elements with thiner films, the authors also described in the previous report<sup>9)</sup> the methods of manufacturing c-axis-oriented thin films of [(1x)PbTiO<sub>3</sub> + x MgO] (x=0.015 ~ 0.090) (hereinafter referred to as "PMT").

The object of the current report dose not lie, as is taken from PLT thin films of Takayama, et. al.,<sup>2,3,5)</sup> in increasing the pyroelectric coefficient P due to a decline in Tc of thin films. It is however, expected an increase in P whose composition is quite close to pure PbTiO<sub>3</sub>, with c-axis-oriented disposition and favorable crystallizability as the cause.<sup>9)</sup>

Some PMT thin films analogous to those prepared in our previous report<sup>9</sup> were used as samples for the detailed investigations carried out in our current study on the presence or absence of natural polarization. The changes of P at Tc after the previously-mentioned thermal history and the pyroelectric properties were also examined, referring further to the usefulness of these thin films as pyroelectric materials.

# 2. Experimental Procedure

# 2.1.Measurement Samples

The samples used in the current experiment were PMT thin films in a composition of  $[(1-x)PbTiO_3 + xMgO]$  (x=0.015 ~ 0.090), which were prepared by the method previously reported<sup>9)</sup> and provided with upper and lower

electrodes.

#### 2.2. Measurement of Pyroelectric Constants

The constants  $\varepsilon_r$ , tan $\delta$  and P were determined using the standard methods for measuring static pyroelectric properties.<sup>10,12</sup> Fig.1 is schematic diagram of the circuit used for the automatic measurement of static pyroelectric properties in the current experiment. Although the diagram presents two systems, namely pA meter and LCR meter, for drawing conveniences' sake, the actual measurements was confined to the use of only one system by switching the HP-IB cable every time.

2.2.1. Measurement of Specific Inductive Capacitance,  $\epsilon_r$ , and Dielectric Loss, tan $\delta$ 

After the sample was set in an electric furnace (RIGAKU-made ET8411H),  $\varepsilon_r$  and tan  $\delta$  were measured by an LCR meter (YHP-made 4274A) at room temperature with the frequency fixed to 1kHz and the power at about 25V/cm (actual value);  $\varepsilon_r$  was obtained by the following equation:

$$\varepsilon_r = Cd/S\varepsilon_0 \quad \dots \quad (1)$$

where, C is the electrostatic capacity [F], d is the thickness of the measurement sample [cm], S is the surface area of an electrode [cm<sup>2</sup>], and  $\varepsilon_0$  is the vacuum dielectric constant (8.854×10<sup>-14</sup>)[F/cm].

### 2.2.2. Measurement of Pyroelectric Coefficients P and Curie Temperature Tc

A sample was placed in an electric furnace, whose pyroelectric current,  $i_p$ , and temperature changes, dT/dt, ranging from room temperature to 600°C, were measured by a picoammeter (YHP model 4140B). Values of P in the neighborhood of room temperature were obtained from the mean values of  $i_p$  during the temperature changes ranging from 15°C to 70°C as well as from dT/dt. Temperature changing, both rising and declining, was set at the velocity of approximately 3°C/min in any temperature range. Using the above parameters, P could be derived from the following equation:

$$P = i_{\rm p} \cdot (\,\mathrm{d}t/\mathrm{d}T\,)/S \,\left[\,\mathrm{C/cm^2K}\,\right]\,\ldots\,\ldots\,(2)$$

where  $i_p$  is the pyroelectric current [A], S is the surface area of an electrode [cm<sup>2</sup>], T is the temperature [K] and t is the time [s].

P's temperature characteristics within the range from room temperature to 600°C were examined so as to define the temperature where P showed the maximum value as Tc.

The temperature of as-sputtered samples was varied from



Fig. 1. Schematic diagram for automatic measurement of static pyroelectric properties.

room temperature to 600°C above Tc in an attempt to investigate the effect of thermal histories when these elements were used as temperature sensors. Furthermore, the changes of P during the course of three temperature cycles (heating and cooling) were measured to evaluate the dependability of each material as a practical sensor element.

#### 2.2.3. Derivation of Figures of Merit (F.M. and F.M.D\*)

Pyroelectric materials are generally evaluated as infrared sensors using  $\epsilon_r$ , tan  $\delta$ , and P which were determined by the above measurements. Indexes such as F.M. and F.M.D\* which are often used in case of the evaluation were obtained from the following equations. F.M. is a performance index corresponding to Rv, voltage sensitivity, while F.M.D\* corresponds to D\*, specific detectivity, namely a ratio of sensitivity to noise.

$$F.M. = P/(C_v \varepsilon_r) [C cm/J] \dots (3)$$

F.M.D<sup>\*</sup> =  $P / \{C_v(\varepsilon_r \tan \delta)^{1/2}\}$  [C cm/J] . . . (4)

where the volume specific heat Cv=3.2J/cm<sup>3</sup>K.<sup>13)</sup>

# 3. Experimental Results and Discussion

Various pyroelectric constants of PMT thin films were measured in accordance with the above-mentioned experimental procedures. A detailed study concerning the pyroelectric properties thus determined is reported hereunder, centering on the composition and film thickness dependability.

# 3.1. Composition Dependency of Relative Dielectric Constant $\epsilon_r$ and Dielectric Loss tan $\delta$

Figure 2 shows the composition dependency of  $\varepsilon_r$  and tan $\delta$ . As shown in this figure,  $\varepsilon_r$  slightly increases along with increases of Mg. This tendency is quite similar to the results of PLT thin films.<sup>2,3,5</sup> As reported previously,<sup>9</sup> the  $\alpha$  value does not depend on the composition of thin films, leading to the thought that  $\alpha$  has only a negligible effect to the results of the current experiment. As Mg increased, tan $\delta$ 



Fig. 2. Relative dielectric constant  $\varepsilon_r$  and dielectric loss tan $\delta$  as a function of PMT film composition.

showed a linear decrease. Tan $\delta$  remained in a range of 0.8  $\sim 1.3\%$  for this 1µm thick sample.

# 3.2. Film Thickness Dependency of Relative Dielectric Constent $\epsilon_r$ and Dielectric Loss tan $\delta$

Figure 3 shows the thin film dependence of  $\varepsilon_r$  and tan $\delta$ for PMT thin films with x=0.045. With  $\varepsilon_r$  increasing slightly along with increases in film thickness, tand decreased markedly in inverse proportion to the increases in the film thickness. These changes are both associated with the microstructure of the thin films; and as shown in (b) and (c) of Fig.8 in our previous report,9) they may be attributable to a discontinuous insular structure<sup>14</sup> which has gradually shifted to a continuous one. In other words, the microisles are scattered when the films are thin, and polarization levels become lower because of low film densities. This might lead to the explanation that  $\varepsilon_r$  decreases, reflecting these situations, while tand markedly increases due to the existence of insular film interfaces. However, in view of Equation (3) and (4) referred to in Section 2-2-3, it may be desirable to have low  $\varepsilon_{\tau}$  and tan $\delta$  levels for pyroelectric materials. It is known also that the total noise of a pyroelectric-type infrared sensor consists of temperature



Fig. 3. Relative dielectric constant  $\varepsilon_r$  and dielectric loss tan $\delta$  as a function of thickness on *x*=0.045 PMT thin films.



Fig. 4. Pyroelectric coefficient P as a function of PMT film composition.

noise, tan $\delta$  noise, and input resistance noise, and that tan $\delta$  noise is dominant in point-type infrared sensors of f>20Hz.<sup>5</sup> Thus, infrared sensors with high resolution can be expected when materials such as these thin films with low tan $\delta$  levels are used as elements.

### 3.3. Pyroelectric Coefficient, P, and Curie Temperature, Tc

# 3.3.1. Natural Polarization of PMT Thin Films

When the sample concerned was treated with different temperatures in accordance with the experimental method described in Section 2-2-2, the pyroelectric current,  $i_p$ , was detected in a perpendiculer direction against PMT thin film/[100]–oriented Pt thin film/(100) MgO single crystal substrate. As described later, the pyroelectric coefficient P obtained by substituting  $i_p$  in Equation (2) was similar to the theoretical value of P derived by Iijima, et al.<sup>15</sup> Based on the above-mentioned findings, it was concluded that the golarization of these thin films was natural,<sup>1,2,3,5</sup> being oriented in a single direction at the time of film formation.

### 3.3.2. Composition and Film Thickness Dependency of Pyroelectric Coefficient P

**Figure 4** shows the composition dependency of the coefficient P for this sample. An increase of P and a decrease of  $\varepsilon_r$  are required to obtain large figures of merit namely F.M. and F.M.D<sup>\*</sup> For the ferroelectric thin films, P has principally, been increased by increasing  $\alpha$  and decreasing Tc.<sup>2,3)</sup> However, as mentioned earlier, the purpose of the present study is to obtain large P, F.M. and F.M.D.<sup>\*</sup> values by contemplating without decreasing the Curie temperature, Tc to increase the  $\alpha$  level. As described later, it is necessary to reduce the *x* concentration (solid solution volume of MgO) in order to maintain the Tc level.

Paying attention to Fig.4, based on these requirements, it is clear that P increased significantly in a range of x=0.015~ 0.045. On the other hand, P was nearly in equilibrium against the increases in the Mg content increased, so far as in a range of x=0.045 to 0.090. Since P exhibited a clearly convex curve in the neighborhood of x=0.045, the optimum condition for the composition x in order to obtain high Tc and large P levels is considered to be x=0.045. Furthermore, it is conceivably possible to obtain the P levels ( $6.5 \times 10^{-8}$ C/cm<sup>2</sup>K) as high as for PLT thin films<sup>5)</sup> by increasing the value of  $\alpha$ .

**Figure 5** shows the film thickness dependency of P for PMT thin films of *x*=0.030 and 0.045. P decreased for the both compositions in reverse proportion to the increases in



**Fig. 5.** Relationship between pyroelectric coefficient P and thickness on *x*=0.045, and *x*=0.030 PMT thin films.
the film thickness. This is presumably because  $\alpha$  exhibited almost no dependence on film thickness mentioned earlier. When the characteristic curves P for the both compositions are compared, they are nearly in coincidence in case of the film thickness of 4µm; however, it is clear that in a situation of x=0.045, P is at a higher level in a range of thicknesses between 1 ~ 3µm. In case of x=0.045 and the film thickness of 2µm, the result was P=5.4×10<sup>-8</sup>c/cm<sup>2</sup>K.

### 3.3.3. Thermal Properties of Pyroelectric Coefficient P, and Curie Temperature Tc

**Figure 6** shows the thermal properties of P in an as-sputtered PMT thin film 1 $\mu$ m in thickness. It is clear from this figure that the temperature indicating the maximum level of P, namely Tc, decreases as Mg increases, and the value of P of Tc varies notably, depending on the compositions. Thus, it is predicted that the spontaneous polarization of this sample, Ps, also depends greatly on the composition. **Figure 7** shows the relationship between Tc and composition. The data of PMT single crystals referred to in the previous report<sup>7)</sup> are also shown for comparison.

Tc levels of PMT thin films and single crystals decreased linearly in accordance with increases in Mg, both at the nearly equivalent rates of about  $11.8^{\circ}$ C/mol% (MgO) for the former and about  $11.4^{\circ}$ C/mol% (MgO) for the latter. The following study is based on these results. Since it is beneficial to broaden the temperature zone to let sensor elements functionate, it is considered also important to minimize the *x* values (solid solution volume of MgO) to maintain high Tc levels against lowering. Crystals oriented parallel to the c-axis of PMT thin films and single crystals may be regarded crystallographically as almost identical



Fig. 6. Relationship between pyroelectric coefficient P and temperature on various PMT thin films.



Fig. 7. Relationship between the Curie point  $T_c$  and PMT film composition.

from the result of lowering rates. Meanwhile, when the Tc of thin films of the same composition was compared to that of single crystals, the Tc of thin films was found to be higher by about 56°C. This may be attributable to the marked inner stresses and distortions<sup>5</sup> that have been generated inside the thin films during their formation; detailed discussions of this matter, however, will be left for future.

### 3.3.4. Changes in Pyroelectric Coefficient P due to Thermal History

When the thermal properties of P for the as-sputtered PMT thin films were measured in the current experiment, a current reversals were observed twice in the thin films of x=0.015 and 0.030 at the temperatures below 400°C. Figure 8 shows the thermal properties of P for as-sputtered PMT thin films with x=0.015, including those annealed in a range from room temperature to 600°C. In this figure, the current reversals can be observed at 322°C and 364°C. However, no current reversal was observed in the thin film cooled to room temperature after it was heated once to a temperature beyond the Tc level. This phenomenon is considered due to the crystalline defects such as numerous vacancies, etc., which existed in the thin films, being absorbed in the crystal grain boundary by annealing.

Figure 9 shows the changes and composition dependency of P at Tc for samples subject to different heating and cooling cycles. For the as-sputtered films, P at Tc, namely



Fig. 8. Relationship between pyroelectric coefficient P and temperature on as-sputtered, and annealed PMT thin film with x=0.015.



Fig. 9. Pyroelectric coefficient  $P_{Tc}$  at the Curie point as a function of PMT film composition.

 $P_{Tc}$ , reached the maximum level at x=0.045.  $P_{Tc}$  was found to decrease significantly, depending on thermal histories up to the temperatures above 600°C. Particularly a significant decrease was recognized in the composition exceeding x=0.060. This may be explained by the partial easing of the distortions created from the differences between the thermal expansion coefficients of the Pt thin film electrode/MgO substrate and the PMT thin film during the film formation. As shown in the figure, since almost no changes of  $P_{Tc}$  were recognized with the second and subsequent thermal cycles, it was concluded that the inner film distortions were partially reduced when the temperature of the thin films was raised once beyond Tc before cooling. In other words, it is believed that the c-axis of the tetragonal system changes from a paralle to a vertical direction against the substrate simultaneously with cooling. In addition, the magnitude of distortion reduced during the first heating and cooling process largely depends on the composition; it is assumed that once reduced, the distortions are only insignificantly reduced again after the second and subsequent processes. It was found from Figs.8 and 9 that these thin films are highly reliable pyroelectric materials with large P levels, showing almost no temperature dependency in a range from room temperature up to about 300°C even after undergoing the heating and cooling process beyond Tc.

### 3.4. Figures of Merit (F.M. and F.M.D<sup>\*</sup>)

F.M. and F.M.D<sup>\*</sup> are the performance indexes of pryoelectric materials corresponding to  $R_v$ , voltage sensitivity for the former, while D<sup>\*</sup>, specific detectivity taken noise into consideration for the latter. F.M. and F.M.D<sup>\*</sup> were derived from of  $\varepsilon_r$ , tanð and P obtained from measuring



**Fig. 10.** Figure of merit F.M. for voltage responsivity and F.M.D<sup>\*</sup> for specific detectivity as a function of PMT film composition.

by using Equations (3) and (4). Figure 10 shows the composition dependency of F.M. and F.M.D.<sup>\*</sup> It is clear from the figure that F.M. and F.M.D<sup>\*</sup> exhibited the high values in case of x=0.045. Figure 11 shows the relationship between figures of merit and the film thickness on x=0.045PMT thin films. It was made from this figure that F.M. and F.M.D<sup>\*</sup> attained the maximums for the sample films of  $2\mu$ m thickness, indicating  $1.5 \times 10^{-10}$ Ccm/J and  $2.1 \times 10^{8}$ Ccm/J, respectively.

As shown in **Table 1**, F.M. and F.M.D<sup>\*</sup> for the thin film samples concerned attained the performances improvement respectively about 2.5 and 2.6 times, compared with those for PMT single crystals<sup>7,8)</sup> and both about 1.5 times higher than that of PLT thin films.<sup>2,3,5)</sup>

We have described in this paper pyroelectric properties of c-axisoriented PMT thin films with favorable crystallizability, whose composition is quite close to that of pure PbTiO<sub>3</sub>, and have also clarified that these thin films are useful materials for highly reliable point-type infrared sensors due to their high P levels with almost no temperature dependence in a range from room temperature to about 300°C, without depolarizing even when they should encounter an abrupt rise in temperatures beyond Tc.

### 4. Summary

Pyroelectric properties of c-axis oriented thin films with compositions of  $[(1-x)PbTiO_3+xMgO]$  (x=0.015 ~ 0.090) prepared by the rf-magnetron sputtering method were studied, leading to the following results:



Fig. 11. Figure of merit F.M. and F.M.D\* as a function of thickness on x=0.045 PMT thin films.

Table 1. Comparison of pyroelectric properties on ferroelectric materials of PbTiO<sub>3</sub> system.

Materials	Tc (°C)	ε,	tanδ (%)	ρ (Ω・cm.)	P (×10 <sup>-8</sup> C/caftK)	Cv <sup>13)</sup> (J/cmłK)	F.M. (X10 <sup>-10</sup> Ccm/J)	F.M.D.* (X10 <sup>-8</sup> Ccm/J)
PMT thin film with x=0.045,2μm thickness	547	112	0.6	5.4×1014	5.4	3.2	1.5	2.1
PMT single crystal with x=0.045 <sup>7).8)</sup>	480	132	0.8	8.9×10 <sup>11</sup>	2.7	3.2	0.6	0.8
PLT thin film with x=0.10, α=0.9 <sup>2).3).5)</sup>	330	200	1.0	_	6.5	3.2	1.0	1.4
PbTiO <sub>3</sub> thin film with $\alpha = 0.8^{11, 51}$	525	97		1.0×1010	2.5	3.2	0.8	_

- 1)  $\epsilon_r$  of these thin films increased as Mg and film thickness increased.
- 2) Tan $\delta$  of these thin films decreased in reverse proportion to increases in Mg and film thickness.
- 3) P of the thin films measured in the current experiment confirmed natural polarization in the upward direction perpendicular to the [100]-oriented Pt thin film/(100) MgO single crystal substrate.
- 4) Tc of these thin films linearly decreased with increases in Mg. The lowering rate was approximately 11.8°C/mol% (MgO), which was in good agreement with that of PMT single crystals.
- 5) It was found that these thin films had large P levels with almost no temperature dependence in a range from room temperature to about 300°C even after a heating and cooling process beyond Tc.
- 6) F.M. and F.M.D\* reached the maximum levels of 1.5×10<sup>-10</sup>Ccm/J and 2.1×10<sup>-8</sup>Ccm/J, respectively, for the sample with x=0.045 and 2µm thick. Their values were estimated at about 2.5 and 2.6 times those of PMT single crystals and about 1.5 times those of PLT thin films.

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# Structure and Physical Properties of Non-Alkali Multicomponent Glasses

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Non-alkali multicomponent glasses in the system SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO-ZnO-TiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> were prepared by the melt quenching method. The composition range was (in wt%), SiO<sub>2</sub>=32.0-38.0, Al<sub>2</sub>O<sub>3</sub>=9.0-18.0, CaO=17.0-23.0, ZnO=12.0-18.0, TiO<sub>2</sub>=10.0-19.0, and B<sub>2</sub>O<sub>3</sub>=2.0-7.0. Composition dependencies of glass transition temperature T<sub>a</sub>, softening temperature T<sub>d</sub>, thermal expansion coefficient  $\alpha$ , and density  $\rho$  were investigated. It was found that an increase in SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> or CaO content increases the  $T_{\rm g}$  and  $T_{\rm d}$  but an increase in ZnO, TiO\_2 or  $B_2O_3$ content decreases these characteristic temperatures. The thermal expansion coefficient decreased with an increase in SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZnO, TiO<sub>2</sub> or B<sub>2</sub>O<sub>3</sub> content, but increased by the addition of CaO. It was speculated that alumina and titania are combined with CaO to produce AlO<sub>4</sub> or TiO<sub>4</sub> tetrahedra, which help SiO<sub>2</sub>-deficient compositions to form a rather stable glass network. [Received June 11, 1990; Accepted August 31, 1990]

**Key-words:** Non-alkali glass, Glass transition temperature, Softening temperature, Density, Thermal expansion

### 1. Introduction

Glasses used in dielectric layers of hybrid IC elements and as glazing glass for thermal heads should be heat resistant up to 900°C, demonstrate an insulating resistance above  $10^{12}$ , have a dielectric constant below 13 and a sufficient migration resistance to control the diffusion of conductor and resistor materials. To satisfy these requirements, nonalkali borosilicate glasses are generally used mainly in combination with alumina ceramics; with conductors made of Ag, Ag-Pd, Au or Ni; with or low-resistance materials such as RuO<sub>2</sub>. By adjusting the glass composition, various properties can be modified; in particular thermal properties such as the glass transition point, softening point and coefficient of thermal expansion can be controlled such that the glasses can be used for specific applications.

Cabal glass, CaO-B<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> (CaO: 10.5 to 44.4mol%, B<sub>2</sub>O<sub>3</sub>: 33.3 to 78.9mol%, Al<sub>2</sub>O<sub>3</sub>: 8.3 to 25mol%) having a high insulation resistance of above  $10^{11}$  at 450°C, has been studied in detail by Owen<sup>11</sup> and Hirayama.<sup>21</sup> Searstone et al. reported on the structure and water-resisting properties of a CaO-B<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass (CaO: 25mol%, B<sub>2</sub>O<sub>3</sub>: 10 to 45mol%, Al<sub>2</sub>O<sub>3</sub>: 25mol%, SiO<sub>2</sub>: 5 to 40mol%) which was prepared adding SiO<sub>2</sub> to improve the chemical resistance of the Cabal glass.<sup>31</sup> Unfortunately this glass exhibited some undesirable properties such as the evaporation of B<sub>2</sub>O<sub>3</sub> during melting, the erosion of furnace materials, and an unfavorable water resistance. Thus, this study attempted the development of a non-alkali glass having a new composition which would control excessive reactions when used in combination with materials of conductors, resistors and so on.

### 2. Purpose

Using CaO-B<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass system as a base, we replaced the B<sub>2</sub>O<sub>3</sub> mostly with ZnO and added TiO<sub>2</sub> as a nuclei producing agent to make an SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO-ZnO-TiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glass system. Using this system, we studied the effects of the different components on the properties and structure of the system by varying the concentration of the components.

### 3. Experimental Method

#### 3.1. Preparation of Glass

Starting materials for the preparation of the glass were quartz sand (99.8% SiO<sub>2</sub>), aluminium hydroxide (99.8% Al(OH)<sub>3</sub>), calcium carbonate (99.5% CaCO<sub>3</sub>), zinc oxide (99.5% ZnO), titanium dioxide (99.9% TiO<sub>2</sub>), and boric acid (99.8% H<sub>3</sub>BO<sub>3</sub>). Materials were weighed in accordance with desired compositions to produce about 300g of glass melt, and dry mixed for 20min in a V-type stainless steel mixer having a capacity of 1 liter. To melt the glass, a 10% rhodium containing platinum crucible having a capacity of 300cc was charged with one-third of the batch in 20-min intervals and heated for 2hrs at 1450°C in an electric furnace (kanthal super heat generator). To obtain homogeneity, the melt was thoroughly stirred twice with a platinum stirrer while being heated. The melted glass was poured onto an iron plate, molded into a disk, cooled gradually, and cut into specimens for measurement of properties.

#### 3.2. Composition

The base glass composition in terms of weight percentage (mol%) was SiO<sub>2</sub>: 35(39.8), Al<sub>2</sub>O<sub>3</sub>: 15(10.1), CaO: 20(24.4), ZnO: 15(12.6), TiO<sub>2</sub>: 13(11.1) and B<sub>2</sub>O<sub>3</sub>: 2(2). We made 13 additional specimens by varying the component concentrations by 3 to 6 weight %. They are shown in **Table 1** in weight% and mol%.

Figure 1 shows the glass regions of the three-component system:  $SiO_2$ - $Al_2O_3$ - $CaO^{4)}$ . If the glass in the present study is considered to be a quasi-four-component system  $SiO_2$ - $Al_2O_3$ -CaO- $(ZnO+TiO_2+B_2O_3)$ , the composition of  $SiO_2$ - $Al_2O_3$ -CaO ratio can be plotted as in the figure. The  $\bullet$  represents the composition of the base glass and the  $\bigcirc$  are

Table 1. Glass composition in wt% (mol%). Glass No. 0 indicates the base glass. Each component was changed normally in ±6wt% range.

Glass No.		0	1		2		3		4		5		6	
	Bas compo	ic sition	+3w Si	t% D <sub>2</sub>	-3w Si	t% 0 <sub>2</sub>	+ 3 w A 1	t% ₂03	-3w A 1	t% 203	-6w A1	t% 203	+3w1 Cat	t%)
	wt%	mo1%	wt%	mo1%	wt%	mo1%	wt%	mo1%	wt%	mo1%	wt%	mo1%	wt%	mo1%
Si0 <sub>2</sub>	35.0	39.8	38.0	43.0	32.0	36.7	33.7	38.9	36.2	40.8	37.5	41.7	33.7	38.0
A1203	15.0	10.1	14.3	9.5	15.7	10.6	18.0	12.2	12.0	8.0	9.0	5.9	14.4	9.6
CaO	20.0	24.4	19.1	23.1	20.9	25.6	19.3	23.8	20.7	24.9	21.4	25.5	23.0	27.8
ZnO	15.0	12.6	14.3	11.9	15.7	13.3	14.5	12.3	15.5	12.9	16.1	13.2	14.5	12.0
Ti02	13.0	11.1	12.4	10.6	13.6	11.7	12.6	10.9	13.5	11.4	13.9	11.7	12.5	10.7
B 2 0 3	2.0	2.0	1.9	1.9	2.1	2.1	1.9	1.9	2.1	2.0	2.1	2.0	1.9	1.9

Glass No.		7	8		9		1	)	1	1	1	2	13	
	- 31	wt%	+ 3 w	t%	- 3 w	t%	+6 w 1	t%	+ 3 T	wt%	- 3 T	wt%	+ 5 w	t%
	00	10		r	611	, 				102		102	02	
	wt%	mo1%	wt%	mo1%	wt%	mo1%	wt%	mo1%	wt%	mo1%	wt%	mol%	wt%	mo1%
Si0 <sub>2</sub>	36.3	41.6	33.8	38.7	36.2	41.0	32.6	37.5	33.8	38.7	36.2	41.0	33.2	37.9
A1203	15.5	10.5	14.4	9.8	15.5	10.4	13.9	9.4	14.5	9.8	15.5	10.4	14.2	9.5
CaO	17.0	20.9	19.3	23.6	20.7	25.1	18.6	22.9	19.3	23.6	20.7	25.1	19.0	23.1
ZnO	15.6	13.2	18.0	15.2	12.0	10.0	14.0	11.9	14.5	12.2	15.5	13.0	14.2	12.0
Ti02	13.5	11.7	12.6	10.8	13.5	11.5	19.0	16.4	16.0	13.8	10.0	8.5	12.4	10.6
B <sub>2</sub> O <sub>3</sub>	2.1	2.1	1.9	1.9	2.1	2.0	1.9	1.9	1.9	1.9	2.1	2.0	7.0	6.9



Fig. 1. Glass regions by the melt quenching method in the SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-ZnO-B<sub>2</sub>O<sub>3</sub> system. Glass regions are shown in the SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub> molar ratio. Hatched area indicates the glass region by Imaoka,<sup>4)</sup> and × marks indicate the glass compositions by Searstone and Isard,<sup>3)</sup> and  $\bullet$  mark shows the base glass, and O marks the present glasses.

the other glass compositions. The shaded portion represents the glass region of the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO system obtained by Imaoka's air cooling.<sup>4)</sup> The x marks represent the glass compositions of the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO-BaO<sub>3</sub> glasses prepared by Searstone et al.<sup>3)</sup> The compositions in the present study are nearly in the center of the glass region of the 3-component system SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO and much closer to pure SiO<sub>2</sub> than the compositions prepared by Searstone et al.

### 3.3. Measurement of Properties

A thermomechanical analyzer (TMA8141BS Rigaku Denki) was used to measure thermal expansion employing a 10g load and a 10°C/min heating rate. Quartz bars were measured as reference samples, and the standard sample size was about 3×3×15mm. Glass transition temperature, Tg,

was obtained from the inflection point on the thermal expansion curve, and softening temperature, Td, was obtained from the maximum of elongation. We also obtained thermal expansion coefficient within the range 30° to 350°C from the gradients of the thermal curves. The reproduction accuracies of expansion coefficient, glass transition temperature and load softening temperature were ±1.0×10-7/°C, ±2.0°C and ±5.0°C respectively. For each comosition, properties were measured three times to obtain a mean value. Densities were measured by using glass samples about 8×8×2mm in distilled water at room temperature via the Archimedian method. The measuring accuracy was Viscosities of flat samples (10×2×50mm) ±0.01g/cm.3 were measured within the range  $10^9$  to  $10^{12}$  PaS (750° to 650°C) with a beam bending viscometer employing a heating rate of 3°C/min.<sup>5)</sup>

### 4. Test Results

#### 4.1. Measurement of Properties

Glass transition Temperature Tg, and softening temperature, Td, were respectively obtained from the inflection and yield points on the thermal expansion curves. **Table 2(a)** summarizes the results of measurements of Tg, Td, thermal expansion coefficient  $\alpha$ , and density  $\rho$ . Table 2(b) shows the change in measured valves of these properties due to a lwt% variation in each component.

### 5. Discussion

#### 5.1. Composition Dependence of Properties

Table 2(b) only shows variations in properties obtained with respect to the main component specificially varied from the base composition. However, it is not sufficient to

(0 0 1

correlate quantitative variation in properties (such as glass transition temperature, softening temperature, thermal expansion coefficient and density) with the variation in the specified component since (for example) an increase in SiO<sub>2</sub> by 1wt% also causes the percentages of other components to change. To analyze the effect of only one component, we specified compositions by their mol ratio of component MxOy to SiO<sub>2</sub>. This enabled us to keep the concentrations of other components constant (in samples other than Glasses #1 and 2) when varying the amount of the specified component. **Table 3** summarizes the variations in properties ( $\Delta$ Tg,  $\Delta$ Td,  $\Delta\alpha$ , and  $\Delta\rho$  from the base composition) due to a variation in composition ( $\Delta$ MxOy/SiO<sub>2</sub>) from the base composition.

**Figure 2** shows Tg, Td,  $\alpha$ , and  $\rho$  plotted against  $\Delta$ MxOy/SiO<sub>2</sub>. Tg,  $\alpha$ , and  $\rho$  all changed nearly linearly with a positive or negative gradient with  $\Delta$ MxOy/SiO<sub>2</sub>. Td exhibited a non-linear relationship with  $\Delta$ CaO/SiO<sub>2</sub>; the cause of this is not known.

Tg,  $\alpha$ , and  $\rho$  can be expressed as approximate functions of material compositions. Within the range of compositions tested as shown below, measurement errors are also indicated, at the end of the functions. The errors were within the measurement errors. Using these equations not only permits variations in properties with component variations to be understood directly, but also enables variations to be calculated easily. For Td, the signs of the component terms other than  $\Delta CaO/SiO_2$  were the same as those for Tg.

$$\Delta T_{g} / {}^{\circ}C = 26.9 (\Delta Al_2O_3 / SiO_2) + 29.4 (\Delta CaO / SiO_2) - 102 (\Delta ZnO / SiO_2) - 33.3 (\Delta TiO_2 / SiO_2) - 175 (\Delta B_2O_2 / SiO_2) \pm 0.9$$

$$10^{\circ}\Delta\alpha'^{\circ}C^{-1} = -28.0(\Delta A_{12}O_{3}'/SiO_{2}) + 41.8(\Delta CaO/SiO_{2}) + 9.8(\Delta TiO_{2}/SiO_{2}) + 9.8(\Delta TiO_{2}/SiO_{2}) \pm 1.3 \\ \Delta\rho/g \cdot cm^{-3} = -0.3(\Delta A_{12}O_{3}/SiO_{2}) \pm 0.2(\Delta CaO/SiO_{2}) + 0.8(\Delta ZnO/SiO_{2}) + 0.3(\Delta TiO_{2}/SiO_{2}) - 0.6(\Delta B_{2}O_{3}/SiO_{2}) \pm 0.008 \end{cases}$$

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#### 5.2. Contributions of Components to Properties

The results in Table 2(b) indicate that with increasing  $SiO_2$  and  $Al_2O_3$  concentrations, the transition temperature and the temperature softening point rose, while the expansion coefficient decreased. As the CaO content increased, the transition temperature and the softening temperature again rose, but the expansion coefficient increased. As the contents of ZnO and TiO<sub>2</sub> increased, the transition temperature decreased while the expansion coefficient slightly increased. With an increase in the  $B_2O_3$  content, the glass transition and the softening decreased as did the thermal expansion coefficient.

In general, glass transition temperature rises as the viscosity increases. To determine if the glasses in this system followed the same rule, we measured viscosities. **Figure 3** shows the low-temperature viscosities of several glasses in relation with temperature measured using a beam bending method.<sup>51</sup> As the Al<sub>2</sub>O<sub>3</sub> content increased from that in the base composition, the viscosity increased. Increases in SiO<sub>2</sub> or CaO, however, scarcely affected the viscosity. Adding TiO<sub>2</sub>, ZnO, or B<sub>2</sub>O<sub>3</sub> decreased the glass viscosity. These results suggested that changes in Tg correspond to viscosity changes.

Table 2(a). Compositional dependence of glass transition temperature  $T_{fs}$  softening temperature  $T_{ds}$  linear thermal expansion coefficient  $\alpha$  and room temperature density  $\rho$  of the glasses.

Glass No.	0	1	2	3	4	5	6	7	8	9	10	11	12	13
Tg/℃	672	675	668	674	671	669	676	669	665	680	667	669	674	649
Td∕℃	718	728	710	720	716	715	732	727	714	731	715	714	721	697
10 <sup>7</sup> α/°C <sup>-1</sup>	64.5	60.7	67.5	62.9	66.5	67.8	69.6	60.7	64.5	64.5	66.1	65.2	64.2	62.5
ρ/g·cm <sup>-3</sup>	3.11	3.06	3.16	3.09	3.13	3.14	3.13	3.09	3.17	3.06	3.15	3.13	3.08	3.03

Table 2(b). Glass property change caused by an 1wt% increase of additive component.

	+1wt%Si02	+1wt%A1203	+1wt%CaO	+1wt%Zn0	+1wt%Ti02	+1wt%B203
∆ Tg/℃	1.2	0.6	1.2	-2.5	-0.8	-4.6
∆ Td/℃	3.0	0.6	0.8	-2.8	-0.7	-4.2
10 <sup>7</sup> Δ α /°C <sup>-1</sup>	-1.1	-0.5	1.5	0	0.2	-0.4
$\Delta \rho / g \cdot cm^{-3}$	-0.017	-0.006	0.007	0.018	0.008	- 0.016

Table 3. Change in glass property with composition change  $\Delta M_x O_y/SiO_2$  from the base glass.

Glass No.	1	2	3	4	5	6	7	8	9	10	11	12	13
10 <sup>2</sup> Δ A1 <sub>2</sub> 0 <sub>3</sub> / Si0 <sub>2</sub>	-3.1	3.6	6.2	-5.7	-11.1	0	0	0	0	0	0	0	0
10 <sup>2</sup> ∆ Ca0 / SiO <sub>2</sub>	-7.4	8.8	0	0	0	12.0	-11.0	0	0	0	0	0	0
10 <sup>2</sup> ∆ Zn0∕ SiO <sub>2</sub>	-3.9	4.5	0	0	0	0	0	1.7	-7.2	0	0	0	0
10 <sup>2</sup> Δ TiO <sub>2</sub> / SiO <sub>2</sub>	-3.4	4.0	0	0	0	0	0	0	0	15.8	7.7	-7.2	0
10 <sup>2</sup> Δ B <sub>2</sub> O <sub>3</sub> / SiO <sub>2</sub>	-0.6	0.7	0	0	0	0	0	0	0	0	0	0	13.2
∆ Tg/℃	3	-4	2	-1	- 3	4	- 3	-7	8	- 5	- 3	2	-23
∆ Td/℃	10	- 8	2	- 2	- 3	14	9	-4	13	- 3	-4	3	-21
10 <sup>7</sup> ∆ α/°C <sup>-1</sup>	-3.8	3.0	-1.6	2.0	3.3	5.1	-3.8	0	0	1.6	0.7	-0.3	-2.0
Δρ/g·cm <sup>-3</sup>	-0.05	0.05	-0.02	0.02	0.03	0.02	-0.02	0.06	-0.05	0.04	0.02	-0.03	-0.08

One of the dominant factors determining level of viscosity is the activation energy of viscous fluidity which is the energy required to move one unit of the fluid, and is considered to be closely related to the bonding energy between atoms. Table 4 shows the single-bond strengths of the oxides concerned.<sup>6)</sup> While the Al-O single-bond strength in Al<sub>2</sub>O<sub>3</sub> is as large as 101-79kcal/mol, the Ti-O, Zn-O, and Ca-O single-bond strengths are smaller, 73-32kcal/mol. Although the B-O single-bond strength in B<sub>2</sub>O<sub>3</sub> is as large as 119kcal/mol, the effective bonding force is considered to be much smaller because B<sub>2</sub>O<sub>3</sub> glasses have a laminar structure at a low bonding level. However, there is no assurance that given a B<sub>2</sub>O<sub>3</sub> content as low as 2 to 7mol%, the B<sub>2</sub>O<sub>3</sub> glass will have such a laminar structure. If the B-O-B bond is severed by non-bridged oxygen resulting from the combination of B<sub>2</sub>O<sub>3</sub> and CaO, the mean bonding strength will decrease as B2O3 increases. This understanding of bond strengths implies that as SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> having high single-bond strengths increase, the glass transition temperature and the softening temperature rise. However, there is one exception: as CaO with low singlebond strength increased, viscosity scarcely decreased and the Tg point did not fall. This suggested that the addition of CaO resulted in something different from simply the production of a Ca-O bond. One of the factors that could explain this is the formation of a 4-coordinate Al via the reaction:  $[AIO_6]+CaO \ [AIO_4-Ca].^{7-12}$  The O<sub>2</sub> ions in CaO would be used to form Al-O-Al bonds, causing Ca-O bond to be broken. This explains that the addition of CaO prevents viscosity from decreasing.

#### 5.3. Glass Transition Temperature and Expansion Coefficient

An empirical relationship,  $\alpha \times Tg^2 \approx$  constant exists between the glass transition temperature and the expansion coefficient. For example, for typical oxide and chalcogen glasses  $\alpha \times Tg^2 \approx 5.8 K$  (absolute temperature).<sup>13)</sup> Figure 4 shows the relation between  $\alpha$  and Tg for the glass compositions in the present study along with the curve for  $\alpha \times Tg^2 = 5.8 K$ . Within the narrow range of composition variations in the present study, the above-mentioned relationship between  $\alpha$  and Tg held as the contents of SiO<sub>2</sub>



Fig. 2. Changes in glass properties from that of the base glass as a function of composition change  $\Delta M_aO_s/SiO_2$  ( $M_aO_p=Al_2O_3$ , CaO, etc). (a) denotes glass transition temperature  $T_{g_3}$  (b) softening temperature  $T_{d_3}$  (c) thermal expansion coefficient  $\alpha$ , and (d) density  $\rho$ .

and  $Al_2O_3$  varied; the relationship, however, did not hold when the CaO, ZnO and  $B_2O_3$  concentrations were varied.

#### 5.4. Density

If the addition of a component to a glass does not cause the coordination number of the ions in the glass to change, the density of the glass will generally increase upon adding a component having a higher density than that of the basic composition; conversely, the density will decrease upon adding a component having a lower density than the basic composition. Thus, by measuring variations in the density of the glass with respect to the densities of oxides added, additional information regarding the structure of the glass may be obtained.

**Table 5** shows the densities of added components in a crystalline or vitreous state. The density of the glass of the basic composition in this study was  $3.11g/\text{cm.}^3$  SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> vitrify independently, and their densities in either a vitreous or crystalline state are smaller than the vitreous density of the basic composition. Thus, the density of the glass was expected to decrease as long as the coordination of the added component did not change or changed slightly. The actual results were as expected. Al<sub>2</sub>O<sub>3</sub> in an independent crystalline state has a higher density of the glass to decrease. This can be understood assuming that Al<sub>2</sub>O<sub>3</sub> is combined with CaO to form an Al<sub>2</sub>O<sub>3</sub>-CaO structure whose



Fig. 3. Temperature - viscosity curves of the non-alkali multicomponent glasses measured by the beam-bending method.

density, 2.96g/cm<sup>3</sup>, is smaller than the density of the base glass. The coordination of the Al in the Al<sub>2</sub>O<sub>3</sub>-CaO structure is 4. On the other hand, CaO, ZnO, and TiO<sub>2</sub>, whose independent crystalline states have higher densities than the base glass, all caused the glass density to increase. If CaO selectively combines with Al<sub>2</sub>O<sub>3</sub> to form Al<sub>2</sub>O<sub>3</sub>-CaO, the glass density should decrease as the CaO concentration increases. The observed increase in density suggested that CaO also combined with TiO<sub>2</sub> or B<sub>2</sub>O<sub>3</sub> to form a structure having a higher density than the base glass. As described later, TiO<sub>2</sub> probably combines with non-bridged oxygen into a 4-coordinate TiO<sub>4</sub>. The measured density of this compound is not available and not shown in Table 5. As for ZnO, it may independently form a vitreous network.

#### 5.5. Structure

We now examine vitreous structure of the present system. Needless to say,  $SiO_2$  is a typical component which vitrifies independently. It has been reported that Al ions combine with alkaline or alkaline earth ions to form a 4-coordinate AlO<sub>4</sub> structure.<sup>7-12)</sup> In light of the results in 5.2 and 5.4, it

Table 4. Single bond strength in some oxides.<sup>6)</sup>

Bond	Single bond strength
	kcal.mol <sup>-1</sup>
B - 0	119
Si-0	106
A1-0	101-79
Ti-0	73
Zn - 0	36
Ca-0	3 2



Fig. 4. Plots of thermal expansion coefficient against glass transition temperature  $T_g$  obtained for the present glasses ( $\bullet$ ) along with some other glasses. Solid curve shows the calculated curve according to an equation  $\alpha$ :  $T_g^2$ =constant.<sup>(3)</sup>

Table 5. Comparison of densities among the related compounds, crystalline or vitreous.

Density/g·cm <sup>-3</sup>									
Compound	SiO <sub>2</sub>	A1203	CaO	A1203 · Ca0	ZnO	Ti02	B 2 0 3		
Crystalline	quartz 2.65	corundum 3.99	3.4	2.96	5.78	rutile 4.23	2.46		
Vitreous	2.2						1.84		

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is assumed that in the present system, Al<sub>2</sub>O<sub>3</sub> combines preferentially with CaO to form a 4-coordinate AlO<sub>4</sub> vitreous network. It is known that in the presence of alkaline earth ions, B and Ti ions become 4-coordinate.14-20) In a glass, CaO can possibly take on the following four roles: (1) if CaO can combine with B<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> to form 4-coordinate BO4 and AlO4 with bridging oxygens and 4-coordinate TiO<sub>4</sub> containing non-bridging oxygen;<sup>16-20)</sup> (2) it can contribute to bring non-bridging oxygens to  $SiO_2$ (=Si-O-Ca); (3) it can contribute to bring non-bridging oxygens to B<sub>2</sub>O<sub>3</sub> (=B-O-Ca); or (4) it can cause the formation of 6-coordinate TiO<sub>6</sub> containing non-bridging oxygen.<sup>17-20)</sup> It has also been shown that adding  $TiO_2$  to  $SiO_2$ glass causes the thermal expansion coefficient ( $\alpha$ ) to decrease.<sup>21)</sup> It is assumed that Ti<sup>4+</sup> ions in SiO<sub>2</sub> glass are 4-coordinate and solid dissolved in place of Si4+ ions.21-23) However, in this study as the TiO<sub>2</sub> content increased,  $\alpha$  also increased. Thus, it is more reasonable to assume that TiO<sub>2</sub> combined with CaO to form 4-coordinate TiO<sub>4</sub> containing non-bridging oxygens rather than being solid dissolved in the SiO<sub>2</sub> skeleton.

B<sub>2</sub>O<sub>3</sub>, on the other hand, can combine with CaO to form (1) 4-coordinate BO<sub>4</sub> or (2) 3-coordinate BO<sub>3</sub>. In the presence of a large excess of CaO (mol ratio CaO/B<sub>2</sub>O<sub>3</sub>=12), the composition curve of the 4-coordinate boron ratio N<sub>4</sub> for the B<sub>2</sub>O<sub>3</sub>-M<sub>2</sub>O system (M: alkaline metal)<sup>14</sup> indicates that B is more likely to form a 3-coordinate structure containing non-bridging oxygen than to become 4-coordinate. As for ZnO, since the zinc in crystalline ZnO is 4-coordinate, ZnO in glass can possibly exist as ZnO<sub>4</sub> tetrahedra.

### 6. Conclusion

- Non-alkaline SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO-ZnO-TiO<sub>2</sub>-B<sub>2</sub>O glasses were prepared by the melt quenching method in the composition ranges of SiO<sub>2</sub>: 32 to 38, Al<sub>2</sub>O<sub>3</sub>: 9 to 18, CaO: 17 to 23, ZnO: 12 to 18, TiO<sub>2</sub>: 10 to 19 and B<sub>2</sub>O<sub>3</sub>: 2 to 7wt%. The composition dependency of glass transition temperature Tg, softening temperature Td, thermal expansion coefficient α, and density d were studied while measuring low-temperature viscosities. Tg and Td increased as components SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO increased, and decreased as components ZnO, TiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> increased. Thermal expansion coefficient decreased as components SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and B<sub>2</sub>O<sub>3</sub> increased, and increased as components TiO<sub>2</sub> and CaO increased.
- Equations for quantitatively representing the variations in properties were formulated as a function of component

content.

3) We assumed that in glass, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> combined with CaO to form AlO<sub>4</sub> tetrahedra containing bridging oxygens or TiO<sub>4</sub> tetrahedra containing non-bridging oxygens, and assisted in forming a vitreous skeleton with a relatively low SiO<sub>2</sub> density.

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## Preparation of ZrSiO<sub>4</sub> Powders by Sol-Gel Process (3) – Preparation Conditions of ZrSiO<sub>4</sub> Composition Precursor Gels from Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> and Zr(O<sup>i</sup>C<sub>3</sub>H<sub>7</sub>)<sub>4</sub> Alkoxides –

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ZrSiO<sub>4</sub> powders were prepared using a sol-gel processing from partially hydrolyzed Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> and Zr(O<sup>i</sup>C<sub>3</sub>H<sub>7</sub>)<sub>4</sub> solutions. The optimum conditions for obtaining precursor gels with ZrSiO<sub>4</sub> composition were as follows: concentration of mixed solutions; 0.25mol/l, stirring time of alkoxide solutions: 6h, pH of the hydrolysis water: 5.5, H<sub>2</sub>O/alkoxide molar ratio: 10 and stirring time of solutions after hydrolysis: 3h. The precursor powders prepared by using these conditions were converted into ZrSiO<sub>4</sub> powders in about 20% yield at 1200°C for 2h by the addition of 1.5wt% ZrSiO4 seeds. Furthermore, the formation rate of ZrSiO<sub>4</sub> became remarkably higher through "Hedvall effect" bringing about the transition from amorphous silica to crystalline silica at 1250 to 1350°C, and the powders prepared by firing at 1500°C for 2h have become an almost single phase of ZrSiO4 and the particle size of 0.3 to 0.6µm is revealed.

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**Key-words:**  $ZrSiO_4$ , Sol-gel process, Alkoxide, Precursor gel,  $Si(OC_2H_5)_4$ ,  $Zr(O^iC_3H_7)_4$ 

### 1. Introduction

Zircon (ZrSiO<sub>4</sub>) is a composite oxide ceramic material, known for its low thermal expansion coefficient and high resistance to thermal shocks. For it to fully exhibit its inherent properties, it is necessary to synthesize high-purity ZrSiO<sub>4</sub> powder, which differs from the natural products containing impurities.

This synthetic powder has been produced mainly by putting into practice the sol-gel process in which tetraethylsilicate (Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>) and zirconium oxychloride octahydrate (ZrOCl<sub>2</sub> · 8H<sub>2</sub>O) are used<sup>1-5</sup>) as well as by the hydrothermal process.<sup>6</sup> However, scarcely any researchers, besides the authors<sup>7</sup> have discussed synthesis of ZrSiO<sub>4</sub> powder by the sol-gel process using metal alkoxides as the starting materials. This process uses Si-alkoxides and Zr-alkoxides possessing different hydrolysis characteristics as the materials, therefore it was essential either to prepare the composite metal alkoxide of uniform composition or to form a precursor copolymer of different alkoxides from which a precursor gel of uniform ZrSiO<sub>4</sub> composition could be prepared by the method of hydrolysis.

In the preparation of Zr-O-Si glass ceramic materials from Si and Zr alkoxides, a uniform metal alkoxide solution of Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> (including that partially hydrolyzed) and zirconium tetrapropoxide (Zr(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>) were prepared and the mixture was then either hydrolyzed or allowed to stand in the air for gelation.<sup>8-12)</sup> Lately, the process of hydrolysispolymerization reaction has been attracting attention for the preparation of a uniform Zr-O-Si composite metal alkoxide.<sup>13,14)</sup>

In this study, attempts have been made to prepare the  $ZrSiO_4$  powder by the sol-gel process from a mixed solution of partially hydrolyzed  $Si(OC_2H_5)_4$  and  $Zr(O^{i}C_3H_7)_4$ , in which the effects of alkoxide concentrations, stirring time, quantity of water for hydrolysis, solution pH and stirring time for the hydrolyzed solution were investigated. The precursor powder of ZrSIO<sub>4</sub> composition was calcinated at 1200° to 1500°C for 2h into ZrSiO<sub>4</sub> powder in order to follow the product yield as the criterion to assess the preparation conditions.

### 2. Experimental Procedure

The metal alkoxides as the starting materials were zirconium tetra-isopropoxide  $(Zr(O^iC_3H_7)_4, ZPr^i, Kojundo Kagaku)$  and  $Si(OC_2H_5)_4(TEOS, Kojundo Kagaku)$ .

TEOS was partially hydrolyzed, using H<sub>2</sub>O in which HCl was added as a catalyst before it was mixed with ZPr<sup>1</sup>, because it is used to be hydrolyzed more slowly than ZPr<sup>i</sup>. The partial hydrolysis was made by using the mixed solution at the rate of  $H_2O/EtOH/HCl = 2/2/0.1$  times for each mole of TEOS and stirring for reflux at 70°C for 2h. With respect to the pretreatment of ZPr<sup>i</sup>, it was added to i-BuOH which was heat-treated at 70°C in a nitrogen flow and stirred at 95°C for 3h reflux. The partially hydrolyzed TEOS solution was added to the i-BuOH solution at the molar ratio of ZrO2/SiO2=1, and the mixture was in a nitrogen flow stirred at 70°C for 1 to 24h for reflux processing. Concentration of the mixed alkoxide solution was set at 0.2mol/l, except in case of investigating the effects of alkoxide concentration on to the yield rate of ZrSiO<sub>4</sub>. The H<sub>2</sub>O-EtOH solution (H<sub>2</sub>O/EtOH =  $2 \sim 20/2$  by mole for the total number of moles of alkoxides), adjusted to pH 5.5 with hydrochloric acid, was added dropwise to the mixed alkoxide solution which was heated to 50°C, and the mixture was stirred for 0.5 to 10h in order to effect hydrolysis and polymerization/condensation of the alkoxides. It was then evaporated to remove the solvent and dried at 200°C. The dried precursor gel thus prepared was crushed by an agate mortar, dispersed in an alcohol solution, stirred and evaporated to remove alcohol and water. This procedure was repeated twice. The powdered sample thus prepared was heated in a Tammann oven at 4°C/min to 600°C, at which it was calcinated for 5h. The calcinated powder was totally amorphous, as was revealed by X-ray diffraction analysis.

Commercial grade ZrSiO<sub>4</sub> powder (98% pure, containing Hf of 0.3% Fe, Ti and Al of 0.06% and Y of 0.03% as impurities, Kojundo Kagaku) was added to the calcinated powder to 1.5wt %, and the mixture, after being crushed and mixed by an agate mortar, was heated in a box type high-temperature air oven at 20°C/min to 1200°~ 1500°C, at which it was calcinated for 2h, cooled at 20°C/min to 900°C and then allowed to cool to the room temperature in the oven.

The ZrSiO<sub>4</sub> yield was determined by an X-ray diffractometer (Rigaku Denki's RAD-C System). The four peaks appearing at a diffraction angle 20 in a range from 26 to 33° in the X-ray diffraction patterns, relevant to ZrSiO<sub>4</sub> (200), m-ZrO<sub>2</sub> (111, 111) and t-ZrO<sub>2</sub> (101), were used as the standards to determine relative intensity from each peak, and then the yield  $\alpha_{ZrSiO_4}$  was determined by the equation  $\alpha_{ZrSiO_4} = I_{Zr(200)}/(I_{ZR(200)} + I_{M(11)} + I_{M(11)} + I_{T(101)})$ , where subscripts ZR, M and T stand for ZrSiO<sub>4</sub>, m-ZrO<sub>2</sub> and t-ZrO<sub>2</sub> respectively and the numerals in the parentheses was plane index.

### 3. Results and Discussion

#### 3.1. Effects of Mixed Alkoxide Solution Stirring Time

TEOS, which can be hydrolyzed more slowly than ZPr<sup>i</sup>, was pretreated in the presence of HCl (HCL/TEOS= 0.01/1 mol/mol) as the catalyst for partial hydrolysis. ZPr<sup>i</sup>, was dissolved in i-BuOH under reflux to replace a part of its side-chain groups with isobutoxy groups in order to increase steric hindrance. The mixed solution of TEOS and ZPr<sup>i</sup> thus prepared was stirred under reflux, in an attempt to prepare a uniform solution of ZrSiO<sub>4</sub> composition (ideally, as the precursor-forming solution for the production of ZrSiO<sub>4</sub>). It was used as the sample to investigate the effects of the mixed alkoxide solution stirring time on the ZrSiO<sub>4</sub> yield rate.

Figure 4 shows the relationship between ZrSiO<sub>4</sub> yield and stirring time of the mixed alkoxide solution, which after being stirred at 70°C for 1 to 24h under reflux, was hydrolyzed with a H<sub>2</sub>O-EtOH solution (mixed solution/total alkoxides = 10/1 mol/mol) for further stirring at room temperature for 1h and calcinating at 1300°C for 2h. With of i-BuOH solution of ZPr<sup>1</sup> being at this time added to TEOS (partially hydrolyzed with H<sub>2</sub>O double in molar quantity), the solution became slightly turbid, because of the preferential hydrolysis of ZPr<sup>i</sup> with a small quantity of H<sub>2</sub>O remaining in the TEOS solution without being completely



Fig. 1. Effect of stirring time of mixed alkoxide solution on the formation rate of ZrSiO<sub>4</sub> obtained by firing the precursor gels at 1300°C for 2 h.

consumed through hydrolysis .13) ZrSiO<sub>4</sub> yield increased as the stirring time advances up to around 3h but thereafter it remained almost unchanged irrespective of the time of stirring. This stirring time of 3h is considered to have been necessary for the exchange between EtOH, i-PrOH and i-BuOH and side chains of Si- and Zr-alkoxide, 15,16) and for the formation of ZrSiO<sub>4</sub> precursor possessing the Zr-O-Si bond as the product of the reactions between Zr-alkoxide and TEOS oligomers.<sup>13)</sup> Considering, in particular, that the stirring time of the mixed alkoxide solution for which ZrSiO<sub>4</sub> yield increased corresponding roughly to that needed by the exchange of the side chains of Zr(OBu<sup>n</sup>)<sub>4</sub> in EtOH,<sup>16</sup> most of the alkoxide molecules present in the mixed solution were in the form of the TEOS oligomers (certain ethyl groups may be partly substituted for isopropyl groups) and Zr(OEt)<sub>4</sub>. It was concluded, based on the above discussions, that at least three hours were required for stirring in order to prepare an uniform solution of ZrSiO<sub>4</sub> composition by these alkoxide compounds.

#### 3.2. Effects of pH Level of Water for Hydrolysis and of Concentration of Mixed Alkoxide Solution

Water of varying pH levels (0.5 interval within the range between 4.0 and 6.0) was added for hydrolysis to the mixed alkoxide solution and the resultant precursor powders of the ZrSiO<sub>4</sub> composition were calcinated at 1300°C for 2h after being analyzed by a scanning electron microscope. The mixed alkoxide solution, after being stirred for 10h under was reflux, hydrolyzed with a H<sub>2</sub>O-EtOH mixture (ten times in molar quantity over the total alkoxides and adjusted at a given pH level) and then stirred at the room temperature for 1h. The SEM analysis indicated that the size of the particles were smaller when the mixed alkoxide solution was hydrolyzed with the water having a pH of 5.0 and 5.5, with the ZrSiO<sub>4</sub> becoming higher in case of other pH conditions.

Accordingly the mixed alkoxide solution which was made varied in concentration (0.1 to 1.0mol/l), after being stirred for 10h under reflux, was hydrolyzed with a H<sub>2</sub>O-EtOH mixture (10 times in molar quantity over the total alkoxides) of pH = 5.5, and then stirred at the room temperature for 1h, in order to prepare the precursor powder of the ZrSiO<sub>4</sub> composition. The powder was then calcinated at 1300°C for 2h, to follow the effects of concentration of the mixed alkoxide solution on ZrSiO<sub>4</sub> yield. The result was shown in **Fig.2**. The yield remained almost unchanged at the concentration between 0.1 to 0.5mol/l, but thereafter decreased in inverse proportion to increases in concentration. This decreases in yield depend on the precursor gel



Fig. 2. Relation between concentration of mixed alkoxide solution and the formation rate of ZrSiO<sub>4</sub> obtained by firing the precursor gels at 1300°C for 2 h.

prepared from the mixed alkoxide solution of high concentration (0.75 and 1.0mol//), which might have been apt to arouse partial gelation at the time of hydrolysis as the cause of non-homogeneity in composition. These results suggested that the adequate concentration of the mixed alkoxide solution was within a range from 0.1 to 0.5mol// in order to prepare the homogenized precursor gel of the ZrSiO<sub>4</sub> composition.

#### 3.3. Effects of H<sub>2</sub>O/Alkoxide Ratio

In the sol-gel process,  $H_2O/alkoxide$  ratio is one of the most important factors that affect morphologies (gel structures) of the hydrolysis-polymerization/condensation products.

Figure 3 shows a relation between H<sub>2</sub>O/alkoxide ratio and the yield rate of ZrSiO<sub>4</sub>, which represents the result that the powder prepared under the condition of changing the former ratio within a range from 2 to 20 was calcinated at 1300°C for 2h. As shown, the yield rate of ZrSiO<sub>4</sub> scarcely was affected by the above-mentioned ratio. This was presumably because a sufficient quantity of water was given from the first stage, satisfying the requirements of hydrolysis/concentration of mixed alkoxide, with the actual H<sub>2</sub>O/alkoxide ratio at the hydrolysis being 4 times or more in molar amount (representing the total of 2 times for the partial hydrolysis of TEOS, and 2 to 20 times for the hydrolysis of the mixed alkoxide in molar amount).

These results were not contradictory to the general observations that hydrolysis of TEOS and Zr(OBu)<sub>4</sub> would proceed sufficiently with water (H<sub>2</sub>O/TEOS = around 2mol/mol) in the presence of HCl as the catalyst for the former<sup>13,17-19</sup> and with water (H<sub>2</sub>O/Zr(OBu)<sub>4</sub> = 1 ~ 2 mol/mol) for the latter,<sup>20)</sup> and that the hydrolysis of the Zr-O-Si mixed alkoxide would advance in proportion to increases in the H<sub>2</sub>O/alkoxide ratio to form nearly spherical agglomerates at a ratio of 4mol/mol or more.<sup>13)</sup>

#### 3.4. Effects of Stirring Time for Hydrolyzed Solution

It is generally known that hydrolysis-polymerization/condensation of alkoxide is promoted as the time advances, resulting in grain growth and in agglomeration, and that a surplus quantity of water for the hydrolysis accelerates hydrolysis and polymerization/condensation (gelation) of the still unreacting species remaining in the solvent.<sup>21)</sup> It is anticipated in the synthesis of ZrSiO<sub>4</sub> from TEOS and ZPr<sup>i</sup> as the starting materials that formation of the precursor gel of ZrSiO<sub>4</sub> composition is greately affected by the change in the passing of time of hydrolysis – polymerization/conden-



Fig. 3. Relation between  $H_2O/alkoxide$  molar ratio and the formation rate of ZrSiO<sub>4</sub> obtained by firing the precursor gels at 1300°C for 2h.

sation of these starting materials. Hydrolysis of TEOS proceeds in proportion to acid concentration<sup>22)</sup> and its polymerization/condensation rate increased as the solution pH level increased<sup>22,23)</sup> (for example, it is slow at pH = 2 and fast at pH = 5<sup>19</sup>). In case of Zr(OBu)<sub>4</sub> and Zr(OPr)<sub>4</sub>, it was difficult to control hydrolysis-polymerization/condensation with H<sub>2</sub>O/alkoxide ratio, and it is reported that the gel structures have been affected by the quantity of water used.<sup>15,20,24)</sup>

The attempts were made, therefore, to hydrolyze the mixed alkoxide solution with an excessive quantity of water  $(H_2O/alkoxides = 10mol/mol)$  and to stir the mixture at the room temperature for 0.5 to 10h, in order to prepare the precursor gel. The resultant powder was calcinated at 1300°C for 2h in order to investigate the effects of stirring time of the hydrolyzed solution related to the yield rate of ZrSiO<sub>4</sub>. The results are given in Fig.4. ZrSiO<sub>4</sub> yield increased as the stirring time increased but turned to after the continued stirring over 5h. This relationship between ZrSiO<sub>4</sub> yield and stirring time for the hydrolyzed solution suggested that the process of hydrolysis-polymerization/condensation of the mixed solution of TEOS and Zralkoxide to form the precursor gel of ZrSiO<sub>4</sub> composition was affected by the time-dependent gelation condtions. In other words, stirring for 2 to 3h the hydrolyzed solution accelerated the hydrolysis-polymerization/condensation to form the precursor gel of ZrSiO<sub>4</sub> composition, but stirring for 5h or longer may have caused ununiform composition of the precursor gel, due to decreased viscosity of the mixed solution, resulting from dilution by the solvent and agglomerates with porous gel structures<sup>13)</sup> and an excessive quantity of water present in the solution hence, decreasing the ZrSiO<sub>4</sub> yield.

#### 3.5. Effects of Calcination Temperature

The investigations of the various factors that affected the preparation of the precursor gel of  $ZrSiO_4$  composition have led to the following optimum conditions: 0.25mol/l for mixed alkoxide concentration, 6h stirring time for the mixed alkoxide solution, 5.5 for pH level of the hydrolyzed solution, as the 10mol/mol H<sub>2</sub>O/alkoxides ratio and 3h stirring time for the hydrolyzed solution. The precursor pewder was produced from the precursor gel for ZrSiO<sub>4</sub> composition prepared under the above conditions. This powder was calcinated at varying temperatures (1200° to 1500°C) for 2h after being admixed with 1.5wt% of commercial ZrSiO<sub>4</sub> powder as the seed, in order to investigate the effects of calcination temperature on the ZrSiO<sub>4</sub> yield, which



Fig. 4. Relation between stirring time after hydrolysis and the formation rate of ZrSiO<sub>4</sub> in case of HCI/TEOS molar ratio of 0.01.



Fig. 5. Change of the formation rate of ZrSiO<sub>4</sub> with firing temperature.

continuing to increase though moderately at 1400°C and more, to a 96 – 98% level (almost single ZrSiO<sub>4</sub>) at 1500°C. The yield rate of ZrSiO<sub>4</sub> as a whole beared an S-shaped, curves against calcination temperature.

It is considered that formation of  $ZrSiO_4$  would be promoted by the precursor having Zr-O-Si compositon at 1250°C or less and on the strength of "Hedvall effects" in the course of transformation from amorphous to crystalline phase of silica, at 1250°C to 1350°C, with the solid-phase reactions between nearly crystalline SiO<sub>2</sub> and t-ZrO<sub>2</sub> being the cause of processing at above 1350°C.<sup>2)</sup> These results suggested that it would be possible to produce a quantity of ZrSiO<sub>4</sub> powder from the precursor gel of ZrSiO<sub>4</sub> composition at 1250°C or less, provided that further detailed studies are given to the precursor gel preparation conditions in question.

**Figure 6** shows the SEM photograph of  $ZrSiO_4$  powder prepared by calcinating the precursor gel at 1500°C for 2h. The grain size ranged from 0.3 to 0.6µm.

### 4. Conclusions

ZrSiO<sub>4</sub> powder was synthesized by the sol-gel process from the mixed solution of partially hydrolyzed Si(OC2H5)4 and  $Zr(O^{\dagger}C_{3}H_{7})_{4}$ . The investigations of the various factors that affected the preparation of the precursor gel of ZrSiO<sub>4</sub> composition have led to the following optimum conditions, i.e. mixed alkoxide concentration: 0.25mol/l, stirring time for the mixed alkoxide solution: 6h, pH level of the hydrolyzed solution: 5.5, H<sub>2</sub>O/alkoxides ratio: 10mol/mol, and stirring time for the hydrolyzed solution: 3h. With 1.5wt% of ZrSiO<sub>4</sub> being admixed as the seed, the precursor powder prepared under the above conditions showed calcinated after having been admixed ZrSiO<sub>4</sub> yield of approximately 20% by calcinating at the temperature of 1200°C. Further, the yield rate concerned notably increased at 1250° to 1350°C due to the "Hedvall effects" associated with the transformation of silica from the amorphous to crystalline state resulting in the almost single-phase ZrSiO4 when calcinated at 1500°C for 2h (grains of 0.3 to 0.6µm in size). It is necessary in order to substantially increase ZrSiO<sub>4</sub> yield at a calcination temperature of 1250°C or less to further steady the precursor gel preparation conditions.

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Fig. 6. SEM micrograph of ZrSiO<sub>4</sub> powders prepared by firing the precursor gels at 1500°C for 2h.

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# Equation for the Evaluation of Fracture Toughness by Chevron Notched Beam with Using JIS Type Bending Bar Specimen – Analyzed with the Method by Munz –

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The equations for the evaluation of fracture toughness by chevron notched beam, using the bending bar whose shape is followed as JIS-R1601, are obtained analytically for five different shapes of the notch, with the method by Munz. The accuracy of the equations is tested experimentally with alumina specimens. Except one condition (stand-up type,  $\theta$ =120,°  $\alpha_0$  > 0.6), scattering of the average value obtained from the experiment with every equation is within ±8%, and this scattering is almost same as the relative standard deviation of the fracture toughness of the tested alumina itself, ± 7%.

Then, these equations are useful if we want to evaluate fracture toughness with about this accuracy, even if the specimen is used as either stand-up or lay-down type. [Received June 18, 1990; Accepted October 26, 1990]

**Key-words:** Fracture toughness, Chevron notch, Flexural test, Slice model, Alumina

### 1. Introduction

In evaluating brittleness the biggest drawback of structural ceramics, the measurement of fracture toughness ( $K_{IC}$ ) is considered important; JIS-R1607<sup>1)</sup> of the Japanese Industrial Standards has been applied to the evaluation of  $K_{IC}$ at room temperature. Of the various techniques specified by JIS, SEPB has been adopted as the precision method,<sup>2,3)</sup> and IF as the simplified one;<sup>4-6)</sup> however, the problem of secondary reactions due to anticipated cracking or oxidation has not been solved in the former,<sup>7)</sup> and the applicability of a high temperature experimental equation in the latter has only been tested in a few cases.<sup>8,9)</sup> In addition, a hardness tester for which the IF method is applicable at high temperatures is not widely accepted.

On the other hand, when Chevron Notched Beams are used for the measurement of fracture toughness in the flexural test (hereinafter referred to as the CNB method), 1) the problem of secondary reactions at the notched section disappears, even in measurements at high temperatures, since the notches are mechanically processed; 2) fewer adverse effects are caused by the width of the processed notches; 3) it is possible to achieve stable fracture as well as to evaluate fracture energies; and 4) it is possible to perform the evaluation at high temperatures when provided with equipment for high-temperature flexural tests specified by JIS-R1604.<sup>10</sup> Since the CNB method is characterized by the above advantages, it appears to be an acceptable method for evaluating fracture toughness at high temperatures.

When fracture toughness is obtained by the CNB method, it is usually calculated from the load and the notched shape at the point along the crack length where the shape coefficient,  $Y^*$ , which changes with the propagation of cracking, has a minimum value. However, when the method of Munz et al.<sup>11)</sup> is applied, the calculation becomes more complicated since it requires integrated calculation. Thus, Munz et al. proposed an equation (1) that determines the fracture toughness by a polynomial from the maximum load,  $P_{max}$ , which can be obtained during the experiment.<sup>12)</sup>

where  $S_1$  is the lower span and  $S_2$  is the upper span, and the parameters of the shape of the chevron notch are shown in **Fig.1**. The terms  $\alpha_0$  and  $\alpha_1$  are defined as  $\alpha_0=a_0/W$  and  $\alpha_1=a_1/W$ . Equation (1) makes it possible to easily evaluate the fracture toughness, but as its applicability has only been determined for the shape of test specimen prescribed by Munz et al. (B=3.5mm, W=4.5mm, S\_1=40mm, S\_2=20mm,  $\alpha_0=0.2$  and  $\alpha_1=1.0$ ), it is not yet clear whether it is applicable to a JIS-type test specimen.

Thus, the purpose of the present study was (1) to analytically determine a polynomial in accordance with the method of Munz, et al., for the measurement of fracture toughness of test specimens with chevron notches, which is prepared in JIS flexural tests,<sup>13)</sup> and (2) to confirm experimentally the appropriateness of the equation thus obtained.



Fig. 1. Chevron notch plane section and parameters for the shape of the notch.

### 2. Polynomial Derivation

#### 2.1. Method of Derivation

A polynomial was derived by the method of Munz, et al. First, a relationship between the dimensionless crack length,  $\alpha$ =a/W, of a test specimen with straight cracking and dimensionless compliance, C', was specified by Equations (2) ~ (4).

$$dC'/d\alpha = 2Y^2 \qquad (2)$$
  
$$Y = [(S_1 - S_2)/W] \{(3 \Gamma_M \alpha^{1/2})/[2 (1 - \alpha^{3/2}]\} \} (3)$$

$$\Gamma_{M} = 1.9887 - 1.326 \alpha$$
$$- \frac{(3.49 - 0.68\alpha + 1.35 \alpha^{2}) \alpha (1 - \alpha)}{(1 + \alpha)^{2}} \dots (4)$$

Next, the compliance,  $C_{tr}$ , of a chevron-notched specimen based on the concept of a slice model was calculated. This  $C_{tr}$  is also a function of  $\alpha$ .

$$\frac{1}{C_{\rm tr}} = \left(\frac{\alpha - \alpha_0}{\alpha_1 - \alpha_0}\right) \frac{1}{C(\alpha)} + \frac{k}{n} \sum_{i=m+1}^n \left[\frac{1}{C(\sigma)}\right]_i \quad \dots \quad (5)$$

and C ( $\alpha$ ) equals C'/E'B, where E' is equal to E in a state of plane stress, or E/(1-v<sup>2</sup>) in a state of plane strain (E: Young's modulus, v: Poisson's ratio). The number of slices assumed in this study is 2,000.

The shear coefficient k in Eq. (5) was computed using the polynomial obtained from Bluhm's experiments.

Table 1. Analyzed shapes of the specimens.

10-11-11-11-11-11-11-11-11-11-11-11-11-1			
	B (mm)	W (mm)	θ (deg)
Shape 1	3.0	4.0	60
2	3.0	4.0	90
3	3.0	4.0	120
4	4.0	3.0	90
5	4.0	3.0	120



Fig. 2. Comparison of the fracture toughness values obtained by Equation (1) ( $K_{IC}$  (1)) and Equation (9) ( $K_{IC}$ (9)).

for  $\phi$  in radians.

Next, the shape coefficient,  $Y^*$ , of the chevron notch is calculated using an equation.  $C'_u=E'BC_u$ .

$$Y^* = \left[\frac{1}{2} \left( dC'_{tr} / d\alpha \right) \frac{\alpha_1 - \alpha_0}{\alpha - \alpha_0} \right]^{1/2} \quad \dots \quad \dots \quad (8)$$

Finally, the fracture toughness is obtained from the minimum value of Y  $^{*}$ , or Y  $^{*}_{min}$ .

$$K_{\rm IC} = (P/BW^{1/2}) Y_{\rm min}^*$$
 .... (9)

The shapes currently analyzed are the 5 types summarized in **Table 1**, where shapes 1-3 with W=4 and B-=3 are referred to as "vertical types," and shapes 4-5 with W=3 and B=4 as "horizontal types."

#### 2.2. Results and Discussion

The values of fracture toughness obtained by Equation (1) and Equation (9) were compared using vertical test specimens. As is clear from **Fig.2**, the values obtained from Equation (1) are smaller than those obtained from equation (9) by more than 25% in the range  $\alpha_0 > 0.6$  at  $\theta=90^\circ$ , and  $\alpha_0 > 0.1$  at  $\theta=120^\circ$ . Thus, equation (1) is not applicable to these shapes.

Thus, the analyzed results were fitted to the relationship in Equation (10) to obtain the coefficients,  $A_0$ ,  $A_1$  and  $A_2$ that can be used for the respective shapes.

$$\begin{split} K_{\rm IC} &= (P_{\rm max}/BW^{1/2}) \left(A_0 + A_1\alpha_0 + A_2\alpha_0^2\right) \\ &\times \left[(S_1 - S_2)/W\right] \left(\alpha_1 - \alpha_0\right)/(1 - \alpha_0) \dots \dots \dots (10) \end{split}$$

The results are shown in **Table 2**. Based on this equation,  $K_{IC}$  has units of kg/mm<sup>3/2</sup> when  $P_{max}$  is expressed in kg and the length in mm. In order to obtain  $K_{IC}$  with units of MPa·m,<sup>1/2</sup>  $P_{max}$  must be expressed in MN and the length in m, or the value obtained in units of kg/mm<sup>2/2</sup> must be multiplied by 0.3101.

In our previous report,<sup>15</sup> we calculated the standard compliance using the deflection at the center of a specimen, but adopted the deflection at a loading point as Munz, et al., used in their calculation. Nonetheless, the difference between the two methods was approximately 1% at most. Although we used Bluhm's share coefficients in following the method of Munz, et al., in our current study, we think it may be necessary to conduct future studies by using these coefficients based on more recent reports that have been pub-

Table 2. Coefficients from Equation (10) for each specimen shape.

		A0 A1	A2
Shape 1	0 < α <sub>0</sub> < 0.35	2.91 4.97	11.64
2	0 < α <sub>0</sub> ≤ 0.3	3.01 10.35	-2.92
	$0.3 < \alpha_0 < 0.62$	10.68 -33.85	61.91
3	$0 < \alpha_0 \leq 0.3$	3.39 22.29	-24.20
	$0.3 < \alpha_0 \le 0.6$	8.65 -12.65	36.21
	$0.6 < \alpha_0 < 0.78$	155.7 -484.9	416.0
4	0 < α <sub>0</sub> < 0.33	3.01 4.35	12.81
5	0 < α <sub>0</sub> ≤ 0.3	3.09 9.49	-1.31
	0.3 < α <sub>0</sub> < 0.61	9.75 -29.74	57.26



Fig. 3. The fracture toughness calculated from Equation (10) with changing  $\alpha_0$  on the specimen shape 1 to 5.

lished on Bluhm's share coefficients<sup>16)</sup> subsequent to our report.

Since Bluhm obtained his share coefficients based on the assumption that the Poisson ratio was 0.28, it may be necessary to conduct another study using materials with Poisson ratios largely different from this value.

### 3. Experimental Procedure and Results

#### 3.1. Experimental Methods

A commercially available sintered compact of alumina (purity 99.5%, density  $3.90g/cm^3$ , mean grain diameter  $13\mu$ m) was used as a sample for the experiment. Young's modulus and Poisson's ratio were 376GPa and 0.26, respectively, when measured by the resonance method. Flexural test specimens, with dimensions 4x3x38mm, were provided with chevron notches of different  $\theta$  and  $\alpha$ , using a diamond saw. The saw thickness was 0.1mm. The flexural test was conducted at 4 point bending with an upper span of 10mm and lower span of 30mm. A crosshead was moved at a rate of  $5\mu$ m/min. The fracture of all samples that stably progressed before and after the maximum load under these conditions was confirmed via the curves indicating loading and time.

#### 3.2. Results

Ten samples were tested under the fixed conditions,  $\alpha_0=0.13$ ,  $\theta=60^\circ$ , for vertical type samples in an attempt to ascertain the distribution of fracture toughness measurements on alumina. It was found that the mean value was  $3.82MPa \cdot m^{1/2}$  with a standard deviation of 0.25, or about  $\pm 7\%$  in our samples under the current test conditions.

Figure 3 shows the scatter of calculated values due to variations in  $\alpha_0$  for each shape.  $K_{IC}$  should be constant with respect to changes in  $\alpha_0$ , in view of the scattering of the material itself, and it is almost constant under respective conditions. Figure 4 compares the mean values obtained from respective shapes and their standard deviations. The lowest value obtained was from a vertical type sample with  $\theta$ =120° at  $\alpha_0 > 0.6$ . It appeared that it may be necessary to



Fig. 4. Average  $K_{IC}$  and standard deviation for each specimen shape.

raise the precision level in the measurement of loading, because the area of a ligament was extremely small with fracture occurring at a lower level of loading.

However, when this single condition was excluded, the mean value obtained from respective shapes was 3.68MPa·m<sup>1/2</sup> with a standard deviation of 0.22, and the value furthest from the mean value was within  $\pm 8\%$ . Thus, these polynomials can be fully utilized if the precision in the neighborhood of this level is acceptable.

#### 3.3. Discussions

Opinions differ as to whether the fracture of specimens provided with chevron notches is accurately measured by the value of fracture toughness. In fact, (1) cracks of a certain length have already developed when the maximum



Fig. 5. Change of the crack length when Pmax is applied with changing a on the specimen shapes 1 to 5. Brackets show the range of experiment. (a: vertical type, b: horizontal type)



Fig. 6. Change of experimentally obtained fracture toughness with changing the crack length by the change of the shape of the specimen. Numbers correspond to the shape 1 to 5.

loading occurs, and (2) when the fracture develops stably, cracking rate is not large enough. Case (1) is a problem in relation to R-curves, while (2) is a problem relating to a subcritical crack growth (SCG).

When these effects are taken into consideration, the values obtained from the current experiment alone may not indicate the true fracture toughness. However, the conclusion that can be drawn from Equation (10) in the current experiment is whether a certain "stress inteusity factor that leads to fracture" should be given in case where a specific material is to be fractured under fixed conditions. In this meaning, it is necessary to study the effects which R-curves and SCG have on the current experiment.

1) Effects of R-Curves

The length of cracking that develops under the maximum load can be analytically obtained from the shape of the respective test specimens. Figure 5 shows the changes of  $\alpha_{max} - \alpha_0$ , which is the length of cracking under the maximum load, with changing the shape of the notch (where  $\alpha_{max}$ is equal to  $\alpha$  at the maximum loading). It is clear from the figure that changes in  $\theta$  or sample type (vertical/horizontal) have a larger effect on crack length than does a change in  $\alpha_0$  for a given sample. The mean values and deviations of the crack lengths, and the mean values and deviations of fracture toughness for shapes 1 to 5 are plotted in Fig.6. Since the scattering was significant for some of the specimens used in the current test, the variation of fracture toughness that occurred when the crack length increased was difficult to recognize. Since the comparison here is between specimens with different shapes, particularly those with the different value of  $\theta$ , the above problems, including those concerning share coefficients, need to be further discussed. At that time, it may also become necessary to obtain



5 0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 ao/W

10

Fig. 7. Change of the crack velocity when Pmax appears with changing 0 on the specimen shape 1 to 5. (a: vertical type, b: horizontal type)

R-curves by the other methods.

#### 2) Effects of SCG

The crack velocity at the maximum load can be analytically determined, but this value depends on Young's moduli and fracture toughness values (or stress intensity factor that leads to fracture). Here, the crack velocity, corresponding to 5µm/min of the crosshead speed, was calculated using Young's modulus and the mean value of the fracture toughness of alumina. However, the values are obtained without considering the deformation of metallurgical tools and testers, and then they are merely reference values. Figure 7 shows the changes of the crack velocity as a function of the shapes of the respective test specimens and  $\alpha_0$ . The ratio of maximum to minimum crack velocities was found to be as high as 10 under the current experimental conditions.

The typical value indicating the fatigue parameter of alumina, n, is conceivably  $80 \sim 90^{17}$  but in view of this fatigue parameter, the factor of 10 in the crack velocity may manifest itself as a change in type stress intensity factor leading to fracture of about 3%. The material is seemingly fractured in this experiment in proportion to a fixed stress intensity factor within a range of its own scattering.

The difference in stress intensity factor leading to fracture attributed to the difference of the crack velocity is not necessarily small. It is believed that the plots in Fig.7 merely shift upward on the whole, and no changes can be seen in the maximum/minimum ratios of the velocity even when the crosshead speed is increased. This difference should definitely appear as long as the fracture is being made at a rate corresponding to that of the first region of K<sub>1</sub> ~ V diagram. For the materials with smaller fatigue parameters, it is necessary to allow the fracture at a rate corresponding to that of the experimental conditions as well as the stable fracture conditions.

Since it is clear from Fig.7 that the cracking velocity decreases at a fixed ratio along with an increase of  $\alpha_0$  regardless of the shape of the test specimen currently analyzed, the scattering due to SCG can be avoided if the tests are carried out without causing major changes of  $\alpha_0$ .

It is possible from (1) and (2) that the fracture of alumina observed in the current experiment was not necessarily caused by the magnitude of fracture toughness; however it is conceivable that the fracture progressed with certain stress intensity factor within a range of scattering of the material itself, where the length and crack velocity would not be affected by eventual changes of the shape of the test specimen. Thus, "KIC" of a certain level should be specified in the analytically obtained Equation (10) as a condition of the current experiment. The relationship between the fracture toughness obtained for the test specimens provided with chevron notches and the true fracture toughness cannot be clarified by an analytical study alone, because the possible effects of the length and velocity dependent on the materials. However, it is important to compare them with the values obtained by other measurement methods for further investigations.

#### 4. Summary

A polynomial applicable to the evaluation of fracture toughness for specimens provided with chevron notches for JIS flexural tests was derived from the analytical method of Munz, et al., and experimentally evidenced. The experimental values of fracture toughness obtained from the respective shapes were within a range of  $\pm 8\%$  excluding data for one vertical type sample:  $\theta = 120^\circ$ ,  $\alpha_0 > 0.6$ ), indicating that the polynomial currently obtained was sufficient for applications requiring this degree of precision. However, the compatibility with values obtained by the other measurement methods, and how the share coefficient, k, is specified need to be further studied.

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# Influence of Whiskers' Shape and Size on Mechanical Properties of SiC Whisker-Reinforced Al<sub>2</sub>O<sub>3</sub>

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For whisker reinforced ceramic composites, many toughening mechanisms are proposed. However, it is not clear vet which mechanism mainly contributes to the toughening. In this paper, we tried to explain the toughening behavior by the pull-out mechanism. A model based on the energy balance of crack propagation and frictional energy during whisker pulling-out was constructed for analyzing experimental results. Seven types of SiC whiskers with various sizes and shapes were used for fabricating SiC whisker/Al<sub>2</sub>O<sub>3</sub> composites. Mechanical properties of these composites such as fracture toughness  $K_{\rm IC}$ , effective fracture energy  $\gamma_{\rm eff}$  and 4point bending strength  $\sigma_{f}$ , were measured as a function of whisker dimension or whisker volume fraction. Fractured surfaces and crack propagation paths in these composites were observed in detail. A linear relationship between  $\gamma_{\rm eff}$  and  $r^2/l_{\rm w}$  was obtained (r: radius of whiskers,  $l_w$ : length of whiskers).  $\gamma_{eff}$  also had a linear relationship with the whisker volume fraction. These results seem to support the whisker pull-out model proposed here.  $(K_{1C})^2$ showed linear relationship with  $r^2/l_w$  and whisker volume fraction as well as  $\gamma_{eff}$ . Four-point bending strengths of these composites were not improved in spite of toughening by whisker reinforcement. It is presumed that long whiskers cause to introduce large defects into ceramic matrix.

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**Key-words:** SiC whisker, Al<sub>2</sub>O<sub>3</sub>, Composite, Fracture toughness, Effective fracture energy. Four-point bending strength, Pull-out

### 1. Introduction

Recently, a number of researchers have been extensively studying whisker-reinforced composite materials with a view to increasing the toughness of ceramics, and some have already become commercialized.<sup>1)</sup> Reinforcing with whiskers is expected to increase fracture toughness of the ceramic as the matrix of the composite by several mechanisms; (1) crack deflection, (2) crack bowing, (3) fiber bridging at crack tip, (4) pulling-out of the whiskers, etc. Increased productivity as compared with composites reinforced by long fibers becomes another advantage.

The extensive studies on whisker-reinforced ceramic materials have been initiated due to commercial production of high-quality SiC whiskers being one of the backgrounds. It should be noted, however, as the manufacturers have been producing widely varying whiskers, the shape and size of the whiskers must be optimized, in order to realize the target mechanical properties of ceramic based composites, such as elastic modulus strength, fracture toughness  $K_{IC}$ , etc., It becomes therefore necessary to understand the relations of whisker shape and size to the mechanical properties of composites.

Several researchers have been recently discussing strength and fracture toughness  $K_{\rm IC}$  of whisker-reinforced ceramic composites.<sup>3-6)</sup> However, changes in shape and size of whiskers used in these studies remained within narrow ranges, and the experimental results and their explanation are divided. It is therefore considered that our knowledge concerning toughening mechanism of whisker-reinforced ceramic composites remains low at present.

In this study, seven kinds of SiC whiskers varying widely in shape and size were used to prepare composites with  $Al_2O_3$ , in order to investigate mechanical properties of the composites in relation to the shape, size and volume fraction of whiskers. Based on these results, we further aimed at studying toughening mechanism of the above-memtioned SiC whisker/ $Al_2O_3$  composite materials.

### 2. Whisker Pulling-Out Model

Various mechanisms have been proposed to explain increased toughness of whisker-reinforced ceramic materials. In this study, a model was developed, paying attention to the "fiber bridging and pulling-out" concept, which is characteristics of fiber-reinforced composite materials. Calculation was carried out on the assumption of continuum approximation which follows linear fracture dynamics. This assumption would be adequate when texture size was sufficiently smaller than crack length. The effects of "fiber bridging" and "fiber pulling-out" are to be discussed separately, the former being defined as the phenomenon in which fibers bridging with the crack faces so that the energy release rate (or stress intensity factor) at the crack tips may change, and the latter as the phenomenon in which fiber pulling-out accompanied by crack propagation consumes energies.

### 2.1. Fiber Pulling-Out Effects

1) Behavior of a short fiber

A behavior of a short fiber case in hereby is considered to pull out short fibers of a radius r, which are inserted in an object to a depth of  $l_i$  as shown in **Fig.1**(a). The following equation can be obtained when the fibers is pulled out by an external force  $F_p(u)$ , with dynamical equilibrium being maintained, provided that shear stress  $\tau_i$  acting on the fiber/matrix interface is constant (Fig.1(b)):

where, u is a pull-out length of the fibers.

Work required for pulling out the fibers when a crack is propagating.

It is assumed that each fiber that bridging a crack is perpendicular to the crack face, length of the shorter portion of the fibers parted by the crack (corresponding to the insertion length shown in Fig.1(a)) is constant at  $l_i$ , while the fibers are pulled out to an extent equivalent to a displacement of the crack opening u(x) (Fig.1(c)). Fracture of the fibers is neglected.

A stress given by the following equation is considered continuously distributed in the crack face at the crack tip (Fig. 1(d)):

$$\sigma_{\rm P}(x) = 2V_{\rm f} \tau_{\rm i} \left| l_{\rm i} - u(x) \right| / r \qquad \dots \qquad \dots \qquad \dots \qquad (2)$$

where,  $V_{\rm f}$  is volume fraction of the fibers. The stress produced when the fibers bridging the crack faces being considered to be discontinuous, the continuously distributed stress is multiplied by  $V_{\rm f}$  to take into account the above discontinuity.

Consider a penny-shape crack of radius *C*. Crack opening displacement u(x) is given by the following equation,<sup>7)</sup> based on linear fracture dynamics:

where,  $\alpha$  is contant and length of the portion of the fiber bridging the crack faces L<sub>B</sub> is given by:

$$l_{\rm i} = u (L_{\rm B}) = \alpha \sqrt{L_{\rm B}} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (4)$$

which gives the work  $\Delta W_p$  needed to pull out the fiber when the crack propagates  $\Delta C$ :

$$\Delta W_{\rm P} = \int_{0}^{s} 2 \pi \left(C - x\right) \sigma_{\rm P}\left(x\right) \Delta u\left(x\right) \,\mathrm{d}x$$
$$= 2\pi C V_{\rm f} \tau_{\rm i} l_{\rm i} \left(l_{\rm i}/r\right) \Delta C \left(L_{\rm B} <<\!\!<\!\!\mathrm{C}\right). \quad . \quad . \quad (5)$$

$$\therefore dW_{\rm P}/dC = 2\pi CV_{\rm f}\tau_{\rm i}l_{\rm i} (l_{\rm i}/r) \quad \dots \quad \dots \quad \dots \quad \dots \quad (6)$$

Area of the crack face A is given by:

$$A = \pi C^2, \quad \therefore \quad dA = 2\pi C dC \quad \ldots \quad \ldots \quad \ldots \quad (7)$$

Substituting Equation (7) into Equation (6) yields:



Fig. 1. Schematic illustrations of the fiber pull-out model.

3) Fracture Criterion

Fractures proceed under the conditions of energy release rate  $g \ge fracture$  toughness  $g_e$ , based on energy balance.<sup>7)</sup>

 $dW_{\rm P}/dA = V_{\rm f} \tau_{\rm i} l_{\rm i} (l_{\rm i}/r) \qquad (8)$ 

The work  $W_s$  needed to increase area of propagating non-bridged cracks is given by:

where,  $\gamma$  is surface energy per unit area of the crack. Combining equations (8) and (9) yields:

$$g_{\rm C} = dW_{\rm S}/dA + dW_{\rm P}/dA = 2\gamma + V_{\rm f}\tau_{\rm i}l_{\rm i}(l_{\rm i}/r)$$
 (10)

Increment of fracture toughness  $\Delta g_{\rm C}$  is given by:

The following relationship will hold between energy release rate g and stress intensity factor, based on linear fracture dynamics:<sup>7)</sup>

$$g = K^2/E' \qquad \dots \qquad (12)$$
$$E' = \begin{cases} E \qquad (\rightarrow \text{plane stress})\\ E/(1 - v^2) \qquad (\rightarrow \text{plane strain}) \end{cases}$$

where, E is Young's modulus of a composite and v is Poisson ratio of a composite.

4) Correction of Average Insert Length  $l_i$  and  $V_f$ 

.

The above discussions are based on the assumption that no fiber is broken. However, some fibers are broken while being pulled, and it becomes necessary to correct  $V_r$ , so that only those fibers involved in pulling-out are considered. It is also necessary to consider the relationship between insert length  $l_i$  and actual fiber length  $l_w$ . Therefore, the following corrections have to be made:

The maximum force  $F_{p_{max}}$  needed to pull out a fiber having an insert length  $l_i$  is given by:

The maximum force  $F_{W_{max}}$  to which a fiber can withstand is given by:

where,  $\sigma_F$  is a tensile strength of fiber.

A fiber will be broken, and hence cannot be pulled-out, when  $F_{P_{\text{max}}} \ge F_{W_{\text{max}}}$ , or  $l_i \ge r\sigma_F/2\tau_i$ , and it will be pulled out without been broken when  $l_i \le r\sigma_F/2\tau_i$ . In the above discussion, strength of the fibers is assumed to be uniform.

When fiber length  $l_w$  is  $l_w \le r\sigma_r/\tau_i$ ; all the fibers contacted by the cracks will be pulled out without being broken, and no correction of  $V_f$  is required in this case. Assuming that each portion of a fiber is contacted by the crack at the same probability, the following relationship will hold:

Substituting Equation (17) into Equations (11) and (14) yields:

$$\Delta g_{\rm C} = (1/16) V_{\rm f} \tau_{\rm i} l_{\rm W} (l_{\rm W}/r) \quad . . . . . . . . . . (18)$$

$$\Delta (K_{\rm IC}^2) = (1/16) E' V_{\rm f} \tau_{\rm i} l_{\rm W} (l_{\rm W}/r) \quad . \quad . \quad . \quad . \quad . \quad (19)$$

When  $l_i \leq r\sigma_F/\tau_i$ :

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A fiber will be pulled out when contacted by a crack at the portion within  $r\sigma_{F}/2\tau_{i}$  from each edge, but will be broken when contacted at any other portion. Therefore:

Substituting these equations into Equations (11) and (14) yields:

$$\Delta g_{\rm C} = (1/16) V_{\rm f} (\sigma_{\rm F}/\tau_{\rm i})^2 \sigma_{\rm F} r (r/l_{\rm W}) \quad . \quad . \quad . \quad (22)$$

$$\Delta (K_{\rm IC}^2) = (1/16) E' V_{\rm f} (\sigma_{\rm F}/\tau_{\rm i})^2 \sigma_{\rm F} r (r/l_{\rm W}) \quad . \quad . \quad (23)$$

Equations (18) and (22) suggest that  $\Delta g_c$  attains the maximum ( $\Delta g c_{max}$ ), when  $l_W/r = \sigma_F/\tau_i$ , and is given by:

The above two equations suggest, based on the "fiber pulling-out model," that toughness will be increased by (1) use of as large fibers as possible, so long as their shape almost satisfies the condition of  $l_w/r = \sigma_f/\tau_i$ , (2) increasing volume fraction of fibers  $V_{f_5}$  (3) use of high-strength fibers, and (4) sufficiently decreasing shear stress at the fiber/matrix interfaces relative to fiber strength.

#### 2.2. Bridging by Fibers

Stress intensity factor  $\Delta K$  is correlated with compressive stress  $\sigma(x)$ , based on linear fracture dynamics, when  $\sigma(x)$  is present over a length of  $L_B$  from the edge of the penny-shape crack possessing a radius *C*:

$$\Delta K = -\left(\frac{2}{\sqrt{\pi C}}\right) \int_{0}^{t_{n}} \left\{ (C-x) \sigma(x)/\sqrt{x(2C-x)} \right\} dx$$
(26)

Stress intensity factor  $\Delta K$  is given by the following equation in the absence of the above compressive stress  $\sigma(x)$  at the crack tip, when an external stress  $\sigma_A$  is applied to the penny-shape crack from an infinite distance:

Therefore, stress intensity factor of the crack, in the presence of the stress  $\sigma(x)$  at the crack tip, is given by:

$$K = K_0 + \Delta K \qquad \dots \qquad (28)$$

Crack opening displacement u(x) is given by, based on linear fracture dynamics:

$$u(x) = (4/E') K \sqrt{x/2\pi}$$
 .... (29)

Substituting Equation (29) into Equation (2) gives the stress  $\sigma_{B}(x)$ , which is produced when the crack tips are bridged by a fiber:

$$\sigma_{\rm B}(x) = 2V_{\rm f}\tau_{\rm i} \left\{ l_{\rm i} - (4/E') K \sqrt{x/2\pi} \right\} / r \quad \dots \quad (30)$$

Combining Equations (26) and (30) yields:

$$\Delta K = -(6/\sqrt{\pi C}) \left( V_{\rm f} \tau_{\rm i}/r \right) \left( l_{\rm i} \sqrt{2 \ C L_{\rm B}} \right) \left( L_{\rm B} << C \right)$$
(31)

The length of the fiber portion involved in the bridging is given by the following equation, on the assumption that the fiber is pulled-out to the exent of crack opening displacement u(x):

Combining Equations (31) and (32) gives  $\Delta K$ :

$$\Delta K = -3 V_{\rm f} \tau_{\rm i} \left( l_{\rm i}/r \right) l_{\rm i} \left( E'/K \right) \quad \dots \quad \dots \quad (33)$$

Combining Equation as (28) and (33) gives K:

$$R = 3 V_{\rm f} (\tau_{\rm i}/\sigma_{\rm A}) (E'/\sigma_{\rm A}) (l_{\rm i}/r) (l_{\rm i}/C) \quad \dots \quad \dots \quad (34)$$

where,  $0 \le R \le 1$ 

$$K = (\sigma_{A}/\pi) \sqrt{\pi C} (1 + \sqrt{1 - R}) \quad ... \quad (35)$$

Comparing Equation (27) with Equation (35) suggests that the external stress  $\sigma_A$  apparently becomes, when the crack faces are bridged by a fiber. In other words, the parameter *R* represents the effects of decreasing stress intensity factor (stress-shielding effects). Equation (34) suggests that *R* is affected not only by the material-specific properties, such as  $V_f$ ,  $\tau_i$ , E',  $l_i$  and r, but also by fracture toughness measuring conditions, such as  $\sigma_A$  and *C*.

### 3. Experimental Procedure

#### 3.1. Materials

Powdered Al<sub>2</sub>O<sub>3</sub> used as the matrix for the composite was Taimei Kagaku Kogyo's Taimicron TM-100 ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>>99.9%, primary particle diameter: 0.01µm, BET specific area: 140m<sup>2</sup>/g, according to the catalog).

Seven types of whiskers were used (Tateho Kogyo's SCW#1-S, SCW#1-105-0.7, Tokai Carbon's Toca Whisker TWS-400 and Shin-Etsu Kagaku's KSC-40, KSC-41 and KSC-42). **Table 1** presents the catalog values in shape and size. The ESCA analysis of these fibers indicated that the quantity of oxygen present on the surfaces was almost the same and sufficiently small. Each whisker type was of single β-SiC crystals, as revealed by the TEM-aided electron beam diffraction analysis.

#### 3.2. Sample Preparation

Figure 2 shows the production process. Volume fractions of the SiC whiskers were adjusted at 0, 5, 10 and 20%. Mixture by a tumbling mixer and high-speed drying by a rotary evaporator were conducted so that the whiskers' shape and size may not be changed and the uniform dispersion in the matrix may be secured. Temperature for hotpressing was controlled in such a way as to change in order to have at least the 99% level of the density which is predicted from the composition rule, that is, at 1500 for the monolithic Al<sub>2</sub>O<sub>3</sub> and at 1600, 1650 and 1750°C for the SiC whisker/Al<sub>2</sub>O<sub>3</sub> composite samples containing the whiskers at 5, 10 and 20%, respectively. Other conditions were: 33MPa as the pressure and 1h as the time of preservation, in Ar gas atmosphere.

Table 1. Dimensions of SiC whiskers.

whisker	sample name and the supplyer	diameter	length	aspect ratio
1	KSC-41 (Shinetsu Chem. Ind.)	0.19 Jum	6.4 µm	34
2	KSC-40 (Shinetsu Chem.Ind.)	0.23 µm	7.8 µm	34
3	SCW#1-S (Tateho Chem. Ind.)	0.35 µm	17.1 µm	49
(4)	TOKA WHISKER (Tokal Carbon Co. Itd.)	0.35 µm	35 µm	100
5	SCW#1-105-0.7 (Tateho Chem. Ind.)	0.85 µm	19.0 µm	22
6	TWS400 (Tokal Carbon Co. Itd.)	1.1 µm	45 µm	41
(7)	KSC-42 (Shinetsu Chem. Ind.)	2.1 µm	51 µm	24

These data are average values referred to catalogues.

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#### 3.3. Evaluation Procedure

- Density: Apparent density was determined by the Archimedes' water-displacement method. Each sample was found to have an apparent density of at least 99% against the theoretical composite density.
- Young's Modulus: A strain gauge (Showa Sokki-made gauge of 1mm in length) was used during the measurement of strength in accordance with JIS R1602.
- 3) 4-point bending strength was measured, based on JIS R1601 under the conditions of internal span: 10mm and external span: 30mm. In case of a hot-pressed whisker-reinforced composite sample, whiskers showed two-dimensional random orientien in the plane perpendicular to the pressing direction.<sup>8)</sup> Each sample, therefore, was cut in such a way as to let the tensile plane set at a right angle to the hot-pressing direction, so that the main cracks might be propagated in the direction perpendicular to the whisker orientation plane. The tensile plane was finished by grinding longitudinally with a #600 diamond wheel.
- 4) Fracture toughness K<sub>IC</sub>: The above sample (3x4mm) was tested by the 3-point bending method in order to determine fracture toughness K<sub>IC</sub> under the conditions of span: 30mm and cross-head speed: 0.005mm/min. This sample was provided with a chevron notch so as to make the main cracks propagate in the direction perpendicular to the whisker orientation plane. In analysing, the following equations of "straight through crack assumption"<sup>9</sup> were used:

$$K_{\rm IC} = P_{\rm max}/(B\sqrt{W}) \times Y^*_{\rm min}(\alpha)$$
 .... (36)

$$Y^{*}(\alpha) = Y(\alpha) \times \left\{ (\alpha_{1} - \alpha_{0})/(\alpha - \alpha_{0}) \right\}^{1/2} \quad . \quad (37)$$

where

- $K_{\rm IC}$  : fracture toughness,
- $P_{\text{max}}$  : maximum load,
- B : sample width,
- W : sample height,
- $Y(\alpha)$ : shape factor of the sample possessing a straight through crack,
- $\alpha_1$  : relative depth of the chevron notch bottom,
- $\alpha_0$  : relative depth of the chevron notch tip,
- $\alpha$  : relative crack length, and



Fig. 2. Flow chart-of the process preparing SiC-whisker/Al<sub>2</sub>O<sub>3</sub> composites.

 $Y^*_{\min}(\alpha)$ : the minimum value of  $Y^*(\alpha)$ .

The following Wakai equations were used to represent the above-cited  $Y(\alpha)$ ,<sup>10</sup> taking into consideration the sample shape.

$$Y(\alpha) = 3 L/2W$$

$$\times (A_0 + A_1 \alpha + A_2 \alpha^2 + A_3 \alpha^3 + A_4 \alpha^4) \sqrt{\alpha} \quad (38)$$

$$A_i = a_i + b_i \times \ln (L/W - c_i) \quad \dots \quad (39)$$

where, L is span distance.

 Effective fracture energy y<sub>eff</sub>: Effective fracture energy y<sub>eff</sub> was determined from the load-crosshead displacement

	$A_0$	$-A_1$	$A_2$	$-A_3$	$A_4$
$a_i$	1.493	3.091	14.46	24.37	24.88
$b_i$	0.1468	-0.1745	-0.5167	-0.7781	-0.5196
C <sub>i</sub>	3.434	3.225	3.247	3.278	3.286

curve and projected area of the ligament for those samples in which the cracks propagated semi-statically until they were finally broken:

where,

- A: projected area of the ligament, and
- U: work done by the load.
- 6) Observation of fracture mode: The mirror-polished sample was indented by a Vickers indenter at a load of 20kgf in order to observe propagation of the cracks by a scanning electron microscope. Furthermore, the fracture faces of the samples for the measurement of  $K_{\rm IC}$  were observed, in an attempt to correlate fracture mode with  $K_{\rm IC}$ .

### 4. Results and Discussions

The Al<sub>2</sub>O<sub>3</sub> matrix varied in grain size according to the shape, size and contents of the whiskers but within a fairly narrow range from 2 to 6µm. In the following discussions, therefore, the difference is considered to be sufficiently small to affect  $K_{\rm IC}$ ,  $\gamma_{\rm eff}$  and bending strength levels significantly. It is also assumed that the whiskers used in this study would be uniform in strength and surface conditions, irrespective of type.

### 4.1. Effects of Whisker Shape and Size on $K_{IC}$ and $\gamma_{eff}$

It was known that a sufficiently large compressive residual stress was produced in the radial direction in a SiC-whisker/Al<sub>2</sub>O<sub>3</sub> composite material caused by the differences in the thermal expansion coefficients between SiC and Al<sub>2</sub>O<sub>3</sub><sup>,11</sup> suggesting that pulling-out of the whiskers was associated with a large shear resistance at the interfaces. In case of a experiment based on a simple "fiber pulling-out model," it was considered to result in  $l_w/r \ge \sigma_F / 2\tau_i$  when shear resistance stress  $\tau_i$  at the interfaces was comparatively higher than the fiber strength  $\sigma_{\rm F}$ . This meant that  $\Delta gc$  was in proportion to  $r^2/l_w$  from Equation (22). Assuming that the externally applied force was totally consumed to produce the fracture faces, leading to the relationship of  $g_c$  $\approx 2\gamma_{\rm eff}$ ,  $\gamma_{\rm eff}$  was plotted against l(Fig.3). Furthermore,  $K_{\rm IC}^2$ was also plotted against  $r^2/l_w$ , in consideration of Equation (23).



(radius)<sup>2</sup>. (length)<sup>1</sup> ∕ nm

Fig. 3. Effective fracture energy  $\gamma_{eff}$  of SiC whisker  $20vol\%/Al_2O_3$  composites as a function of whiskers' dimension.



Fig. 4. (Fracture toughness  $K_{\rm IC}$ )<sup>2</sup> of SiC whisker 20vol%/Al<sub>2</sub>O<sub>3</sub> composites as a function of whiskers' dimension.

There was noticed a fairly good linear relationship between  $\gamma_{\rm eff}$  and  $r^2/l_{\rm w}$ , which meant that only the simple "fiber pulling-out model" would account for increased toughness of the SiC-whisker/Al<sub>2</sub>O<sub>3</sub> composite material comparatively well, with "fiber bridging" being not taken into consideration. In this study, measurement of  $K_{\rm IC}$  and  $\gamma_{\rm eff}$  were condudcted by using a cheveron notch beam, thus leading to the situation where the size of the textures represented by the whiskers and matrix grains were sufficiently smaller than the length of the main cracks. These represented the evaluation by the formulae (34) and (35) under the condition where the "fiber bridging" effects tended to be reduced. Meanwhile, there occurred values smaller than expected from a linear relationship were shown only for those reinforced with whiskers of type 7 (average size: 2.1µm, average length: 51µm) in Table 1.

 $K_{\rm IC}$  of which tended to be lower than that anticipated by the linear relationship. This probably resulted from the composites' lower Young's modulus (343GPa for those reinforced with the whiskers of type O and 387 to 413GPa for others), from Equation (23). For reference only, it was noted that there was a good correlation between  $K_{\rm IC}^2$  and  $2E\gamma_{\rm eff}$ . One of the reasons for the lower Young's modulus of the composites reinforced with the O type whisker was the presence of micro-cracks produced by a large residual stress.

# 4.2. Effects of Volume Fractions of SiC whiskers in $K_{\rm IC}$ and $\gamma_{eff}$

The SiC-whisker/Al<sub>2</sub>O<sub>3</sub> compoite materials were prepared with the SiC whiskers of types ③, ⑥ and ⑦, where volume fractions  $V_f$  were adjusted at 5, 10 and 20%, in order to measure  $K_{IC}$  and  $\gamma_{eff}$ , and the results were compared with the model computation based on the "fiber pulling-out model". As equations (22) and (23) indicated that  $\Delta g_c$  and  $\Delta (K_{IC}^2)$  were in proportion to  $V_f$  and  $\gamma_{eff}$ ,  $K_{IC}^2$  was plotted against  $V_f$  (Figs.5 and 6).

These figures showed that both  $K_{\rm IC}$  and  $\gamma_{\rm eff}$  were linearly correlated with V<sub>f</sub>, thus backing up the validity of the simple "fiber pulling-out model". In the relationship between  $K_{\rm IC}^2$  and  $V_{\rm f}$ , the gradient of the straight line for the composites reinforced with the whiskers of type @ was smaller than that predicted from the whisker shape, which was also caused by lower Young's modulus, as discussed earlier.

### 4.3. Behavior of Crack Propagation

It was observed from **Fig.7** that crack propagation was effected the more by whiskers the more in the composite accompanied by the phenomena of so-called toughening behavior such as crack branching, crack deflection and pulling-out of the whiskers. It was also noted that the cracks ran relatively straight in the samples whose  $K_{\rm IC}$  and  $\gamma_{\rm eff}$  values should no significant improvement.

Figure 8 presents the result of fracture surface observa-



**volume fraction of whiskers Fig. 5.** Effective fracture energy  $\gamma_{eff}$  of SiC whisker/Al<sub>2</sub>O<sub>3</sub> composites as a function of whiskers' volume fraction. (whisker 3, 6, 7 See Table 1.)



Fig. 6. (Fracture toughness  $K_{1C}$ )<sup>2</sup> of SiC whisker/Al<sub>2</sub>O<sub>3</sub> composites as a function of whiskers' volume fraction. (whisker 3, 6, 7 See Table 1.)



Fig. 7. Typical SEM observations of crack propagation introduced by Vicker's indentor. (3 and 7 show whiskers' numbers in composite. See Table 1.)



Fig. 8. Fractured surfaces of SiC whisker 20vol%/Al<sub>2</sub>O<sub>3</sub> composites observed by SEM. (1, 6 and 7 show whiskers' numbers in composite. See Table 1.)



Fig. 9. 4-point bending strength sr of SiC whisker 20vol%/Al<sub>2</sub>O<sub>3</sub> composites as a function of whiskers' length.

tion. The monolithic  $Al_2O_3$  sample showed the mixed fracture mode, i.e. intergrain and intragrain fractures, while in the SiC-whisker/ $Al_2O_3$  composite samples, the intragrain fracture seems to have been predomenant in the matrix. It

was also observed that the fracture surface was more deflected in the composite sample than in the monolithic  $Al_2O_3$  sample, indicating that the SiC whiskers prevented crack propagation. The intragrain fracture seems to have predominated in the matrix. Particularly, crack defection was found more drastic in the composite sample of higher toughness, with the whiskers being found to be pulled out more. In the samples of low  $K_{IC}$  and  $\gamma_{eff}$ , the fracture surface was relatively smooth, leaving the extingished traces where whiskers are supposed to have been broken.

#### 4.4. Bending Strength $\sigma_f$

Bending strength  $\sigma_f$  for each sample was plotted against whisker length, as shown in Fig.9, indicating that  $\sigma_f$  decreased as the whisker length was increased.

Stress intensity factor  $K_1$  at the crack tip when an external force  $\sigma_A$  was applied to a crack of radius *C* on a semi-infinitely expanding surface was given by the following equation:

$$K_1 = 2.44/\pi \times \sigma_A \sqrt{\pi} C \qquad \dots \qquad \dots \qquad \dots \qquad \dots \qquad (41)$$

Fracture toughness  $K_{IC}$  was given by the following equation, on the assumption that the sample was broken totally by a stress  $\sigma_{f}$ :

40

length of whiskers / µm

Fig. 10. Equivalent crack length of SiC whisker 20vol%/Al<sub>2</sub>O<sub>3</sub>

monolithic Al<sub>2</sub>O<sub>3</sub>

60

80

equivalent

50



20

Fig. 11. 4-point bending strength sf of SiC whisker/Al<sub>2</sub>O<sub>3</sub> composites as a function of whiskers' volume fraction. (whisker 3, 6, 7 See Table 1)

$$K_{\rm IC} = 2.44/\pi \times \sigma_{\rm f} \sqrt{\pi C} \qquad (42)$$

As shown in Fig.10, radius of the critical crack which was determined from  $K_{\rm IC}$  and  $\sigma_{\rm f}$  values was plotted against whisker length. It was understood from this figure that length of the critical crack on the surface took on an increasing trend as the whisker length increased. Several reasons are cited hereunder for the decreased bending strength, in spite of an expectation of improvement in  $\sigma_{\rm f}$  due to increased  $K_{\rm IC}$ .

The whisker/matrix interface present in the plane on which the maximum tensile stress was acted served as the starting point of fracture, thus leading to the defect size which became larger in proportion to increases in the whisker length.

With a residual tensile stress being present in the matrix of a SiC-whisker/Al<sub>2</sub>O<sub>3</sub> composite sample,<sup>11)</sup> it was considered that the size of inclusions had a relation to the formation of fine cracks by residual stress,<sup>12)</sup> producing fine cracks more easily as the whisker size increased. This, coupled with external force, caused the sample to be broken at a low load.

Thus, it is considered that increasing whisker length accelerated production of the fine cracks, which possibly originated fractures, leading to the decreased bending strength. Further, in case of changing  $V_{\rm f}$  using the same type of whiskers (**Fig.11**), it is considered that while under the same conditions as mentioned above, increases in  $V_{\rm f}$ caused  $K_{\rm IC}$  improvement, affecting the bending strength of also to improve.

### 5. Conclusions

- Δ(K<sub>IC</sub><sup>2</sup>) and Δγ<sub>eff</sub> changed in proportion to r<sup>2</sup>/l<sub>w</sub> (K<sub>IC</sub>: fracture toughness, γ<sub>eff</sub>: effective fracture energy, r: whisker radius and l<sub>w</sub>: whisker length). This result could be explained with the simple "fiber pulling-out model".
- 2) Δ(K<sub>IC</sub><sup>2</sup>) and Δγ<sub>eff</sub> were also in proportion to V<sub>f</sub> (V<sub>f</sub>: volume fraction of the whiskers in the composite sample). This results could also be explained by the above-mentioned simple "fiber pulling-out model".
- 3) Observation of crack propagation and the fracture surfaces indicated that the phenomena related to toughness increases such as deflection of the main crack plane and pulling-out of the whiskers, were noted more in the sample as its toughness was reinforced and that the whiskers were broken to a significant extent in the sample whose  $K_{IC}$  and  $\gamma_{eff}$  had not significantly improved.
- Bending strength σ<sub>r</sub> might have tended to decrease as the whisker length was increased, conceivably because cracks originating fractures were produced more in a longer whisker.
- 5) When the same type whiskers were used,  $K_{IC}$  increased in proportion to the increases in  $V_f$  so as to let bending strength  $\sigma_f$  appear to take on an increasing trend accordingly.

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# Low Temperature Sintering of Spherical Silica Powder by Hydrothermal Hot-Pressing

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Powder of spherical silica particles prepared by hydrolysis of tetraethylorthosilicate was sintered by the hydrothermal hot-pressing method at low temperatures below 350°C. Densification of the powder was accelerated by the increase in reaction temperature and pressure. Formation of necks and deformation of particles were observed in fractured surface of a sintered body produced at high pressure (49MPa). Water contained in the starting powder was essential to the densification by hydrothermal hot-pressing.

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**Key-words:** Hydrolysis of tetraethylorthosilicate, Spherical silica particles, Hydrothermal hot-pressing, Low temperature sintering, Linkage of particles, Role of water

### 1. Introduction

Hydrolysis of tetraethylorthosilicate with ammonia as the catalyst will give well-dispersed, spherical silic particles of uniform size.<sup>1-5)</sup> Such a monodisperse system would provide an ideal feed for controlling the microstructures of sintered ceramic materials.<sup>6)</sup> Pressureless sintering was normally used to treat the monodispersed, spherical silica particles and it has been reported that ceramics can be sufficiently densified at a relatively low temperature in a range between 1000 and 1100°C.<sup>7-10</sup>

However, Shimodaira et al.<sup>(1),12)</sup> have successfully treated monodispersed spherical silica particles under hot isostatic conditions and produced opal-like materials by forming necks between the particles. This approach used tar pitch as the pressure-propagating medium, where the largest neck grew to a size about 40% of the particle diameter under the sintering conditions of 155°C and 14.4kg/cm<sup>2</sup> for 198h. The observation of the fractured surface, however, revealed that the structures were fractured around the necks, indicating insufficient sintering.<sup>(1)</sup>

The authors have developed a hydrothermal hot-pressing mehtod in which an external pressure was applied to the powder of an inorganic compound kept under hydrothermal conditions in an autoclave, in order to squeeze water present in the gaps between the particles and, at the same time, to promote densification and thereby to solidify the powder by bonding fast the particles to each other by the actions of water under high pressure and high temperature conditions.<sup>13,14</sup> Attempts have been performed to apply the above method to the solidification of radioactive wastes.<sup>14,15</sup> In addition, the mechanisms involved in the densification of borosilicate glass powder containing some quantities of modified oxides of network structures have been investi-

gated.<sup>16,17)</sup> More recently, the method has been applied to the processing of spherical silica particles prepared by the hydrolysis of tetraethylorthosilicate, leading to the discovery of the neck portions between the particles.<sup>18)</sup> In this study, the effects of hydrothermal hot-pressing on the sintering behavior of the spherical silica particles were investigated. As a result, it was found that increasing the reaction temperature and pressure accelerated densification and the starting powder.

### 2. Experimental Procedure

### 2.1. Preparation of Starting Materials

The starting material was prepared by hydrolyzing tetraethylorthosilicate in the presence of ammonia as the catalyst, following the procedure proposed by Shimodaira et al.<sup>33</sup> Two types of solution were prepared, one was a methyl alcohol solution of tetraethylorthosilicate ( $115cm^3$ ) dissolved in methyl alcohol ( $480cm^3$ ) and the other an aqueous solution of ammonia and ethyl alcohol or a mixture of ethyl alcohol ( $136cm^3$ ), concentrated ammonia water ( $NH_325\%$ ,  $200cm^3$ ) and distilled water ( $40cm^3$ ), were stirred for 1h in a constant-temperature bath kept at  $20^{\circ}C$ . The white, turbid liquid resulting from the mixing of these solutions was centrifuged at 1500rpm and the separated precipitates were dried at  $120^{\circ}C$ . The resultant solid blocks were crushed in a mortar, placed in ammonia water and then dried at  $80^{\circ}C$  in order to prepare the starting material for sintering.

The changes in the starting material under heat were observed by a thermogravimetric analyzer (Rigaku), infrared absorptiometer (IR-430, Shimadzu)and X-ray diffractometer (Rotorflex, Rigaku).

### 2.2. Preparation of Sintered Samples

Figure 1 illustrates the autoclave used for hydrothermal hot-pressing. The autoclave body consisted of carburized blister steel, 1.4cm in diameter. The sample in the autoclave could be pressed directly by the upper and lower pistons and this pressure expands the gland packing, to keep the vapor pressure within the autoclave at a desired level. Each piston was provided with a void space, through which water contained in the sample was emitted. The external walls of the autoclave were lined directly with a sheath type flexible heater to heat the sample.

The starting powder (2g), dried at 80°C, was pressed at normal temperature and 98.1MPa for 10min in the autoclave. It was then heated, while kept at a given pressure (9.8 to 49.0MPa), to a given reaction temperature (100 to  $350^{\circ}$ C) at 10°C/min and held for a given time (0 to 12h) at given temperature and pressure. It was then allowed to



Fig. 1. Autoclave for hydrothermal hot-pressing.

1: push rod, 2: thermocouple well 3: piston, 4: sample, 5: space for water retreat, 6: gland packing, 7: body.



Fig. 2. SEM photograph of starting material.

cool, while kept at a given pressure.

#### 2.3. Characterization of Sinter Samples

Each columnar sinter sample was measured for its height and was exposed to a load of 100gf for 15sec by a micro-Vickers hardness equipment (MVK-E III, Akashi) in order to measure its hardness by its indentation size. It was then measured for its compressive strength by a versatile tester (REH-100, Shimadzu) and the fractured surfaces were observed by a scanning electron microscope (SEM; S-530, Hitachi).

### 3. Results and Discussion

#### 3.1. Properties of Starting Powder

The starting powder used for sintering consisted of spherical particles of approximately  $0.2\mu$ m in diameter (**Fig.2**). It was amorphous, as far as the X-ray analysis results indicated. **Figure 3** shows the weight loss of the starting material under heat. A weight loss accompanied with a broad endothermic peak was observed at around 120°C and a total weight loss of 5% was recorded until the sample was heated to 200°C. No significant loss was observed between 200° and 300°C and the weight decreased again slowly between 300° and 700°C. The sample had lost 9.3% of its original weight until it was heated to 900°C. The weight loss observed at below 200°C was considered to result from dehydration of adsorbed water and the sample heated to 250°C gained a weight when it was allowed to

cool in air, to a higher amount than the original weight of the sample dried at 80°C. The weight loss observed at 300°C or above was conceivably associated with the dehydration/condensation of silanol groups. Figure 4 presents the infrared absorption spectral patterns of the various samples. The starting powder possessed absorption bands at 800, 950, 1100, 1200, 1400 and 1630cm<sup>-1</sup> in a wave number range from 700cm<sup>-1</sup> to 1700cm<sup>-1</sup>. The absorptions at 800, 1100 and 1200cm<sup>-1</sup> were relevant to  $Si-O^{5}$  and that at 950m<sup>-1</sup> to Si-OH.<sup>5,19,20)</sup> Those at 1400 and 1630cm<sup>-1</sup> were relevant to -NH4+ and O-H in free water, respectively. The starting powder contained ammonia, in addition to water. The absorption relevant to ammonia, although observed in the sample dried at 120°C, disappeared when the sample was heated to 250°C. The absorption at 950cm<sup>-1</sup> showed no change with samples heated at 250°C in air, but disappeared when the sample was heated at 900°C.

### 3.2. Effects of Hydrothermal Hot-Pressing Conditions on Sinters

Figure 5 and 6 shows the effects of reaction temperature and pressure on height, Vickers hardness and compressive strength of the sinters. Height of the columnar sinter sample was used as a measure of densification, instead of density, because the hydroscopic nature of the sitner tended to give an erroneous density value.

Increasing the reaction temperature accelerated densification, as revealed by the decreased sinter height. It also increased Vickers hardness and compressive strength. Increasing the reaction pressure also accelerated densification



Fig. 3. Weight loss of starting material.



Fig. 4. Infrared spectra of (a) spherical particles heated at 900°C for 12h, (b) sintered body produced at 250°C and 19.8MPa for 1h, (c) spherical particles heated at 250°C for 12h, (d) starting spherical particles.



Fig. 5. Effect of reaction temperature on compressive strength, micro-Vickers hardness and height of columnar sintered body produced at 19.8MPa for 1h.



Fig. 6. Effect of reaction pressure on compressive strength, micro-Vickers hardness and height of columnar sintered body produced at 250°C for 1h.

notably – a shrinkage of approximately 15% was attained at 50MPa, as shown in Fig.6 – and enhanced the mechanical properties of the sinter. The sinter prepared at 250°C, 49MPa and 1h possessed an apparent density of around  $1.5g/cm^3$  (about 65% that of quartz glass), compressive strength of 200MPa and Vickers hardness of 1.8GPa.

It was found by continuous monitoring of linear shrinkage that the sample shrinked rapidly during the heating process but very slowly at the reaction temperature. **Figure 7** shows the effects of reaction time at 250°C on the sample height, indicating that the reaction became almost saturated in 3h. It was also shown that  $1 - (1-X)^{1/3}$  changed linearly with reaction time, where X was shrinkage rate of the sample. These results suggested that the process was represented by a solid-liquid heterogeneous reaction, whose rate was determined by surface reaction. The hydrothermal solid reaction of glass powder also has exhibited similar phenomena.<sup>14</sup>

**Figure 8** presents the SEM photographs of the fractured surfaces of the sintered samples. The necks were formed between the particles in order to connect them, even in the sample prepared under the hydrothermal conditions of 250°C, 19.6MPa and 1h. At a higher pressure, the particles

were deformed in such a way that they filled gaps between packed spherical particles and, at the same time, the necks were formed, in order to accelerate densification by reducing the number of pores.

#### 3.3. Role of Water

Water played a vital role in the hydrothermal hot-pressing method. Water for this method has been supplied by adding a material capable of releasing water of hydration to the starting material.<sup>21,22)</sup> In this study, no water was added to the spherical silica particles as the starting material, which contained adsorbed water desorbable at 200°C or less, in expectation that the starting material could release water required by the hydrothermal process. It was found that water was released from the sample even at 100°C; this sufficiently densified the sintered sample and allowed Vickers indentation. In the absence of water, e.g., when the



Fig. 7. The height change of columnar body with time at 250°C and relation of  $1-(1-X)^{1/3}$  and time.



Fig. 8. SEM photographs of fractured surfaces of sintered bodies produced at 250°C and 19.8MPa for 1h(a), and at 250°C and 49.0MPa for 1h(b).

sample was pressed under heat after the gland packing was removed or treated after it had been dried at 250°C to remove adsorbed water, no shrinkage reactions were observed and the sample was not solidified but merely compacted. These results showed that water released from the starting material contributed to formation of the necks.

The changes in sinter height, Vickers hardness and compressive strength with reaction temperature (Fig.5) were similar to each other in that they changed little in a range from 200° to 300°C. These results were in good agreement with the gravimetric changes of the starting material under heat. In other words, the spherical silica particles shrinked in the hydrothermal hot-pressing process to enhance mechanical properties of the sinter, as water was released. Higashi et al. have reported that monodispersed silica particles as starting materials increased in density under heat.<sup>5)</sup> Therefore, increased density accompanying dehydrdrtation was also considered to contribute to the shrinkage of the starting material. The sinter prepared at 250°C possessed a reduced infrared absorption at 950cm<sup>-1</sup>, relevant to Si-OH (Fig.4), indicating that dehydration of silanol group was promoted under pressure. Dehydration of silanol groups at the contact points between the particles conceivably promoted bonding between the particles.

Tseng and Yu<sup>9)</sup> have attempted to sinter spherical silica particles at 1000°C in various atmospheres and found that densification was promoted in the presence of steam, hence, the Si-O-Si bond was opened by hydrolysis in a steam atmosphere to produce silanol groups. This phenomena was accompanied with decreased surface tension and, in particular, viscosity of the starting material, which accelerated densification. The starting material used in this study, contained a large quantity of silanol groups, was low in viscosity, and viscous or plastic motion was predominant even at low temperatures around 250°C under an elevated pressure, which accelerated densification. Water released from the starting material worked to decrease viscosity and thereby facilitate mass transfer.

### 4. Conclusions

The water-containing mono-dispersed spherical silica particles, around  $2\mu$ m in diameter, prepared by the hydrolysis of tetraethylorthosilicate, were sintered at a low temperature (350°C or less) by the hydrothermal hot-pressing method. The well-solidified sinter was produced even at 100°C by the hydrothermal hot-pressing, where the starting material was pressurized in the presence of water released from the starting material. In the absence of water, the starting material was not sufficiently sintered at elevated pressure and temperature. Increasing the temperature under the hydrothermal hot-pressing conditions accelerated densification of the sinter, as water was released from the starting material, increasing its Vickers hardness and compressive strength. Increasing the reaction pressure also accelerated densification of the sinter as well as mechanical strength. Observation of the fractured surface indicated that necks were formed between the particles and that the particles became deformed under elevated pressure which accelerated densification.

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# Gas Permeability and Bending Strength of Porous SiC Ceramics

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The reaction-sintered porous SiC ceramics with different particle sizes and porosities are prepared, and the effects of particle size and porosity on their gas permeability and bending strength are investigated. For porosities above 0.25, the Ergun's equation well explains the small pressure drop at large particle sizes and high porosities which were achieved by the increased compaction pressure of raw materials. The reduction in porosity down to 0.26 by the addition of free Si under the constant compaction pressure increased the bending strength remarkably, while no change in the pressure drop was accompanied. At a porosity smaller than 0.26, an abrupt increase of the pressure drop was observed without any further increase in bending strength. These observations were examined through the analysis of morphology and pore size distribution. The abrupt change was found to occur at the point where all the smaller pores are filled with Si completely. The preferential filling of Si in smaller pores can be explained by the good wetting of SiC with Si.

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**Key-words:** Silicon carbide, Particle Size, Porosity, Free silicon, Permeability, Pressure drop, Bending strength

### 1. Introduction

Possessing high resistance to corrosion and heat, porous ceramics are being promoted for wide applications in filtration and separation.<sup>1,2)</sup> Among ceramic materials, SiC exhibits a high resistance to corrosion and can be obtained at relatively high levels of purity, so that its porous products are used as dispersion boards for etching gas in IC manufacture.<sup>3)</sup> Also, with respect to high thermal resistance of SiC, SiC/MoSi<sub>2</sub> ceramic composite has been developed.<sup>4)</sup> Porous SiC in the composite plays the role as the matrix for absorbing the sintering molten MoSi<sub>2</sub>.

Porous materials been manufactured by several methods.<sup>5)</sup> The production method by holding the porosities in the initial process of the green molding has been applied widely, because of the simplification for making them. Requirements for the properties of the porous SiC include the controllability of the gas permeation with high accuracy and keeping a certain level of mechanical strength. There have been few studies investigating the effects of various factors on the gas permeability and mechanical strength of the porous SiC manufactured by reaction sintering. The effects of SiC grain size on the porosity by varying the green molding pressure and porosity changes with Si contents variations in reaction sintering on these required properties were investigated while examining, also, they were related with the micro-structure of porous ceramics.

### 2. Test

#### 2.1. Manufacture of Porous Ceramics

The porous ceramics used in the test were manufactured as follows. With respect to the raw material of Sic, one type of  $\alpha$ -SiC abrasives GC#80 and #150 (mean particle dia.: 186 and 69µm) made by Taiheiyo Random was used. The mean particle diameters were obtained from grain size distribution by sifting using tester. SiC and carbon powder, its mean particle dia.: 4µm, made by Chuetsu Kokuen Kogyojo were placed a weight ratio of 95% to 5 in a solvent (acetone) together with 5 parts of stearic acid as an organic binder, mixed well and then dried. The material was then molded (molding pressure: 16-190MPa) into green moldings 37mm in diameter and about 5mm thick. They were then heated to 1500°C, held in a vacuum for 1h and then sintered in contact with the required amount of Si into porous SiC disks.

#### 2.2. Measurement

With respect to gas permeability, O rings were pressed on both sides (surface roughness  $2\mu$ m) of the porous specimens in order to prevent leakage, N<sub>2</sub> gas was passed at a specified rate and the gas pressure at the up stream side was initially measured by using the apparatus shown in **Fig.1**. Then, with the apparatus unloaded, N<sub>2</sub> gas was passed at the same rate and the gas pressure equivalent to the pressure drops in the flow meter and in the piping to the flow meter was measured. Since this pressur could be regarded as the down stream pressure after passing the specimen, its pressure drop was obtained from the difference pressure between both cases, that were measurement with/without the specimen.

Bending strengths were obtained from a 3-point loading test at a crosshead speed of 0.5mm/min by using Autograph AG-5000A made by Shimadzu (specimen surface rough-



Fig. 1. Apparatus for measurement of pressure drop of porous SiC ceramics.

ness: 2 $\mu$ m, w=9, t=5, L<sub>7</sub>=37, L=30). In this test, samples were made from #280 (mean particle dia.:42 $\mu$ m) in addition GC#80 and #150 were also used.

Porosities were obtained from bulk densities calculated from the dimensions and the weights of specimens and the apparent densities obtained by a water absorption method.

Pore diameter distributions were measured by a mercury penetration porosimetry method.

### 3. Test Results and Review

#### 3.1. Effect of Porosity and Grain Size of Raw Material

Figure 2 is a typical optical micrograph of a porous sample used in the test. The microstructure was seen to be composed of SiC (gray), Si(white) and pores (black).

Figure 3 shows pressure drop measurement with varying in porosity and the grain size of the raw material at a constant  $N_2$  gas speed of 0.042m/s (20°C, 0.1MPa). Porosity variations were caused by only variations in molding pressure. The Si level during sintering was constant at approximately 21% of the molding weight independent of



— 100 μm

Fig. 2. Microstructure of porous SiC(GC#150) ceramics prepared and used in this experiment.

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Fig. 3. Effect of porosity on pressure drop at  $N_2$  gas velocity: 0.042m/s for changing particle size.

molding pressure and the grain size. Even at the equivalent level of porosity, pressure drops varied widely with variations in the grain size of raw material. Conventionally to evaluate the gas permeability of porous porcelain, the following equation derived from Poiseuille law was used.

$$\frac{\Delta P}{L} = \frac{32\alpha \,\mu \,u}{d^2 \,\varepsilon} \qquad (1)$$

where

- $\Delta P$  : pressure drop (P<sub>a</sub>),
- L : length (m),
- $\alpha$ : labyrinth coefficient,
- $\mu$  : viscosity (Pa-s),
- μ : flow velocity with a cross section reference (m/s),
- d : pore dia.(m),
- ε : porosity

Equation (1) cannot be applied very freely because it contains parameters difficult to evaluate or measure accurately, such as labyrinth coefficient  $\alpha$  and pore diameter d. Equation (1) also assumed that the gas flow was laminar.

Figure 4 shows pressure drop for varying  $N_2$  flow velocity. In the equivalent porous material, as the cross section based flow velocity increased the actual flow velocity in the pores also increased. Here the relationship between flow velocity and pressure drop cannot be expressed linearly. Pressure drops eventually, deviated upwards from the straight line. These discrepancy became larger, when the greater grain size or the smaller porosity of the specimens were tested. Deviations from the straight line suggested that it was not correct to assume the flow as completely laminar. Taking pressures drops due to laminar and turbulent flows into consideration, in evaluating gas permeability and assuming that Ergun's equation which does not contain any labyrinth factor and porosity parameters was more rational and easier to apply.<sup>70</sup>

$$\frac{\Delta P}{L} = \frac{150 (1-\varepsilon)^2}{\varepsilon^3} \cdot \frac{\mu \mu}{D_p^2} + \frac{1.75 (1-\varepsilon)}{\varepsilon^3} \cdot \frac{\rho \mu^2}{D_p}$$

where

 $\rho$  : fluid density (kg/m<sup>3</sup>)

Figure 5 shows the comparison of experimental pressure drops with the calculated values based on equation (2), by using the mean particle diameter of SiC powder for Dp and



Fig. 4. Relationship between pressure drop and  $N_2$  gas velocity for varying different porosities  $\varepsilon$ .



Fig. 5. Comparison of experimental pressure drop with calculated results based upon Ergun's equation for a constant gas velocity.



Fig. 6. Deviation of calculated particle size from the measured value as changing porosity.

the measured porosity for  $\varepsilon$ . With any grain size of the raw material, there occurred a good consistency between calculated and measured pressure drop values in the porosity range of 0.25 and above, proving that Ergun's equation was applicable. However, in the low porosity range, measured values were higher. To represent this more concisely Dp calculated from measured pressure drops were plotted against porosity  $\varepsilon$ , as shown in **Fig.6**. The horizontal lines in the figure represented mean particle diameters of the raw materials for GC numbers. The calculated Dp was equivalent to the mean particle diameter of the raw material in the porosity range from 0.25 and higher, but was lower in the low porosity range.

**Figure 7**(a) is an optical micrograph representing a case in which Ergun's equation was applicable and (b) was another case in which Ergun's equation was not applicable. Ergun's equation was essentially applicable for filler layers composed of particles. This may be why it was applicable to microstructures as in (a) in which particles still remained, but was not applicable to microstructures as in (b) in which particles were agglomerated together. The fact that calculated Dp was lower than the mean particle diameters of the raw materials in low ranges of porosity, implied a discrepancy resulting from application of Ergun's equation forcibly to cases possessing large deviations from filler layer structures as a prerequisite of Ergun's equation. Therefore, if Ergun's equation was to be representative, there existed a level of gas permeability greatly lowered by the advanced amalgamation of particles and there appeared a irrationality which required a reduction of the particle size, which essentially should have been constant, in addition possessing a reduced porosity.

Figure 8 shows the effect of porosity and the grain size of raw material on bending strength. With respect to the relationship between strength and porosity etc., several expressions have been presented. The related data has been thus summarized into:

where  $\sigma$  is bending strength (MPa) and K<sub>1</sub>, f and B are constants. From the data acquired in the present test, K=522, f=0.19 and B=3.8.



Fig. 7. Microstructures of porous SiC. The porosities were changed by pressing load, i.e. (a): 60 MPa and (b): 190 MPa, in the forming process of green body.



Fig. 8. Relationship between bending strength and porosity for different measured particle size  $D_{p}$ .



Fig. 9. Relationship between pressure drop and porosity for increasing free Si content and compaction pressure in forming. (N<sub>2</sub> gas velocity: 0.015m/s, 20°C, 0.1MPa)



Fig. 10. Effect of porosity on bending strength for increasing free Si content.



### Fig. 11. Microstructure of porous SiC for the different free Si content.

#### 3.2. Effect of Porosity due to Variation in Level of Free Si

For a grain size GC#150 of raw material, the porosity of sintered samples was changed by varying the level of the Si brought into contact, while the press molding was processed by applying the constant compaction pressure of 90MPa.

Figure 9 shows the effect of porosity on pressure drops. The dotted line represented the effect of porosity on pressure drops due to variations in molding pressure equivalent to Fig.3. It had no inflection point, but the curve which was depicted by the correlation of the pressure drop versus porosity for the different Si content possessed inflection. Decreases in porosity due to increases Si content had little effect on pressure drops, when the porosity range was kept larger than 0.26, but in the porosity range below 0.26 pressure drops increased. In other words, the pressure drop curve for the different Si content gave the inflection point at round a porosity of 0.26.

Figure 10 shows the effect of the porosity on bending strength with porosity varied by varying the level of Si. Decreases in porosity due to increases in Si level caused the bending strength to increase greatly in the porosity range larger than 0.26 but hardly any effect in the lower porosity range. Differing from Fig.8, Fig.10 showed an inflection of bending strength and the porosity at which the inflection occurred was nearly the same as that at the inflection of pressure drop in Fig.9.

The above results suggested that at a porosity of about 0.26 there occurred a great change in the microstructures of the sintered specimens. Therefore, the pore diameter distributions were investigated by means of observation under an optical microscope and by using a mercury penetration porosimeter.

**Figure 11** shows optical micrographs with the Si level raised gradually (with porosity decreased). From Fig.11(a), (b) and (c), it became evident that Si preferred to enter smaller pores and from (d), as the level of Si increased, Si also entered larger pores. The porosity in (c) is 0.26, which coincided with that at the inflection seen in Figs.9 and 10.

Figure 12 shows pore diameter distributions. There existed pores with porosities equivalent to the vertical portions of the curves and the porosities for such pores corresponded to the difference of the vertical portions of the curves. Pores



Fig. 12. Relationship between the cumulative porosity and pore diameter for varying free Si content.

in porous specimens were entirely devoid of Si and consisted of 2 types: smaller pores 2 to  $6\mu$ m and larger pores 10 to 20 $\mu$ m. The arrow in the figure indicates the rising direction of Si level. As the Si level increased, Si first filled the smaller pores 2 to  $6\mu$ m and after completion filled the larger pores 10 to 20 $\mu$ m. **Figure 13** shows variations in the ratio between 2 to  $6\mu$ m and 10 to 20 $\mu$ m pores due to decreases in total porosity resulting from increases in Si level. In the porosity range above 0.26, the quantity of smaller pores decreased greatly and in the lower porosity ranges the larger pores decreased. The inflection point occurring at a porosity of 0.26 agreed with the porosity with which the inflection point was observed as the gas permeability and at which bending strength variation occurred.

The above data proved that the factor which had the most effect on gas permeability was the quantity of unfilled and remaining 10 to 20 $\mu$ m pores and that the bending strength was greatly affected by the ratio of 2 to 6 $\mu$ m pores, being increased as the smaller pores were filled with Si, but bending strength hardly increased as the larger pores were filled.

When moldings were brought into contact with a small amount of Si, Si first filled the smaller pores. This was because the contact angle between molten Si and SiC was approximately 40 degrees, very small and showed high wettability. With the same feed of molten Si, the interface energy was smaller when Si filled the smaller pores, in which process the area of contact with SiC became larger. This may be why Si first filled the smaller pores.

### 4. Conclusion

The following effects have been investigated, the grain size of the raw material, compaction pressure in green molding, the level of Si in reactive sintering on the gas permeability and the mechanical strength of porous SiC blocks manufactured by a reactive sintering method; the following conclusions were reached: Porosity varied due to changes in compaction pressure.

- In the porosity range above 0.25, the effect of the grain size of the raw material and porosity on pressure drops could be explained quantitatively by Ergun's formula.
- 2) In the porosity range below 0.25, Ergun's formula was



Fig. 13. Relationship between distribution ratio and whole porosity for increasing free Si content.

not applicable because measured pressure drops were higher than the values by Ergun's formula. Porosity also varied due to changes in the level of free

Si.

- 3) Decreases in porosity due to increases in Si level, produced inflection points at which pressure drop and bending strength changed greatly. For both pressure drop and bending strength, the inflection points occured at equivalent porosities.
- 4) As Si level was gradually raised to the inflection point, Si first filled the smaller pores. Decreases in porosity here caused the bending strength to increase greatly, while hardly affecting the pressure drop. The reason why Si first filled smaller pores was that Si and SiC possess high wettability.
- 5) As Si level was raised above the inflection point, Si filled the larger pores. Decreases in porosity here caused the pressure drop to rise greatly but hardly contributed to increasing the bending strength.

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# Influence of Surface Roughness on Critical Current Density of Bi-Pb-Sr-Ca-Cu-O Superconductivie Thin Films

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Bi-Pb-Sr-Ca-Cu-O superconductive films (Tc≥100K) films were obtained by annealing A  $((Bi+Pb)_{147}Sr_{100}Ca_{0.02}Cu_{1.80}O_x)$  at 850°C which were prepared by rf-magnetron sputtering using multi-targets. The critical current density (Jc) of the annealed films was greatly influenced by the surface roughness of the film. Jc increased proportionally with a decrease in surface roughness, indicating that the decrease of Jc was caused by the rough surface of the film, and by a liquid phase formed during the annealing process. To avoid the formation of the liquid phase and to obtain smooth surface films, low Ca content films B  $(Bi+Pb)_{1,27}Sr_{1,00}Ca_{0,76}Cu_{1,37}O_{x})$  were prepared and annealed at a low temperature (835°C). The surface of the annealed film B was smoother than that of the annealed film A. The obtained films with smooth surface films showed high Jc(=27,000A/cm<sup>2</sup>) at 77K in zero magnetic field.

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Key-words: Bi-Pb-Sr-CA-Cu-O thin film, rf magnetron sputtering, Multi target, Surface roughness, Critical current density

### 1. Introduction

Compounds of Bi-Sr-Ca-Cu-O<sup>1)</sup> and Bi-Pb-Sr-Ca-Cu- $O^{2,3)}$  systems are polymorphs exhibiting a high Tc phase at 110K, a low Tc phase at 80K, and a semiconducting phase with different C-axis lengths. To improve their applicability as materials in electronic devices, various studies are under way to produce thin films with smooth surfaces, for micropatterning, the preparation of weak-links, and device reliability.

At present, Bi system superconductive thin films are mostly prepared by heat treatment. Unfortunately, this heating process roughens the surface of the thin film as well as influencing its superconductive properties, but is necessary to promote film crystallization and gain growth in microbridges. In other words, heat treatment suffers the contradiction of damaging smooth surfaces and yet being favorable for fine micropatterning and the preparation of weak-links.

Nagai, et al.,<sup>4)</sup> have been trying to obtain smooth surfaces by heat treating Bi-Sr-Ca-Cu-O thin films on MgO single crystals.

In this study the authors attempted to produce smooth films without affecting superconductive properties. Thin films were prepared with critical temperatures exceeding 100K to examine the influences of their surface roughness (smoothness) and particle orientation on their critical current density.

### 2. Experimental Procedure

### 2.1. Preparation of Thin Films

Thin films of the Bi-Pb-Sr-Ca-Cu-O system were formed on commercial MgO single crystal substrates by rf magnetron sputtering using a multitarget. The following three targets were used:

- 1) Bi<sub>0.5</sub>Pb<sub>0.5</sub>O<sub>x</sub> (powder mixture of Bi<sub>2</sub>O<sub>3</sub> and PbO);
- CaCu<sub>0.75</sub>O<sub>x</sub> (powder of CaCO<sub>3</sub> and CuO fired at 950°C); and
- 3) SrCu<sub>0.75</sub>O<sub>x</sub> (powder of SrCO<sub>3</sub> and CuO fired at 950°C).

The thin films were prepared by sputtering 1, 2 and 3 to form Bi-Pb-O/Ca-Cu-O/Sr-Cu-O layered structures.<sup>5)</sup> The composition was controlled by adjusting the sputtering time for each target. In this experiment, stacking was repeated 400 times obtaining thin films over the course of the following sputtering periods:

Film A: 1. 8 sec. 2. 58.5 sec. 3. 33.5 sec.

Film B: 1. 10 sec. 2. 50 sec. 3. 40 sec.

The thickness of the film deposited during a single cycle of each target was 5nm, and  $2\mu m$  for the finished product. Prepared thin films were amorphous, and heat treatment was required.

#### 2.2. Annealing of Thin Films

A two-step annealing method was adopted. Film A was primary annealed at 780°, 800°, and 820°C for 2 hours, and then heated at 850°C for 15 hours as the secondary annealing. Film B was primary annealed at 780°C for 2 hours, and secondary treated at 835°C for 15, 24, 65, and 110 hours. The thin films were rapidly heated to each annealing temperature, soaked for 2 hours, and then quenched. In the step, they were rapidly reheated to each secondary annealing temperature, and held there for the specified period of time, followed by cooling in the fumace to room temperature. All annealing of the thin films was carried out in alumina crucibles together with Bi<sub>0.96</sub>Pb<sub>0.24</sub>SrCaCu<sub>1.6</sub>O<sub>x</sub> pellets.

### 2.3. Evaluation of Thin Films

The composition of the obtained thin films was determined by EPMA, and crystalline phases by XRD. The volume ratio of the high Tc phase was calculated using the intensity ratios of the (002) reflection of the XRD patterns.<sup>5)</sup>

The electrical resistance of the thin films was measured

by a four-probe method. in addition, critical current density was measured at 77K in a zero magnetic field and calculated based on a current value when the output voltage exceeded  $1\mu V$  (terminal gap: 2mm).

The orientation of the crystal was evaluated using the rocking curve of the (0014) reflection of the high Tc phase. The micro-structures of thin films were observed by SEM, and the surface roughness was estimated from the maximum height ( $R_{max}$ ) of films (terminal scan: 2mm).

### 3. Results and Discussions

#### 3.1. Annealing of Film A

The composition Film A was determined by EPMA as follows:

 $(Bi + Pb)_{1.47} Sr_{1.00} Ca_{0.92} Cu_{1.80} O_x$ 

Figure 1 shows the relationship between the critical temperature and the critical current density of the thin film after the primary annealing at  $780^{\circ}$ ,  $800^{\circ}$ , and  $820^{\circ}$ C, and after the secondary annealing at  $850^{\circ}$ C for 15 hours. Figure 2 shows the relationship between the surface roughness and the orientation (width at half maximum of a rocking curve).

As previously reported,<sup>5)</sup> XRD patterns indicated that the composition of each thin film was approximately 50% in the high Tc phase, and the critical temperature was over 100K.



Fig. 1. J<sub>c</sub> and T<sub>c</sub> of the Film A annealed at 850°C for 15hr.



Fig. 2. R<sub>max</sub> and half maximum intensity breadth of rocking curve of the Film A annealed at 850°C for 15hr.

Figure 1 shows that the critical current density of the thin film at 77K in a zero magnetic filed decreased from  $667A/cm^2$  to  $160A/cm^2$  as the primary annealing temperature increased. These values were substantially lower than those reported by Tanaka, et al.<sup>6)</sup>

In the second step, the surface roughness of thin films and the orientation of the particles (half maximum intensity breadth of rocking curve) was measured and were considered to affect the critical current density of the thin film. As shown in Fig.2, the surface roughness increased from 5.6 through 11.0 to 11.8 $\mu$ m with an increase in the primary annealing temperature. (i.e. the surface became rougher). On the other hand, the half maximum intensity breadth of the rocking curve of the (0014) reflection of the high Tc phase, decreased from 3.2 to 1.0 and 0.6°, as the primary annealing temperature increased, and improved the orientation of the crystals. In other words, the thin films with higher C-axis orientation had rougher surfaces and lower critical current densities.

These results suggested that the change in the critical current density caused by the primary annealing could be explained as follows:

1) The orientation of particles (platelike crystals) improves when a liquid phase is present during the formation of a high-Tc phase. This liquid phase remains in the thin film after annealing and acts as an insulator, which lowers the critical current density. This indicates that the higher the particles orientation of a thin film, the higher the tendency of the liquid phase to remain around platelike crystals after the secondary annealing. It has been reported that this liquid phase can be formed by a reaction between the semiconductor phase (Bi<sub>2</sub>Sr<sub>2</sub>Cu<sub>1</sub>O<sub>x</sub>) and Ca<sub>2</sub>PbO<sub>4</sub>.<sup>7)</sup>

After the primary annealing, the thin films in this study were also composed of  $Bi_2Sr_2Cu_1O_x$ ,  $Ca_2PbO_4$ , and CuO (**Table 1**), suggesting that the liquid phase was formed during the secondary annealing.

The microstructure in the vicinity of the platelike crystal grain boundary was observed by SEM (Fig. 3) to confirm the existance of a glass phase surrounding the platelike crystals, and binding them to each other. It was concluded that a change in particle orientation generated by different primary annealing temperatures was probably caused by different amounts of the liquid phase being formed. This was based on the fact that there was a difference in the proportion of crystal phases (Ca<sub>2</sub>PbO<sub>4</sub> and CuO) formed by the primary annealing (Table 1). In other words, the larger the amount of Ca<sub>2</sub>PbO<sub>4</sub> generated by the primary annealing, the further the formation of the liquid phase proceeded during the secondary annealing.

2) A second reason for the change in the critical current

Table 1. Crystalline phase of the Film A after preannealing

crystalline_phase preannealing	Ca <sub>2</sub> PbO <sub>4</sub>	Bi <sub>2</sub> Sr <sub>2</sub> Cu <sub>1</sub> 0×	CuO
780°C 2hr	weak	very weak	strong
800°C 2hr	middle	very weak	middle
820°C 2hr	strong	very weak	weak
density is that platelike crystals are piled up in blocks which significantly roughens the film (less than  $0.1\mu m$ before annealing; 5.6-11.8 $\mu m$  after secondary annealing), and causes spots with extremely low cross sections in the thin film. Since the critical current is determined by these cross sections, the pass of the superconducting current becomes smaller, resulting in a lower critical current density.

The fact that the platelike crystals pile up in blocks further supports the involvement of a liquid phase generated by the secondary annealing, and that the degree to which the phenomenon occurs depends on the amount of the generated liquid phase. Additionally, the roughened sur-



750 n m

Fig. 3. SEM photograph of the grain boundary of the platelike crystals for the annealed film.



Fig. 4. XRD patterns of the Film B annealed at  $835^{\circ}$ C for  $15 \sim 110$ hr.

faces of the films with high C-axis orientations are probably due to the substantial formation of the liquid phase during the secondary annealing.

The condition of the film after annealing seems to change as described below depending on the amount of the liquid phase formed in the secondary annealing.

Case of large quantity:	The orientation of the platelike crystals proceeds and they ag- glomerate to roughen the film surface.
Case of small quantity:	The orientation of the platelike crystals does not proceed, and bonding of the platelike crys- tals to one another prevents the surface from roughening.

#### 3.2. Annealing of Film B

#### 3.2.1. Crystalline Phase

The roughened surfaces of the thin films and the low critical current densities are caused by the liquid phase formed during the annealing. It has been reported that Ca and Cu tend to generate a liquid phase as well as precipitating in the grain boundaries.<sup>8-9)</sup>

Consequently, Film B,  $((Bi+Pb)_{1.27}Sr_{1.00}Ca_{0.76}Cu_{1.37}O_x)$  containing less Ca and Cu, was used to control the formation of the liquid phase, and was subjected to a secondary annealing at lower temperatures than was Film A.

**Figure 4** shows the XRD patterns of Film B primary annealed at 780°C for 2hr, and then at 835°C for 15, 24, 65, or 110hr for the secondary annealing.

In each thin film the amount of high–Tc phase generated was small: 0%(15hr), 6%(24hr), 10%(65hr) and 7%(hr). The limited amount of the high–Tc phase formed via a reaction with the liquid phase, suggested that the lower Ca and Cu contents as well as the lower temperature for the secondary annealing tended to suppress the formation of the liquid phase.

#### 3.2.2. Critical Temperature and Critical Current Density

**Figure 5** presents the critical current density and critical temperature of Film B. The critical temperature of the thin film treated for 15hr secondary annealing was 82K. This was due to the fact that the thin film was composed only a low–Tc phase. The critical temperature increased to 106K as the secondary annealing time increased. This indicated



Fig. 5. J<sub>c</sub> of the Film B annealed at 835°C for 15 ~ 110hr.



Fig. 6.  $R_{max}$  and half maximum intensity breadth of rocking curve of the film B annealed at 835°C for 15 ~ 110hr.

that the particles of the high-Tc phase came into direct contact with each other even though the proportion of the phase was small.

The critical current densities of most of Film B were higher than the A films; in particular Film B subjected to secondary annealing for 65hr exhibited a critical current densities of 27,000 A/cm<sup>2</sup>. Longer annealing (110hr) decreased the value to 4,600 A/cm.<sup>2</sup>

#### 3.2.3. Surface Roughness and Orientation

**Figure 6** presents the surface roughness and the half maximum intensity breadth of the rocking curve for Film B. The surface roughness of the thin film increased with increasing secondary annealing times (before treatment 0.1µm or less; after annealing 0.9µm (15hr) ~ 2.4µm (110hr). However, a given period of annealing, the surface roughness of most of the films was substantially lower than that of Film A.

Moreover, the particle orientation showed little change



Fig. 7. SEM photographs of the films:(a) Film B annealed at 835°C for 15hr, (b) Film B annealed at 835°C for 24hr, (c) Film B annealed at 835°C for 65hr, (d) Film B annealed at 835°C for 110hr, (e) Film A annealed at 850°C for 15hr

 $(3.15 \sim 3.20^{\circ})$  for secondary annealing times of up to 65 hr; however, at 110hr, the value dropped to 0.70°, resulting in a substantial improvement in the particle orientation.

The above observations were thought to be due to the small amount of the liquid phase generated by the annealing. The limited formation of the liquid phase suppressed amount of the insulation around the crystal particles, and caused the plate crystals to pile up into blocks and greatly improved the critical current density. Based on the above observations, it appears that decreasing the surface roughness is also effective in improving the superconducting properties of these thin films.

#### 3.2.4. SEM Observation

Figure 7 shows the SEM photographs of Film B for comparison, the SEM photograph of Film A is also presented. All films were primary annealed at 780°C for 2hr.

In each thin film, the platelike crystals are c-axis oriented which agreed with the XRD patterns previously analyzed. The size of the platelike crystals was different for thin films A and B, with the former exhibiting coarser particles.

This suggested that the grain growth in Film A occurred in the presence of a larger amount of the liquid phase than did Film B; i.e., the formation of the liquid phase was less in Film B than in Film A. In addition, in the case of Film B, particles were coarsened by the secondary annealing for 110hr. This was probably due to a prolonged contact with the liquid phase, although limited in quantity. This observation was in good agreement with the orientation results.

# 4. Conclusions

Two kinds of thin films with different composition were subjected to a two-step annealing to prepare Bi-Pb-Sr-Ca-Cu-O superconducting thin films. The effects of surface roughness and particle orientation of these thin films on critical current density were studied obtaining the following results.

#### 1) $(Bi+Pb)_{1.47}Sr_{1.00}Ca_{0.92}Cu_{1.80}O_x$ thin films

Different primary annealing temperatures affected the surface roughness and the orientation of platelike crystals. Critical current density tended to increase with decreasing surface roughness, and decrease with higher particle orientation. These facts suggested that a liquid phase generated during the secondary annealing was closely associated with the property changes.

2) Thin films with low Ca and Cu content

The compound  $((Bi+Pb)_{1.27}Sr_{1.00}Ca_{0.76}Cu_{1.37}O_x)$  was subjected to low temperature secondary annealing to prepare films in which the formation of the liquid phase was suppressed. The obtained films exhibited substantially lower surface roughness as well as improved critical current densities (27,000A/cm<sup>2</sup> at 77K, OT).

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# Metal/dielectric NANOCON Materials (II) – Effects of Additives on Nano-Structure Controlled Magnetic Materials –

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The effect of additives on Nano-structure Controlled materials has been studied. This material consists of Febased (Fe-Si-Al) soft magnetic metal grains completely separated from each other by insulating thin films. The synthesis process is as follows: first, a metal powder was heated to form thin uniform Al-O-N film (~ 10nm). Then the coated powder was compacted and hot-press sintered with additives at a high pressure. The sintered materials had electric resistivities  $(10^6 - 10^8\Omega \cdot m)$  containing  $B_2O_3(+5nm - +20nm)$  higher than that of sintered one without additives.

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**Key-words:** Composite materials, Hot-press sintering, Magnetic materials, Insulating film, Additives

# 1. Introduction

Multi-function material, such as inclined functional materials and "NANOCON" (Nano-Structure Controlled) materials which have improved properties in plural aspects have been developed, based on mono-functional materials in which properties of one aspect, such as electro-magnetism, mechanical strength or thermal stability, is maximized. Various industrial uses for these materials have been discovered for which conventional materials are not entirely applicable.

The NANOCON material means Nano-structure Controlled material, which is artificially controlled through its atomic configuration, composition, crystalline structure, or bonding mode on a nanometer(nm) scale, to realize new functions and characteristics.

The authors have already developed and investigated the electromagnetic properties of NANOCON magnetic materials characterized by their high saturation flux density and high electrical resistance.<sup>1-3)</sup> Materials were prepared by covering metallic magnetic particle surfaces with an insulation layer of inorganic ceramic particles on the order of 10nm, and sintering them to 99% or more of the theoretical density.1-3) The saturation magnetic flux density of the NANOCON magnetic materials was at least 2 times greater than that for oxide-based magnetic materials such as Mn-Zn ferrite. In addition, they exhibited a substantially higher (106 times or more) electrical resistance than metallic magnetic materials; this resulted in a high permeability and low loss in the high frequency region which is inconceivable for mono-functional materials such as Mn-Zn ferrite or metallic magnetic materials.

Since they are bulk materials, they are mass-producible, unlike the magnetic materials of laminated thin-film structures,<sup>4)</sup> and can be used in highly functional electronic devices such as magnetic cores in high-frequency power sources which occupy certain volume, for which laminated thin-film materials are rarely applicable.

The NANOCON magnetic material prepared in this study had a structure in which the metallic magnetic particles were separated from each other, each being covered by a non-magnetic insulation layer. This structure provided a magnetic circuit in which the thickness of the insulation layer is one of the most important factors which determines the permeability of the sinter, together with the shape of the metallic particles (determines the demagnetizing factor), the particle size, (related to skin effect depth), and sinter density. In particular, the absolute value of the permeability crucially depends on the thickness of the non-magnetic film.

Figure 1 shows the relationship between the DC permeability of the NANOCON magnetic material and the thickness of the non-magnetic insulation film, calculated using the Ollendorf equation.<sup>5)</sup> It is assumed that each metallic particle is spherical and 20 $\mu$ m in diameter (demagnetizing factor N=1/3); the relative DC permeability of the metallic particle itself is 1×10,<sup>4</sup> that of the insulation film is 1; and the relative density of the sinter is 100% (porosity: 0%).

The relationship suggests that it is necessary to keep thickness of the insulation film at 20nm or less, in order to secure a relative permeability of  $\mu$ =500 or more. It has been demonstrated that a sinter exhibits a high electrical resistance and a relative permeability of 300 to 400 if the thickness of the insulation film is maintained around 30nm. Inoue et al.<sup>3</sup> reported that it is necessary to reduce the thickness of the insulation film to 10nm in order to realize still higher permeabilities.<sup>3)</sup>



Fig. 1. The relationship between a permeability at dc of Nano-Structure Controlled Magnetic Materials and their thickness of insulating film, calculated from equation of Ollendort<sup>4</sup>.

#### higher permeabilities.3)

Figure 2 shows the composition of the insulation film coating the magnetic alloy particles; the distribution of elements along the thickness of the sample was determined by AES analysis. These results indicated that Al, O and N are present in the vicinity of the surface of alloy particle, which consists mainly of Fe. Al is nitrided and oxidized preferentially over the particle surfaces, and Fe or Si is rarely present in the insulation film. Furthermore, the metallic particle is considered to have a fairly uniform composition inside, based on the scarcity of oxygen and nitrogen diffusing into the metallic particle, and the fact that the composition-sensitive magnetic properties (in particular, permeability) are essentially unchanged after being covered with the insulation film.

These spherical particles, when hot-press sintered, are



Fig. 2. The Auger depth profile of the Fe-Si-Al particle after forming an insulting film.



Fig. 3. The photographs of scanning electron micro-scope (SEM) of (a) particle-boundary fracture surface, and (b) lapped and etched surface of the hot-press sintered body.

plastically deformed into polyhedrons separated from each other by the insulation film. **Figure 3** presents the SEM photographs of the ground and fractured surfaces. It is also noted that the sinter was highly densified, with few pores in the interfaces between the particles or in the triple point regions.

For a NANOCON material to have a high relative permeability of 500 to 1000 in the high-frequency region, it should be high in density and electrical resistance even when its particles are covered with very thin (around 10nm) insulation films.

In this study, the authors have attempted to prepare a thinner insulation film and to dope it with various additives to enable accurate control of the characteristics of the NANOCON material. The subsequent investigation of the microstructures and electro-magnetic properties of these materials will also be discussed.

#### 2. Experimental Procedure

The starting material was a magnetic alloy spherical powder (Sanyo Tokushu Seiko) containing Fe as the main ingredient, with very small quantities of Al and Si, atomized into a nitrogen gas atmosphere and passed through a 250mesh-sieve resulting in a powder with an average particle size of around 20µm. Figure 4 presents an SEM photograph of the starting powder. The average particle size was estimated from relative surface area measurements determined by the BET method. The starting powder, containing 70ppm of oxygen and 30ppm of nitrogen, was thermally treated at 773–1273K in an N<sub>2</sub>/O<sub>2</sub> gas mixture, with varying oxygen partial pressure, to form a uniform insulation film (several to several tens of nm(s) in thickness) over each particle.

The composition of the insulation film was estimated from the distribution of the elements along the thickness determined by Auger electron spectroscopic analysis (AES). The thickness of the insulation film was determined from the mass analysis results of oxygen from combustion infrared absorption, and of nitrogen from combustion thermal conductance, based on the assumption that the film consisted of Al<sub>2</sub>O<sub>3</sub> and AlN, taking into account Ar ion sputtering rates used in the AES elementary analysis.

Next, trace quantities of special reagent grade B2O3,



Fig. 4. The photographs of scanning electron micro-scope (SEM) of a starting spherical Fe-Si-Al powder.

 $V_2O_5,\,Sb_2O_3,\,PbO,$  and  $Bi_2O_3$  were added (in concentrations of 0.2 to 0.8vol%), under dry conditions, to the particles covered with the insulation film formed under the varying conditions. The mixture, was then hot-pressed to prepare the highly densified sinter having a relative density of 99% or more.

For  $B_2O_3$ , more volatile than the other elements, boron (B), was quantitatively analyzed by the induced coupled plasma (ICP) method.

Sinter microstructures were observed through mirrorpolished surfaces as well as their etched and fracture surfaces using an optical microscope and scanning electron microscope (SEM). A specimen strip was cut from the sintered sample and provided with In-Ga electrodes on the edges to determine its electrical resistivity by the twoelectrode method, using an LCR meter (YHP-4274A). Furthermore, saturation flux density (Bs) of the sinter was determined at room temperature, using a vibration type magnetometer (Toei Kogyo VSM).

The wetability of additives on the insulation film hotpressed at a specified temperature was compared with each other, based on the contact angle to the film.

The hot-pressed sinter, having a relative density of 99.8% or more, was mirror-polished, coated with a 17nm thick insulation film and then treated with trace quantities (several mg) of one of the afore-mentioned additives before being heated at hot-press temperature in an inert gas atmosphere. Each sample was analyzed for contact angle of the molten additive to the insulation film after it was cooled.

# 3. Results and Discussion

Figure 5 shows the relationship between the resistivity and the thickness of the insulation film, where the particles coated with the insulation films were thermally treated under varying conditions to control film thickness in a range  $\delta$ =8 to 100nm, before being hot-pressed. The straight broken line shown in Fig.5 represents the relationship between the resistivity,  $\rho$ , and the film thickness,  $\delta$ , of the

colculated ۶ B,0. 6 4 (Um) 2 C бо 0 - ity 0. 0 ng film non-additives 10<sup>10</sup> Ωm -6 -8 500 1000 100 200 10 20 50 2 5 thickness of insulating film  $\delta$  (nm)

Fig. 5. The relationship between electric resistivity  $\rho$  and thickness of insulating film  $\delta$  of Nano-Structure Controlled Magnetic Materials with additives and without additives. The insulating film is composed mainly of Al-O-N compound. magnetic NANOCON model, where it is assumed that the 20µm thick metallic conductor and insulation film (with a thickness on the order of several nm(s)) are connected in series; the electric resistivity of the former being  $8 \times 10^{-7} \Omega$  - m, and that of the latter on the order of  $10^{10}\Omega$  m based on the assumption that the film consists of Al<sub>2</sub>O<sub>3</sub> and AlN. For the additive-free sinters, however, the resistivity was higher than  $10^6\Omega$  m, which was sufficiently close to the calculated level, when the thickness of the film exceeded 30nm, but dropped sharply as the film thickness decreased to  $10^0\Omega$  m

The spherical metallic particles, when hot-pressed into a highly densified sinter body, were plastically deformed into polyhedrons, as shown in Fig.3, increasing the surface area. As a result, the insulation film of inorganic materials was made brittle by fracture around the greatly deformed metallic particles. Thus, the metallic particles could come into contact with each other very easily through the broken film. if the film was sufficiently thin. Assuming that there was a pin hole of 100nm in diameter on each metallic particle which would allow these particles to come into contact with each other, the resistivity would be reduced to a value as low as  $10^{-2}\Omega$ ·m. This suggests that the resistivity of the sinter would be greatly affected by the presence of pin holes, even if their size is on the order of several nm(s). On the other hand, increasing the thickness of the insulation film would prevent the metallic particles from coming into contact with each other, keeping the resistivity of the sinter at a high level.

In an attempt to prevent direct contact of the metallic particles during the hot-pressing process, the particles coated with a 17nm thick insulation film of an aluminum oxinitride were further coated with various oxide additive particles to an estimated thickness of around 40nm(0.8vol%).

Resistivity of some of these samples is shown in **Fig.5**, where the film thickness equals the original insulation film thickness plus the coating powder thickness.

The resistivity was  $7 \times 10^{-3} \Omega$ ·m for the additive-free sample (marked with min Fig.5), which increased to the order of  $\rho = 10^7 \Omega$ ·m when the insulated particles were coated



Fig. 6. The relationship between electric resistivity rand thickness of insulating film  $\delta$  of Nano-Structure Controlled Magnetic Materials with B<sub>2</sub>O<sub>3</sub> and without additives. The insulating film is composed mainly of Al-O-N compound.

Table 1. The contact angle (wettability) of additives on the insulating Al-O-N surface after heat treatment. Also an electric resistivity of Nano-Structure Controlled <u>Magnetic Materials with each addi-</u>

Additives	m. p.	Contact Angle	$\rho  (\Omega \cdot m)  \  \  / \delta = 5.7 \ n \ m$
B2 03	294℃	5	2×1 0'
V205	658°C	9 0	3×1 0-4
S b 2 O 3	656°C	6 0	8×1 0-5

with  $B_2O_3$  powder prior to the sintering process. The resistivity of the samples covered with additives other than  $B_2O_3$  was on a level with, or slightly lower than, that of the additive-free sample.

Figure 6 shows the relationship between the resistivity and the thickness of the insulation film, where each sample was coated with a 9nm thick insulation film of an aluminum oxinitride and then with varying quantities of B<sub>2</sub>O<sub>3</sub> powder prior to sintering. The resistivity of the B2O<sub>3</sub>-free sample is also shown (marked with O), for comparison. Resistivity increased to  $10^7 \Omega \cdot m$  at a total film thickness of 14nm (9nm of the insulation film and 5nm of the B<sub>2</sub>O<sub>3</sub> powder layer). This compares with a thickness of around 30nm for the B<sub>2</sub>O<sub>3</sub>-free sample needed to attain the same level of resistivity (dotted line in Fig.6).

One of the reasons for the increased resistivity of the  $B_2O_3$ -containing sample is that the insulation film was almost entirely covered with a thin layer of  $B_2O_3$  powder which acted to repair those portions of the insulation film broken as a result of the extensive plastic deformation of the metallic particles during the sintering process, thereby preventing the metallic particles from contacting with each other directly. For an additive to efficiently protect the Al-O-N insulation film, it should be sufficiently wettable with the film at the hot-pressing temperature. The contact angle with the insulation film at the hot-pressing temperature was measured to screen various additives; the results are given in **Table 1**.

All of the additives tested were low-melting oxides which liquefied at the hot-pressing temperature. Of these,  $B_2O_3$  had the lowest contact angle (around 5°), and was thus more wettable with the insulation film. The oxide film containing  $Sb_2O_3$  scarcely reacted with the Al-O-N insulation film, and was separated easily from the film. The  $V_2O_3$  film, on the other hand, remained as a powder on the Al-O-N film after it was thermally treated near at the hot-pressing temperature; its contact angle with the film was 90°.

Yamaguchi et al.<sup>6)</sup> have treated mixtures of AlN and an oxide (such as  $B_2O_3$ , PbO, or  $Bi_2O_3$ ) at varying oxygen partial pressures, to observe the oxidation of AlN. They reported that the oxidation of AlN was accelerated by  $Bi_2O_3$  and PbO, but decelerated by  $B_2O_3$ , conceivably because it was liquefied and covered the AlN particles.

In an attempt to investigate the conditions of  $B_2O_3$  in the sinter, the distributions of the elements on the fracture face in the thickness direction were measured by AES analysis of a sample cut along the grain boundary interface. Added  $B_2O_3$  was found to have penetrated into the insulation film of Al, O, and N, and distributed on the surface as shown in **Fig.7**.

Varying quantities of B<sub>2</sub>O<sub>3</sub> were also added to the uninsulated (untreated) particles, but it failed to form an insula-



Fig. 7. The Auger depth profile of the particle-boundary fracture surface of the hot-press sintered body, composed of Fe-Si-Al particles and Al-O-N insulating film with additive of B<sub>2</sub>O<sub>3</sub>.

tion film to maintain the high resistance (or to prevent contact of metallic particles). In fact, the particles coated only with B<sub>2</sub>O<sub>3</sub> (to a thickness of 80nm) were found to have a resistivity of 10<sup>0</sup>Ω·m. In other words, the addition of B<sub>2</sub>O<sub>3</sub>, prior to the hot-pressing process, to metallic particles insulated with a film of Al, O, and N, controlled the chemical reactions of the Al-N-O film, because B<sub>2</sub>O<sub>3</sub> is sufficiently wettable with the insulation film to cover it with a liquid phase. The pin hole defects on the order of several nm(s) in the insulation film would thus be repaired by B<sub>2</sub>O<sub>3</sub>.

The  $B_2O_3$ -containing magnetic NANOCON material was also confirmed to have a saturation flux density of approximately 1T (10,000G) at room temperature by a vibration type magnetometer (VSM), which indicated that its structure tended to keep the magnetic properties within the metallic particles.

# 4. Conclusions

Various additives were used to coat the high-density NANOCON magnetic material, consisting of Fe-based metallic magnetic particles coated with a high-resistance insulation film. The relationship between the thickness of the insulation film and the resistivity of the sinter was subsequently investigated. The addition of  $B_2O_3$  to the insulated particles resulted in the sinter exhibiting a high resistivity of  $10^8\Omega$ -m with a thinner (14nm) film than the film of Al-O-N alone.

These results indicated that the added  $B_2O_3$  repaired the defects of the fracture-brittled insulation film, as a result of the plastic deformation of the metallic particles during the hot-pressing process. The authors are now planning to elucidate the effects of  $B_2O_3$  on magnetic properties, in particular permeability, of the sinter as well as the mechanisms involved.

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# Preparation and Mechanical Properties of TiB<sub>2</sub> Composites Containing Ni and C

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Mechanical properties of pressureless sintered TiB<sub>2</sub> containing Ni and C were investigated. Ni and C play an important role in the densification of TiB<sub>2</sub>. Sintered TiB<sub>2</sub> containing 7.5wt% (14Ni:1.5C) exhibited a bending strength of 470MPa. Vickers hardness of 17GPa and K<sub>1C</sub> of 4.9MPam<sup>1/2</sup>. The fracture surface of TiB<sub>2</sub> sintered containing Ni and C showed both transgranular and intergranular fracture modes. XRD analysis detected Ni<sub>3</sub> B and TiC phases besides in addition to TiB<sub>2</sub> in the sintered body.

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Key-words: TiB<sub>2</sub>, Ni, C, Pressureless sintering, Densification, Bending strength, Vickers hardness, Fracture toughness

# 1. Introduction

Titanium boride (TiB<sub>2</sub>), a boride of a transition metal belonging to the 4A group, has been attracting much attention as a material for structures exposed to high temperatures, for cutting tools, for surface protection, for wear-resistant parts used in a corrosive environment and for electrodes for aluminum smelting and MHD power generation, because of its favorable properties, such as high melting point, high hardness, chemical stability and electrical conductivity equivalent to that of metallic materials.<sup>1-5)</sup>

A number of researchers have been reporting hot-pressing in the presence of a variety of sintering aids, <sup>6-9</sup>) and composite materials containing  $Al_2O_3$ ,  $ZrO_2$  or Ti (C,N).<sup>10-14</sup>) More recently, ultra-fine particles of mono-thic TiB<sub>2</sub>, prepared by the arc plasma method, have been sintered.<sup>15,16</sup>) However, few researchers have attempted pressureless sintering of TiB<sub>2</sub>, because it is highly covalent-bonded and difficult to sinter under normal conditions.<sup>17,18</sup>) The authors have been attempting to produce highly densified TiB<sub>2</sub> sinter, by pressureless sintering and found that TiB<sub>2</sub> could be highly densified in the presence of both Ni and C. In this study, the effects of Ni and C on the sinterability of TiB<sub>2</sub> and properties of the sinter were investigated.

# 2. Experimental Procedure

# 2.1. Starting Powder and Sample Preparation

The starting powders consisted of TiB2 (Cerac), Ni

(Soegawa Rikagaku) and C (Mitsubishi Kasei). **Table 1** shows their average grain sizes, purities and impurity contents; the average particle sizes and purities were catalogued values, whereas the impurity contents were determined by chemical analysis. Particle size distribution, total oxygen and carbon contents were determined by a microtrack particle size analyzer (Leeds & Northrup) and oxygen and carbon on analyzers (Leeo). The results are given in **Fig.1** and **Table 2**, respectively. The TiB<sub>2</sub> powder possessed a median value of around 5 $\mu$ m. These starting powders were mixed in a given ratio, and ball-milled in a plastic container with nylon balls for 24h, by wet processing in the presence of ethyl alcohol. The mixture, after having been dried, was formed by a monoaxial press at 30MPa and then CIP-treated at 300MPa, in order to prepare a formed shape (about

Table 1. Average particle size and chemical composition of raw materials

materials.			
Material	Average particle size (µ∎)	Purity(%)	Impurity(%)
TiB <sub>2</sub>	2.65	99	Si:0.3,Mg:0.3,Fe:0.2 Al:0.1,Ca:0.01,Cr:0.001
Ni	4.0	99	Fe:0.2,S:0.03,C:0.02 Al:0.01,Si:0.01
C	0.03	99.9	Na:0.01,Ca:0.01,Fe:0.003 Al:0.001,Mg:0.001,Si:0.001



Table 2. Total oxygen and caron contents of TiB2 powder.

Material	Total	oxygen(wt%)	Total	carbon(wt%)
TiB <sub>2</sub>		0.9		0.6

10×10×50mm in size).

### 2.2. Sintering

The formed shape, packed in a carbon vessel, was placed in a resistance furnace provided with carbon heating elements and sintered under the given conditions in an argon gas atmosphere. It was heated at 15°C/min.

#### 2.3. Analysis of Density and Bending Strength

Bulk density of the sinter was determined by the Archimedean method and relative density was obtained by calculating the ratio of bulk density to theoretical density, the latter being based on the arithmetic average of the densities of TiB<sub>2</sub>, Ni and C.

The specimen for the bending test was prepared by cutting the sintered body into a  $4\times3mm$  shape and 40mm long, which was polished by a diamond disc. The 4-point bending test was carried out under the conditions of upper span: 10mm, lower span: 30mm, cross-head speed: 0.5mm/min, and temperature: room temperature. Each specimen was tested 3 to 5 times.

## 2.4. Analysis of Vickers Hardness and Fracture Toughness

Vickers hardness was determined by a Vickers hardness tester (Matsuzawa Seiki, Model MV-1), and the test conditions were load: 5kg and loading time: 20sec. Fracture toughness  $K_{IC}$  was measured by the CN method and determined using the equation proposed by Munz et al.<sup>19</sup>

#### 2.5. Observation of Crystalline Phases and Structures

The bending tested specimen was crushed and analyzed



Fig. 2. Relationship between relative density and Ni content of the composites sintered at 1700°C.



Fig. 3. Relationship between relative density and C content of the composites sintered at 1900°C.

by X-ray diffraction analysis in order to identify the crystalline phases. The sinter structures were observed by a scanning electron microscope (SEM).

## 3. Results and Discussion

#### 3.1. Effects of Ni and C on Sinter Density

 $TiB_2$  containing Ni was sintered at 1400° to 1900° for 1h and the effects of Ni on relative density of the sinter were determined. The results are given in **Fig.2**.

The sintered composite containing 7.5wt% of Ni possessed a significantly higher density than the monolithic TiB<sub>2</sub> phase, at a relative density of 92% when sintered at 1700°C, indicating that addition of Ni was a very effective method of densifying TiB<sub>2</sub>.<sup>8,9)</sup>

Increasing sintering temperature to 1800°C or more, however, tended to produce cracks, lowering sinter density. Furthermore, increasing Ni content beyond 7.5wt% also resulted in swelling and cracking, consequently, lowered sinter density. The swelling and cracking were conceivably caused by the gases generated during the sintering process.

Figure 3 shows the effects of C content on relative density, where each sample was prepared by sintering a  $TiB_2/C$ mixture at 1900°C for 1h. The monolithic  $TiB_2$  sinter, treated at 1900°C, possessed a relative density of 80%. The powder contained about 0.2wt% of Fe and Co as impurities (Table 1), which probably helped to accelerate densification of  $TiB_2$  to such a relatively high level. However, addition of C, was found to decelerate densification, because sinter density decreased simply with C content.

#### 3.2. Effects of Ni and C on Sinter Density

The samples were prepared by sintering the mixed powders at 1700°C, a temperature level which hardly caused swelling or cracking and gave well densified samples, as shown in Fig.2. Sintering time was 1h. **Figure 4** plots relative density against Ni content and carbon content X. As shown, combinations of Ni and C increased sinter density significantly over that of the sinter conter containing Ni alone, indicting that sintering of TiB<sub>2</sub> was greatly accelerated in the presence of both Ni and C. A total aid quantity of 7.5wt% (Ni/C ratio: 14/1 to 14/1.5 by weight) gave relative density as high as 98%.

#### 3.3. Mechanical Properties of Sintered TiB<sub>2</sub> Containing Ni and C

Figure 5 through 7 show bending strength, Vickers hard-



Fig. 4. Relationship between relative density and additive of the composites sintered at 1700°C.



Fig. 5. Relationship between bending strenth and additive of the composites sintered at 1700°C.



Fig. 6. Relationship between Vickers hardness and additive of the composites sintered at 1700°C.

ness and fracture toughness of the  $TiB_2$  composites containing both Ni and C, sintered at 1700°C for 1h.

Bending strength of the composites containing a total of 7.5 to 12.5wt% of Ni and C attained a maximum at an X level of 1 to 2; bending strength was 470MPa at a Ni/C ratio of 14/1.5 by weight for the composites containing a total of 7.5 and 12.5wt% of Ni and C (Fig.5). Thus, bending strength of this composite improved greatly, compared with 150MPa of the monolithic TiB<sub>2</sub> sintered at 1900°C for 1h. The 4-point bending strength of 470MPa was higher than the 3-point bending strength of 400MPa of the sintered, monolithic TiB<sub>2</sub> prepared by the arc plasma process.<sup>(3)</sup>

Vickers hardness and fracture toughness of the sintered composites showed a similar trend as compared to bending strength, attaining a maximum at an X level of around 1.5 (**Figs.6** and 7). The increased hardness and fracture toughness resulted conceivably from increased density. The best

results were; a Vickers hardness of 17GPa and fracture toughness of 4.9MPam<sup>1/2</sup> of a sample containing a total of 7.5wt% of Ni and C (Ni/C:14/1.5).

#### 3.4. Microstructures and Crystalline Phases

Figure 8 presents the schematic models of the surfaces of the monolithic TiB<sub>2</sub>, TiB<sub>2</sub> composite containing 7.5wt% of Ni and the TiB<sub>2</sub> composite containing a total of 7.5wt% of Ni and C (Ni/C:14/1.5), all sintered at 1700°C for 1h, where the pores are shown by solid dots and Fig.9 the SEM images of the fracture surfaces of the same samples.

The fracture surface of the monolithic TiB<sub>2</sub> phase shows relatively many pores in the structure, indicating that bonding between the particles was not promoted extensively (Fig.8 (a)) and the intergranular fracture predominated (Fig.9(a)). For the sintered composite containing only Ni, although bonding between the particles was advanced, there were some pores contained in the structure (Fig.8(b)) and the intergranular fracture predominated as is the case with the monolithic TiB<sub>2</sub> sinter, though the transgranular fracture was observed to some extent (Fig.9(b)). For the sintered composite containing both Ni and C, bonding between the grains was noted, the grains were uniform in size and well densified (Fig.8(c)) and both intergranular and transgranular fractures occurred (Fig.9(c)).

Thus, addition of both Ni and C promoted bonding between the grains, removing pores in order to densify the structure and thereby provide high-strength composites, as shown in Fig.8(c) and Fig.9(c).

Figure 10 presents the X-ray diffraction analysis results of the starting powder and the sintered composite containing both Ni and C. The sintered composite exhibited peaks



Fig. 7. Relationship between fracture toughness and additive of the composites sintered at 1700°C.



Fig. 8. Schematic model on the area (dark) of pore of sintered body surfaces of (a) TiB<sub>2</sub> 100wt%, (b)TiB<sub>2</sub>-7.5wt%Ni and (c)TiB<sub>2</sub>-7.5wt%(14Ni-1.5C) composites sintered at 1700°C.



Fig. 9. Scanning electron micrographs of fracture surface of (a) TiB<sub>2</sub> 100wt%, (b) TiB<sub>2</sub>-7.5wt%Ni and (c) TiB<sub>2</sub>-7.5wt%(15Ni:1.5C) composites sintered at 1700°C.

considered to be relevant to  $Ni_3B$  and TiC, in addition to those relevant to  $TiB_2$ , but no peak was exhibited relevant to Ni or C, which would have indicated the following reaction taking place during the sintering process:

$$TiB_2 + Ni + C \rightarrow TiB + Ni_3B + TiC \dots \dots \dots (1)$$

It was also considered that oxygen (0.9wt%) and carbon (0.6wt%) present in the starting powder as impurities (Table 2) affected the sinterability of TiB<sub>2</sub>. In particular, oxygen considered to be present on the starting particle surfaces was reduced by the action of carbon as the impurity and the newly added aid, to form CO gas.<sup>20)</sup>

Furthermore, Watanabe et al. have reported that addition of TiC accelerated sintering of a 3 component system of TiB<sub>2</sub>-TaB<sub>2</sub>-CoB, because TiC dissolved Ta and oxygen during the sintering process to form (Ti, Ta) (C,O) which reduced the starting powder and, at the same time, C separated



Fig. 10. X-ray diffraction patterns for starting powder and sintered material.

(a): TiB2-7.5wt%(14Ni:1.5C) starting powder

(b): TiB2-7.5wt%(14Ni:1.5C) composite sintered at 1700°C.

out from TiC as a result of the dissolution of oxygen also reducing the starting powder, hence, removing the pores from the structure.<sup>21)</sup>

It was thus considered, based on the above discussions, that TiC formed as a result of the addition of both Ni and C, dissolved oxygen and the mechanisms involved in the densification of  $TiB_2$  were greatly affected by this reduction of oxygen, the formation of solid solutions and the production of TiC and Ni<sub>3</sub>B. These mechanisms should be scrutinized in detail in the future.

#### 4. Conclusions

 $TiB_2$  was sintered pressurelessly in the simultaneous presence of Ni and C, in order to investigate the effects of these sintering aids on the sinterability and properties of the sintered composites.

- Simultaneous addition of Ni and C as the sintering aids accelerated densification of TiB<sub>2</sub> significantly.
- 2) The TiB<sub>2</sub> composite containing a total of 7.5wt% of Ni and C (Ni/C: 14/1.5 by weight), sintered under normal pressure, was more densified and possessed greater bending strength (470MPa), Vickers hardness (17GPa) and fracture toughness K<sub>IC</sub> (4.9MPam<sup>1/2</sup>) than the monolithic TiB<sub>2</sub> sinter.
- Both intergranular and transgranular fractures were observed in the composites containing both Ni and C.
- 4) The X-ray diffraction analysis detected  $Ni_3B$  and TiC, in addition to  $TiB_2$ , in the composites containing both Ni and C.

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# Microstructure and Phase Changes in Yttria-Partially Stabilized Zirconia Crystals Annealed with Electric Current

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4.5mol% yttria-partially stabilized zirconia crystals were annealed between 1500°C and 1800°C (c-ZrO<sub>2</sub> and t-ZrO<sub>2</sub> co-region) with DC electric current in air and microstructure and phase changes were studied using SEM, EPMA and XRD.

Although no significant microstructure and phase changes were observed in samples annealed without current, an opaque tongue-shaped zone was formed at the cathode in samples annealed at high temperature with current and then cooled to room temperature without current. This zone grew through the sample toward the anode with annealing time. The opaque zone was almost the single phase of tetragonal t' phase and contained many microcracks and some large cracks.

On the other hand, when annealed at 1650°C with current and cooled to about 1000°C with current and then to room temperature without current, the single crystal turned brown and did not show microstructure change and transformation to t' phase. When this sample was annealed again without current, an opaque zone of t' phase was formed at the cathode.

It is presumed that the transformation to t' phase occurs when reduced samples are oxidized at high temperature. [Received September 13, 1990; Accepted October 26, 1990]

**Key-words:** Zirconia, Yttria partially stabilized zirconia, Phase transformation, Microstructure, X-ray diffraction, Direct current, Reduction, Oxidation

# 1. Introduction

Excellent mechanical properties such as high strength and high toughness of yttria-partially stabilized zirconia (Y-PSZ) greatly depend on the microstructure of the substance, which in turn largely depends on tetragonal precipitation at high temperatures. There have been various studies on precipitation, but a great deal of unknown details remain.<sup>1-3)</sup>

Y-PSZ contains a tetragonal t' phase possessing a high  $Y_2O_3$  content produced by diffusionless-transformation from the cubic phase, in addition to the tetragonal phase on equilibrium diagrams. Extensive studies have been made on samples obtained by rapid cooling from the single-phase cubic region, presenting interesting problems in connection with precipitation.<sup>4.8)</sup>

One of the important features of zirconia is that it possesses high capability of conducting oxygen ions at high temperatures. For this reason, this substance is used as a solid electrolyte for electricity fuel cells and oxygen sensors. When Y-PSZ being fed with a DC current is annealed at a high temperature, large quantities of oxygen ions move from the cathode to the anode. At high temperatures, it is likely that not only oxygen ions move but also cations diffuse more easily, possibly involving microstructure variations and phase changes.

There have been a lot of reports on Y-PSZ or its electrical properties, but studies on changes in samples due to electric currents supplied are few.

In this study, Y-PSZ crystals grown by an arc-image floating zone method<sup>21</sup> were annealed in air in the tetragondcubic, effect of DC current feed on samples at high temperatures was investigated, while observing the microstructures and identifying the phases of the samples. As a result, it was discovered that even in the 2-phase stable region, current feed caused phase transitions, producing a nearly single t' phase and that this depended on the temperature of heat treatment, the current density fed and the cooling method.

## 2. Experimental Procedure

#### 2.1. Growth of Y-PSZ Crystals

The Y-PSZ samples were 4.5mol%  $Y_2O_3$ -Zr $O_2$  crystals grown by an arc image floating zone method. With respect to the raw materials, Zr $O_2$  powder (99.9%, Soekawa Chemicals) and  $Y_2O_3$  powder (99.9%, Mitsubishi Chemical Industries) were used. Milky-white bar crystals, 3 to 4mm in dia., were obtained at a growing rate of about 50mm/h. Samples 5mm long and 3 to 4mm in dia. were prepared by cutting the grown crystals with a diamond cutter and polishing the cut surfaces with a #3000 polishing machine.

#### 2.2. Heat Treatment with DC Current

Figure 1 shows the structure of the test apparatus manufactured to heat-treat Y-PSZ crystals while feeding with a DC current. The apparatus was composed of a cylindrical hollow zirconia heater 17mm dia. and 8mm dia.  $\times 23$ mm (made by Shinagawa Refractories) to heat Y-PSZ crystals and an auxiliary furnace to preheat the zirconia heater to about 1000°C before feeding a current to the crystals. The zirconia heater had its center lathed to about 13mm dia. so that electrical resistance was increased in order to heat the samples intensely. The apparatus possessed an observation window. The temperatures of the samples were measured with a radiation thermometer (IR-AHIS made by Chino) through the window. The temperatures of heat treatment given below were those of samples. The samples under heat treatment were observed directly

mometer. Samples were annealed in the zirconia heater fed with a DC current with respect to the DC power supply, a stabilized power supply (4702 made by SOAR) or a bridge circuit previously prepared. For the DC electrodes, 6.5mol% Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> grown by an arc image floating zone method were used. This was because metallic electrodes could not be used at high temperatures near the samples.

Heat treatments were carried out in air under the conditions shown in Fig.2. The samples were first heated to around 1000°C in the auxiliary furnace and then heated at a rate of 30°C/min with the zirconia heater fed with a current (between A and B). The temperatures of heat treatment were mainly 1650°C and secondly 1500° and 1800°C. On the phase diagrams, they were in the tetragonal-cubic stable region. When the samples were heated nearly to the heat treatment temperature, the DC current feed was gradually started, ultimately applying 0 to 4A/cm<sup>2</sup> with in 1min (near B). Since the samples were heated by DC current feed, the output of the zirconia heater was adjusted to keep the sample temperature at the specified level and heat treatment continued for 0 to 4h while feeding a DC current (between B and C). After the heat treatment, the DC current feed was turned down ultimately to zero in about 1 min (near C), while adjusting the output of the zirconia heater so that the sample temperature did not change. Subsequently, the samples were cooled at a rate of 30°C/min to room temperature



Fig. 1. Schematic diagram of the apparatus used for annealing during current passage.



Fig. 2. Temperature-time program for heat treatment.

#### (between C and D).

After the heat treatment, some samples were cooled to about 1000°C while receiving a DC current of constant intensity. The heat treatment conditions are shown in **Fig.3**. In the figure, the procedure between A and C was the same as above. During cooling down to about 1000°C between C and D, the DC current feed was continued at  $4A/cm^2$ . The samples were heated to about 1000°C only with DC current feed. This meant that in the process to D, the output of the zirconia heater decreased to zero. After the DC current had been reduced to zero in about 1 min (near D), the samples were cooled rapidly to room temperature.

#### 2.3. Evaluation of Samples

Powder X-ray diffractometer (XRD) (PW1700 by Philips) with Cu K $\alpha$  radiation was used for the determination of phases and latice constants of the samples. For measurements, a Cu bulb was used under the conditions of 30mA and 40kV. Below, tetragonal lattices are described in terms of face-centered lattices based on cubic lattices. Also, cutting samples, polishing the cut surfaces and then etching them at 250°C with phosphoric acid for 3min, were observed by an SEM (JSM-T200, acceleration voltage 25kV, made by JEOL). Also, using an electron probe microanalyzer (XMA-8621, JEOL), samples were submitted for elemental analysis.

# 3. Results and discussion

#### 3.1. Basic Changes in Samples due to Current Feed

Prior to the DC current feed tests, XRD was used to ascertain that the phases of the starting materials and the samples heat treated at 1500°C, 1650°C and 1800°C without current feed were tetragonal and cubic. After heat treatments, the samples showed no changes in appearance and not cracks.

**Figure 4** shows a sample which had received a DC current, 4A/cm<sup>2</sup>, for 1h at 1650°C. Current feed caused an opaque tongue-shaped zone to appear on the cathode side. The sample shown here was observed in transmitted light. The white zone looked dark because light scarcely passed through it. Compared with the starting samples, this zone was very brittle. The polarity was reversed and the same test was repeated; a similar zone existed on the cathode side. This proved that the phenomenon was not due to the appa-



Fig. 3. Temperature-time program for heat treatment.



Fig. 4. Optical photograph of the sample annealed at 1650°C for 1h at 4A/cm<sup>2</sup>. (This photograph was taken by transmitted light and the opaque zone seems black because of its less transparence.)



Fig. 5. SEM photograph of the opaque zone at the cathode in the sample annealed at  $1650^{\circ}$ C for 1h at  $4A/cm^2$ .

ratus. Not only on samples, but the same change also occurred on 6.5 mol%  $Y_2O_3$ -Zero<sub>2</sub> used as the electrodes.

Figure 5 is the SEM photograph of the opaque zone on the cathode side of a sample energized for 1h. It showed a number of mcirocracks about 0.1µm wide and 5 to 10µm long. That the zone looks opaque may be because light was scattered by microcracks. A few cracks about 2mm long were often found in the areas which were not opaque on the cathode side or in the surroundings of the opaque zone. They were observed through a telescope in the radiation thermometer to occur not during DC current feed but directly after it was stopped (directly after C in Fig.2). The microcrack's seen in the opaque zone might have also been caused directly after the current feed had been stopped.

 $Y_2O_3$  concentration in the white zone was quantified by a ZAF method with EPMA as 4.2mol%, comparable with the 4.5mol% for the starting material.

**Figure 6** shows a diffraction pattern in the (400) region in the opaque zone on the cathode side, together with those for crystals as grown and a sample only heat treated. The diffraction pattern for crystals as grown clearly shows tetragonal (004) and (400) peaks and a cubic (400) peaks, proving that two phases coexisted. The diffraction pattern for the sample only heat treated also showed the coexistence of tetragonal and cubic phases, proving that the heat treatment did not affect the phases of samples.

The diffraction pattern for the opaque zone produced by current feed on the cathode side showed no cubic diffraction peaks but tetragonal ones. Tetragonal peaks for the crystals as grown and the sample only heat treated were only slightly seen between  $\alpha_1$  and  $\alpha_2$  peaks of tetragonal (400) peaks. Compared with the diffraction lines for the crystals as grown, the tetragonal (004) and (400) peaks were shifted toward the high- and low-angle sides respectively and it was assumed that the tetragonal phase here differed from that on the equilibrium diagram. Tetragonal lattice constants and c/a ratios were a=5.105A, c=5.161A, c/a=1.011 for the opaque zone, showing that tetragonal here having a small axial ratio had been produced.

There have been a number of reports on the tetragonal phase in  $Y_2O_3$ -ZrO<sub>2</sub> system transformed diffusionlessly obtained by rapid cooling from the cubic stable region<sup>5-8</sup>) (called t'phasse by Lanteri et. al.<sup>13</sup>)). The tetragonal lattice constant and c/a ratio obtained here for the opaque zone of the energized samples were close to the values of rapid cooled samples of  $Y_2O_3$  content 4.5mol% reported above.

Thus, from the results of EPMA measurement, it was found that the tetragonal phase produced on the cathode side by energization was the t' phase.

As conduction time increased from 0.5 to 1, 2 and 4h under the same heat treatment conditions, the opaque zone on the cathode side spread gradually toward the anode. This was schematically shown in **Fig.7**. The opaque zones consistently were the t' phases.

Common features of the report on FSZ coloration in Ar by energization and the results obtained here were a tongue shape of the affected zone on the cathode side and its hourly growth.<sup>14,15</sup> However, what differed from these reports was that there was no coloration of samples and phase changes were detected. In those reports, the coloration was ascribed to metallic colloids produced by oxygen deficiencies or reductions. In the present study, the samples were heat treated in air. If they had been reduced, they were also further oxidized. This may be the reason for the results obtained differing from others. However, no mention of phase changes in other reports may be for the following reasons:



Fig. 6. X-ray diffraction profiles of (400) reflections in samples. (a) as grown, (b) annealed at  $1650^{\circ}$ C for 2h at OA/cm<sup>2</sup> and (c) opaque zone at the cathode in the sample annealed at  $1650^{\circ}$ C for 2h at 4A/cm<sup>2</sup>.

 $\blacktriangle$  : (004)<sub>t</sub>,  $\blacksquare$  : (400)<sub>c</sub>,  $\blacksquare$  : (400)<sub>t</sub>



**Fig. 7.** Sketch of opaque zone formed during current passage of 4A/cm<sup>2</sup> at 1650°C.



Fig. 8. X-ray diffraction profile of (400) reflections in the sample annealed at  $1800^{\circ}$ C for 4h at  $6A/cm^2$ .

 $\blacktriangle$  : (004)<sub>t</sub>,  $\blacklozenge$  : (400)<sub>c</sub>,  $\blacksquare$  : (400)<sub>t</sub>

phase changes in other reports may be for the following reasons: the t' phase was formed when  $Y_2O_3$  concentration was lower than about 7mol%.<sup>4)</sup> In the other reports, the composition of the samples was FSZ (8-12mol%  $Y_2O_3$ -ZrO<sub>2</sub>) and the temperature was lower: about 800°C.

#### 3.2. Effect of Heat Treatment Temperature

At 1650°C, the t' phase was formed by energizaiton. To investigate changes due to different heat treatment temperatures, a DC current was fed  $4A/cm^2$  to the samples at  $1500^\circ$  and  $1800^\circ$ C. On the samples heat treated at  $1500^\circ$ C and at  $1650^\circ$ C, there appeared opaque brittle zones on the cathode side and the phase formed was the t' phase. With a current density of  $2A/cm^2$ , similar changes were also observed. At  $1800^\circ$ C, heat treatment with energization at a rate of  $4A/cm^2$ , and 2 phases, tetragonal and cubic, coexisted in the samples.

As the samples were further heat treated at 1800°C for 4h with 6A/cm<sup>2</sup>, a tongue-shaped opaque zone appeared on the cathode side of each sample. At 1800°C, unlike 1650° and 1500°C, the opaque zones were hardly brittle and partly penetrable to light; the opaque zones at 1650° and 1500°C appeared white and were hardly penetrable to light. The phases as observed by XRD were tetragonal and cubic, but the t' phase was not detected. The diffraction pattern is shown in **Fig.8**. Samples were cut in parallel with electric fields and the cut surfaces were polished and etched. Figure 9 is an SEM photograph of one of them. It showed holes about 1 to  $5\mu$ m. No such holes were detected in samples heat treated without energization or with energization at  $4A/\text{cm}^2$ . Such holes were not seen on surfaces only polished but on surfaces polished and etched. The white appearance of samples may be due to a number of distributed parts, ready to be etched, produced by energization.

Within the test range, at 1800°C, there was very little or no transition to the t' phase. This may be for the following reasons. If samples were fed with  $6A/cm^2$  at 1800°C or  $4A/cm^2$  at 1650°C, the electric fields applied to the samples are nearly the same around 3V/cm, according to the reported values of the electric conductivity of 5 mol  $Y_2O_3$ - $ZrO_2^{11}$ ). If it was assumed that phase transition only depended on current density or the level of electric field, so the t' phase must be produced at 1800°C -- but in reality it was not. This required more detailed investigation.

#### 3.3. Changes on Anode Side of Samples

In section 3-1, energization time was varied from 0.5 to 1, 2 and 4h. The anode side of the samples, observed with the unaided eye, showed no change with energization times 0.5 and 1h but they appeared slighly opaque with longer energization times, suggesting that the same changes had occurred.

**Figure 10** shows diffraction patterns in the (400) region on the anode side of samples energized at  $4A/cm^2$  for 2 and 4h at 1650°C. The one for the sample with 2-h energization was so broad that diffraction lines for phases cannot be separated from each other. The other for 4-h energization, though broader than that on the cathode side, showed the diffraction figure for the t' phase. In summary, it was assumed that phase transition occurred preferentially on the cathode side. The front of phase transition was beyond the white zone and both proceeded gradually toward the anode side.

#### 3.4. Effect of Energization During Cooling

In the preceding section current feed was stopped at the end of energized heat treatment (in Fig.2) and then the samples were cooled. In the heat treatment in Fig.3, energization was continued during cooling, in which the samples turned brown overall without any boundaries between prominent and unprominent changes. The phases were tetragonal and cubic, and the t' phase was not detected. The samples showed no microcracks but a few cracks (about 2mm overall) existed.



**Fig. 9.** SEM photograph of the sample annealed at 1800°C for 4h at 6A/cm<sup>2</sup>.



Fig. 10. X-ray diffraction profiles of (400) reflections in the anodes in the samples annealed at  $1650^{\circ}$ C at  $4A/cm^{2}$  for (a) 2h, (b) 4h. : (004),  $\blacksquare$  : (400),

tion, the same samples turned milky-white as they were originally, possessing white brittle zones produced on the cathode side as in the samples in section 3-1. These zones were identified as the t' phase.

Since the zone turned to the t' phase in section 3-1 spread during energization, it was probable that a transition to the t' phase occurred during energized heat treatment or a zone inclined to turn to t' phase was produced during the same treatment and turned to the t' phase after energization. As mentioned earlier, during cooling with energization, the samples remained tetragonal and cubic. Thus, it seemed reasonable to assume that the t' phase was not produced during energization but rather after energization had been stopped.

It has been reported that when reduced in  $H_2$ - $N_2$ ,  $ZrO_2$  became colored.<sup>16,17</sup> This was the same phenomenon as in energization. Thus, energization was assumed to reduce samples. In the present study, the samples colored during the process remained tetragonal and cubic. The t' phase was produced in the samples not colored during the process. The relation between energization, colonization and t' phase production was in summary assumed as follows. The t' phase was produced while samples, released from reduction upon the stoppage of energization, were being oxidized again. The zone inclined to turn to the t' phase, mentioned earlier, was assumed to be the part strongly reduced by energization.

The samples energized during cooling remained reduced until they were cooled to a relatively low temperature. This is why the t' phase was not produced in them. When they were further heat treated without energization, they were oxidized, causing the t' phase to be produced.

## 4. Conclusion

While applying a DC current,  $4.5 \text{mol}\% \text{ Y}_2\text{O}_3\text{-}\text{ZrO}_2 \text{ crys-tals}$  grown by an arc image floating zone method, were annealed in tetragonal and cubic co-region, and the following results were obtained:

1) When samples, after heat treatment with energization, were cooled without energization, tongue-shaped opaque

and brittle zones were produced on the cathode side. During energization, they expanded and spread toward the anode.

- 2) A t' phase possessing the same composition as that of the original samples was produced in the white zones. It was produced more readily at lower temperatures of heat treatment.
- The samples cooled with energization turned brown overall and their compositional phases were tetragonal and cubic.
- 4) A transition to the t' phase occurred upon stoppage of energization. It was assumed that such transitions occurred while samples, released from the state of reduction upon the stoppage of energization, were being oxidized again.
- (A report at annual convention of Ceramics Association of Japan, May 199)

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# Mechanical Properties of Mullite–β-Silicon Nitride Whisker Composite Ceramics

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Mullite composite ceramics reinforced with (0-50)vol%  $\beta$ -silicon nitride ( $\beta$ -Si<sub>3</sub>N<sub>4</sub>) whisker were prepared by hot pressing between 1500° and 1650°C under 30MPa for 30min, and the mechanical properties (bending strength, hardness, modulus of elasticity, fracture toughness) of these composites were investigated. Fully densed composites containing up to 40vol% whisker were obtained at 1600°C. X-sialon phase, which was thought to be produced by a reaction between mullite and B-Si<sub>3</sub>N<sub>4</sub>, was detected in the composite fired at 1650°C. Room temperature bending strength increased with increasing whisker content and showed a maximum value (about 630MPa) at 40vol%, which was 80% higher than that of monolithic mullite. These composites had more excellent high temperature strengths than monolithic mullite. The hardness and modulus of elasticity of dense sintered bodies also increased with increasing whisker content. The fracture toughness (about 4MPa·m<sup>1/2</sup>) of a composite with a  $\beta$ -Si<sub>3</sub>N<sub>4</sub> whisker content of 40vol% was more than two times larger than that of monolithic mullite due to crack deflection and pull-out of whiskers in the fracture process. The  $\beta$ -Si<sub>3</sub>N<sub>4</sub> whiskers in the composites were aligned preferentially in the direction normal to the hot pressing direction so that mechanical properties of the plane normal to the hot pressing direction were superior to those of the plane parallel to the hot pressing direction. [Received July 16, 1990; Accepted September 26, 1990]

# 1. Introduction

Ceramic materials have been attracting much attention as structural materials, because of their high resistance to heat and chemicals and high strength at high temperatures. Mullite has low specific gravity (3.15g/cm<sup>3</sup>) and has been characterized by its lower thermal expansion coefficient compared to that of alumina and possesses strength stability over a wide temperature range. The fracture toughness of mullite, however, is low<sup>11</sup> at 2MPa·m,<sup>12</sup> which has greatly limited its industrial use as a structural material. One of the approaches previously investigated to improve its fracture toughness has been reinforcement with silicon carbide whiskers.<sup>241</sup> In this study, silicon nitride whiskers were used in place of silicon carbide whiskers, in order to investigate mechanical properties of the hot-pressed composites.

# 2. Experimental Procedure

#### 2.1. Starting Material and Its Preparation

The starting mullite powder (Chichibu Cement, MP-20) had a stoichiometric chemical composition of 3Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub> and an average grain size of 1.46µm. The  $\beta$ -silicon nitride whiskers (Ube Industries, SN-WB) were approximately 1µm in diameter and 10 to 30µm in length. These starting powders were ball-milled in the presence of ethanol for 24h and the mixture was dried and then passed through a 16-mesh sieve (opening size: 1mm). The  $\beta$ -silicon nitride whiskers were added to the mullite powder in the following quantities: 10, 20, 30, 40 or 50% by volume.

#### 2.2. Sintering

Hot pressing was used as the sintering process. The mixed powder was packed in a graphite mold, pressed to a given pressure, then heated at around  $70^{\circ}$ C/min to a given temperature, at which it was held for a given time and allowed to cool after the pressure was released. The sintering temperatures were 1500° to 1650°C, the pressure was 30MPa and holding time was 30min. The sintered sample size was approximately 20×40×5mm.

#### 2.3. Analytical Procedure

The sintered sample thus prepared was polished with a #200 diamond wheel and its bulk density was measured by the Archimedean method with water.

For the strength test, the tensile face of the sintered sample was polished with a #800 diamond grind plate into  $3\times4mm$  square specimen and 3-point bending test was carried out for a 30mm span and a load rate of 0.5mm/min. The test for high-temperature strength was performed while each specimen was held at a given temperature for 10min in air .

The hardness was determined by a Vickers hardness tester at 98N for 30sec and the modulus of elasticity by the bending resonance method (JIS R1602) on  $1\times4\times40$ mm specimens.

Fracture toughness was determined by the IF and SEPB methods(JIS R1607), under 98N load and 30sec for the specimen mirror-polished with 1 $\mu$ m diamond paste in the former, and under the 3-point bending test with a 30mm span and 0.5mm/min load rate for the 4×3mm square precrocked specimen in the latter.

# 3. Results and Discussion

#### 3.1. Sinterability and Strength

Figure 1 shows the effect of sintering temperature on density and bending strength of the monolithic mullite and the composite containing 40vol% of the  $\beta$  silicon nitride whiskers. Relative density of the composite was based on the theoretical density, i.e., the arithmetic average of the theoretical densities of mullite and  $\beta$ -silicon nitride (3.15 and 3.19g/cm<sup>3</sup>, respectively). These samples possessed similar densities at similar temperatures, and were highly

densified at 1600°C and higher. The bending strength increased as sintering temperature increased, attaining a maximum at around 1600°C and tending to decrease thereafter. The decreased strength conceivably resulted from grain growth of the monolithic mullite but other causes should also be considered in addition to grain growth for the composite, as was the case with a  $\beta$ -silicon nitride whisker/alumina system.<sup>5)</sup> Figure 2 shows the X-ray diffraction patterns of the starting mixture and the sinters treated at 1600° and 1650°C. Patterns of mullite only were detected in the sintered monolithic mullite treated at 1650°C or less. Mullite and  $\beta$ -silicon nitride appeared in the composite



Fig. 1. Effect of sintering temperature on relative density and bending strength.



Fig. 2. X-ray diffraction patterns of composites fired at 1600°C and 1650°C.

sintered at 1600°C, but X-Sialon (Si<sub>12</sub>Al<sub>18</sub>O<sub>39</sub>N<sub>8</sub>) was also found, in addition to the above, in the composite sintered at 1650°C. It is therefore believed that the decreased strength of the composite sintered at 1650°C, as shown in Fig.1, was caused by the formation of X-Sialon in addition to growth of the matrix grains. X-Sialon was conceivably formed by the reaction between mullite and  $\beta$ -silicon nitride:

$$3(3Al_2O_3 \cdot SiO_2) + 2Si_3N_4 \rightarrow Si_{12}Al_{18}O_{39}N_8$$
 (1)

The results shown in Figs.1 and 2 indicate that the optimum sintering temperature for the composites of this study is around 1600°C.

Figure 3 shows the effect of silicon nitride whisker content on density and bending strength of the composites sintered at 1600°C. They were highly densified at a silicon nitride content of 40vol% or less, but increasing the silicon nitride content further tended to decrease the composite density, to 95% at 50vol%. The bending strength increased as silicon nitride content increased from around 350MPa for monolithic mullite to a maximum of around 630MPa at a silicon nitride content of 40vol%, which was roughly 1.8 times that of the monolithic mullite. In comparison, Ruh et al, have reported that the bending strength of the silicon carbide whisker/mullite composite was 1.4 times higher than that of the monolithic mullite at a whisker content of 30vol%,2) and Kumazawa et al. have reported that the bending strength of a composite of mullite of stoichiometric composition was 1.4 times greater than that of the monolithic mullite at a silicon carbide content of 10 to 30vol%.4)

Figure 4 shows the effect of testing temperature on the bending strength of the monolithic mullite and the composite containing 40vol% whiskers. The bending strength of the monolithic mullite was 330MPa at 1200°C and 290MPa at 1300°C. However, that of the composite containing 40vol% of the whiskers, which showed the highest room-temperature strength among those prepared in this study, was 500MPa at 1200°C and 420MPa at 1300°C. Thus, the composite possessed 1.5 times as much bending strength than the monolithic mullite at high temperature, although it declined slightly faster with increasing temperature. Kumazawa et al. observed that bending strength at



Fig. 3. Relative density and bending strength of mullite- $\beta$ -Si<sub>3</sub>N<sub>4</sub> whisker composite fired at 1600°C.



Fig. 4. High temperature bending strength of monolithic mullite and mullite- $\beta$ -Si<sub>3</sub>N<sub>4</sub> whisker composite with 40vol% whisker.



Fig. 5. Effect of whisker content on the Vickers harness and modulus of elasticity of mullite- $\beta$ -Si<sub>3</sub>N<sub>4</sub> whisker composite fired at 1600°C.

1300°C of the silicon carbide whisker/mullite composite decreased as silicon carbide content was increased.<sup>4)</sup>

#### 3.2. Hardness and Modulus of Elasticity

Figure 5 shows the effect of silicon nitride whisker content on hardness and modulus of elasticity of the composites sintered at 1600°C. Hardness showed a dependence on whisker content similar to that of bending strength. It increased as whisker content increased from 11.6GPa of the monolithic mullite to 16.3GPa at a whisker content of 40vol%, but decreased thereafter to 11GPa at 50vol% due to decreased density. The modulus of elasticity also increased with whisker content up to 40vol%, because of the higher modulus of elasticity of  $\beta$ -silicon nitride.

#### 3.3. Fracture Toughness

**Figure 6** shows the effect of silicon nitride whisker content on fracture toughness of the composites sintered at 1600°C. The monolithic mullite possessed a fracture toughness of 1.6MPa·m<sup>1/2</sup> determined by the IF method and 1.9MPa·m<sup>1/2</sup> determined by the SEPB method. Increasing the whisker content increased fracture toughness to 4.1MPa·m<sup>1/2</sup> both by (IF and SEPB methods) at a whisker content of 40vol%, but decreased thereafter, accompanied by decreasing density. In comparison, Ruh et al. observed that fracture toughness of a mullite composite containing 30vol% of silicon carbide whiskers was 4.6MPa·m,<sup>1/2</sup> which was approximately twice that of the monolithic mullite.<sup>21</sup> Wei et al. observed that fracture toughness of a mullite composite containing 20vol% of silicon carbide whiskers was also approximately twice that of the monolithic mullite.<sup>31</sup>



Fig. 6. Effect of whisker content on the fracture toughness of mullite- $\beta$ -Si<sub>3</sub>N<sub>4</sub> whisker composite fired at 1600°C.



Fig. 7. Crack appearance caused by Vickers indentation. (A): monolithic mullite, (B): mullite-40vol%  $\beta$ -Si<sub>3</sub>N<sub>4</sub> Whisker composite.



Fig. 8. SEM micrographs of fractured surfaces. (A): monolithic mullite, (B): mullite-40vol%  $\beta$ -Si<sub>3</sub>N<sub>4</sub> whisker composite.

Figure 7 shows the crack extension from the Vickers indents of the monolithic mullite and the composite containing 40vol% whiskers. The cracks run almost straight in the monolithic mullite but are deflected in the composite. Figure 8 shows the fracture faces of the same samples shown in Fig.7. An intragrain fracture in the mullite matrix was found in each sample. Whisker pull-out was also observed in the composite. The notably increased toughness of the composite, therefore, is believed to result from crack deflection and pull-out of whiskers as has been discussed by Wei et al with composites containing SiC whiskers.<sup>2)</sup>

#### 3.4. Effects of Whisker Orientation on Mechanical Properties

Figure 9 shows the SEM photographs of a composite treated with a boiling 50% NaOH solution, in order to remove the mullite matrix. The β-silicon nitride whiskers were randomly oriented along the plane normal to the hotpressing axis, but many whiskers were oriented in a direction normal to the hot-pressing axis in the plane parallel to the axis. This whisker orientation has been frequently observed in hot-pressed whisker-reinforced composites.3,5-8) This phenomenon conceivably resulted from the shrinkage of whiskers in a specific direction while being hot-pressed, orienting them preferentially in the direction normal to the hot-pressing axis. It has been reported that the structural orientation of whiskers produced anisotropy induced mechanical properties in a silicon carbide whisker/alumina composite.<sup>8)</sup> Therefore, mechanical properties in the planes normal and parallel to the hot-pressing axis were investigated for the mullite composite containing 40vol% silicon nitride whiskers. The results are shown in Table 1. The composite possessed bending strength, fracture toughness and hardness higher in the plane normal to the hot-pressing



Fig. 9. Surfaces of mullite- $\beta$ -Si<sub>3</sub>N<sub>4</sub> whisker composite treated with a boiling 50% NaOH solution (A) normal and (B) parallel to hot pressing axis.

Table 1. Mechanical properties of mullite-40vol%  $\beta$ -Si<sub>3</sub>N<sub>4</sub> whisker composites with surface normal and parallel to hot pressing axis.

1997		
	Normal to hot-pressing axis	Parallel to hot-pressing axis
Bending strength (MPa)	633	591
Fracture toughness (MPa·m <sup>1/2</sup> ) (IF method)	4.08	3.98
Vickers hardness (GPa)	16.3	15.2

axis than in the plane parallel to the axis, as was the case with the silicon carbide whisker/alumina composite.

# 4. Conclusions

The mixture of mullite and  $\beta$ -silicon nitride whiskers was hot-pressed, in order to investigate mechanical properties of the composites.

- The optimum sintering temperature was 1600°C and the composites containing 40vol% or less of the whiskers were highly densified. X-sialon was found in the composite sintered at 1650°C, as the product of the reaction between mullite and β-silicon nitride.
- Room-temperature bending strength of the composite increased as whisker content increased, to 630MPa at 40vol%, which was approximately 1.8 times that of the

monolithic mullite. The composite also possessed also high temperature bending strength 1.5 times that of the monolithic mullite at 1300°C.

- Increasing the whisker content also increased hardness and modulus of elasticity of the highly densified composites.
- 4) Increasing the whisker content also increased fracture toughness of the composites by virtue of the increased effects of crack deflection and whisker pull-out. Fracture toughness of the composite containing 40vol% of the whisker was more than twice that of the monolithic mullite.
- 5) The whiskers in the composite were preferentially oriented in the direction normal to the hot-pressing axis and the mechanical properties were higher in the plane normal to the hot-pressing axis than in the plane parallel to the axis.

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# Silicon Carbide Coating on Alumina Film Using Polycarbosilane

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Silicon carbide coating was applied to a thin high purity alumina film which was produced from aluminum alkoxide sol by the sol-gel method. This alumina film was treated with a polycarbosilane solution and heattreated at 1200°C. The bending strength of the coated alumina film was improved, and no electrical resistivity change was observed in the thickness direction. [Received April 5, 1990; Accepted September 26, 1990]

**Key-words:** Alumina, Silicon Carbide, Polycarbosilane, Coating

# 1. Introduction

Ceramics having the advantage of electrical, thermal, mechanical and dimensional properties have been applied as substrates in microelectronics.<sup>1)</sup> Alumina sheet is widely used for a hybrid IC, a high-frequency circuit and thermal dissipation substrates, etc. Recently a 100µm or less thick alumina film has been produced from aluminum alkoxide by the sol-gel process.<sup>2)</sup> The alumina film produced responds to a high functional demand. But this extreme thinness brings another problem in use for high functional techniques. The problem is the particular fragility that ceramics have. The alumina film needs some improvement in strength. One of the improvements is to coat some materials of high strength on the film. Thus we can expect some improvements on the point of intensity if an alumina film is coated with silicon carbide.

In this report an attempt is made to coat alumina films with silicon carbide which is prepared by heat-treatment of polycarbosilane. Reports of this type of trial, that is to coat silicon carbide onto alumina base using polycarbosilane as silicon carbide precursor, have never been published before.

# 2. Experimental Procedure

#### 2.1. Preparation of Polycarbosilane

Polydimethylsilane was synthesized by the dechlorination reaction of dimethyldichlorosilane with metallic sodium in a nitrogen atmosphere,<sup>3,4)</sup> and the conversion of this polydimethylsilane to polycarbosilane was done as follows: a two liter, three-neck stainless steel vessel was fitted with a motorstirrer, a reflex condenser and a nitrogen inlet and outlet, and this vessel was set in a heating mantle. The temperature in the vessel was measured using a thermometer beforehand. 100g of polydimethylsilane was put in the vess sel and heated at  $350^{\circ}$ – $370^{\circ}$ C in a nitrogen atmosphere. As the result of polymerization for over 20hr, a glassy polymer was obtained, which yielded about 55%, and the molecular weight for dilute benzene solution obtained by cryoscopic method was about 1600.

#### 2.2. Impregnation with Polycarbosilane

The purity, bulk density and thickness of the alumina films which were prepared from aluminum alkoxide sol by the sol-gel process were 99.9%, 3.90g/cm<sup>3</sup> and 100µm, respectively. The alumina films with the dimensions of 42mm×42mm were cleaned ultrasonically with benzene and acetone and dried. A solution was prepared by mixing 8g of polycarbosilane with 50g of xylene in a beaker and the alumina films were immersed in it. Moreover, the beaker with alumina films was put in the desicator to evacuate by rotary pump so that the efficiency of impregnation for alumina film was improved. The alumina films impregnated with polycarbosilane solution were taken out from the beaker and dried at room temperature in air. Then they were heated by steps at 110°C, 150°C and 200°C in a drying oven in air. Thus, polycarbosilane which covered alumina films was structurally crosslinked by oxygen in air, and lost its fluidity. The coated films were put on the set in a furnace in order to avoid sticking to each other, and heat-treated at temperatures from 1200° to 1400°C in a nitrogen atmosphere.

#### 2.3. Measurement

X-ray diffraction measurement was done by the reflection method on the coated alumina film. Scanning electron microscopy (SEM) was applied to explore the surface of the samples. The bending strength was measured for pieces 30mm long and 10mm wide which were out by laser beam by three point bending with 20mm lower span at a crosshead speed of 0.5mm/min. The details of calculation are shown in JIS R1601.

The electrical resistivity was measured at room temperature for the direction of thickness at a fixed voltage (10V) using a dc power supply. Indium-gallium was used for electrical contacts.

# 3. Results and Discussion

First, polycarbosilane which was synthesized in this experiment was examined to determine whether it had been converted to silicon carbide through heat-treatment. The polycarbosilane heat-treated at the temperature in the range of  $1200^{\circ} - 1400^{\circ}$ C appeared black, and its density was 2.47 – 2.51g/cm.<sup>3</sup> These values are lower than those from theoretical density of silicon carbide. The X-ray diffraction

patterns of this heat-treated polycarbosilane are shown in **Fig.1**. The common diffraction lines can be seen such as  $2\theta=26.5 - 26.55^{\circ}$ ,  $35.5 - 35.7^{\circ}$ ,  $60.0 - 60.4^{\circ}$ ,  $71.7 - 72^{\circ}$ . The line of  $2\theta=26.5 - 26.55^{\circ}$  is attributed to low quartz, but other lines fit  $\beta$ =SiC. The formation of low quartz is caused by oxygen fixed in polycarbosilane through crosslinking in air.

When alumina films impregnated with polycarbosilane were heat-treated at 1200° and 1300°C in a nitrogen atmosphere, the surfaces of the films appeared black as shown in **Fig.2**. From the X-ray diffraction measurement of the coated alumina film heat-treated at temperatures in the range of  $1200^\circ - 1400^\circ$ C, all diffraction lines were attributed to the alumina itself. The diffraction lines of silicon carbide were not observed, regardless of the black surface of the films. The disappearance of diffraction lines of silicon carbide suggests that the coating phase is very thin and struc-



Fig. 1. X-ray powder diffraction patterns of silicon carbide from polycarbosilane by heat-treatment at various temperature. a: HTT 1200°C, b: HTT 1300°C, c: HTT 1400°C

turally amorphous, and also amorphous silica may exist together with silicon carbide in the coating phase. It is apparent that quartz formation takes place in the X-ray diffraction patterns in Fig.1.

Figure 3 shows the SEM photographs of the coated black surfaces (Fig.3 - b, c) and the fracture surfaces (Fig.3 - b', c') compared with the original alumina film (Fig.3 - a, a'). The coated films differed in the appearance of the surfaces, which looked smooth, dense and flat. Comparing the coated surface of the sample at 1200° with that at 1300°C, the sample at 1200°C was better than the other in appearance, that is, micro-pores were seen in the sample at 1300°C. It is considered that the formation of micro-pores is related to the continuous structural change of coat phase. In the process of the conversion of polycarbosilane to silicone carbide by pyrolysis, it is recognized that CO gas is generated at temperatures above 1300°C as crystallization proceeds.<sup>3)</sup> From the observation of the fracture surfaces, we saw the border-line of alumina phase and coat phase clearly, and the coat phase was about 1µm thick. The coated surface of the sample at 1400°C cracks and comes off from the alumina base as shown in Fig.4. This phenomenon may be due



Fig. 2. Appearance of the surfaces of alumina thin sheet before (a) and after (b) coating by silicon carbide from polycarbosilane by heat-treatment at 1200°C.



Fig. 3. SEM micrographs of the surfaces (a, b, c) and fracture surfaces (a', b', c') of alumina thin sheets before and after coating by silicon carbide from polycarbosilane by heat-treatment at 1200° and 1300°C. a, a': Original, b, b': HTT 1200°C, c, c': HTT 1300°C



Fig. 4. SEM micrographs of the surface of alumina thin sheet coated by silicon carbide from carbosilane by heat-treatment at 1400°C.

mostly to dimensional and structural changes of the coated surface or alumina base which occur by the process of crystallization. From the aforementioned observations, we can say the 1200°C is apparently an appropriate heat-treatment temperature for coating.

The bending strength of coated alumina films at 1200° and 1300°C were examined. This test was done for eight pieces of each sample. The mean value of bending strength of the original film was 497MPa, while the values of bending strength of coated film at 1200°C and 1300°C were 583MPa and 562MPa. This result shows that the increase in bending strength depends on coating with silicone carbide. Particularily the bending strength of alumina film coated with silicon carbide heat-treated at 1200°C was larger than that at 1300°C. This result thus fits the SEM observation in Fig.3.

From the electrical resistivity measurement there was no change between the original and coated films. Both electrical resistivities were above  $10^{14}$  cm.

In conclusion, a high quality alumina film of oxide ceramics was coated with silicon carbide converted from polycarbosilane by heat-treatment at relative low temperature. This was effective to improve the fragility and surface conditions of the alumina film.

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# Very High-Pressure Sintering of Cubic Boron Nitride with PSZ Additive

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High pressure sintering under the condition corresponding to the thermodynamically stable region for cubic boron nitride in a phase diagram of boron nitride was studied to demonstrate the availability of PSZ as a sintering additive of cubic boron nitride. In a specimen without additives, because of rigidity of cubic boron nitride, the sufficiently high pressure was not applied on the surface of cubic boron nitride particles effectively except for the portion of surface where the cubic boron nitride particles contacted with each other, where inversion into hexagonal boron nitride occurred. In PSZ-added specimens, however, PSZ behaved as a pressure transmitting medium to the surface of cubic boron nitride particles. Consequently, phase transition into hexagonal boron nitride was prevented. On the other hand, part of partially stabilized high temperature phase t-ZrO<sub>2</sub> of PSZ underwent conversion into stable phase m-ZrO<sub>2</sub> for the specimens doped with PSZ less than 12vol%. The cubic boron nitride sintered body with PSZ of 12vol% had the highest microhardness of above Hv2300. It was concluded that PSZ was effective as a sintering additive to obtain cubic boron nitride sintered bodies with a compact texture.

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**Key-words:** Very high pressure sintering, Cubic boron nitride, PSZ, X-ray diffraction, Vickers microhardness

# 1. Introduction

Cubic boron nitride (cBN) is known for its extreme hardness, which is equivalent to that of diamond. However, unlike diamond, cBN may be used to machine various metallic materials, such as based on iron and has been attracting attention as a material for the manufacture of tools for machining those materials difficult to machine by ordinary tools and for improving machining accuracy. Large, single crystals of cBN, have not been produced on a commercial scale and only the sintered form has been used for machining tools.<sup>1)</sup> Common sintering aids for cBN are metals such as Co and Inorganic compounds such as TiN and TiC. Few researchers have reported oxide-based sintering aids, in particular PSZ known for its intense toughness. PSZ, when successfully used as a sintering aid, may exhibit its inherent properties to improve the toughness of cBN.

In this study, the authors have attempted to prepare the toughness high cBN sinters by the very-high-pressure solid phase sintering process using PSZ as the sintering aid and consequently investigated its effectiveness.

# 2. Experimental Procedure

The flow diagram to prepare the cBN sintered compacts is shown in Fig.1. The cBN starting powder was of #8000 (General Electric, cBN type I, catalogued grain size: 0 -1µm) and the PSZ starting powder was Y<sub>2</sub>O<sub>3</sub> (3mol%)doped, partially stabilized zirconia (Toyo Soda, TZ-3Y). The aggregated particles of the PSZ powder was several dozen microns in size and that of the primary particles was approximately 1µm or less, which was approximately equivalent to that of the primary particles of the cBN powder. PSZ was added to cBN, 0, 5, 12 or 30% by volume, mixed in an alumina mortar in the presence of acetone for approximately 30min and then degassed under heat and a vacuum for drving, in order to prepare the starting material. The starting material was formed uniaxially in a metal mold at 50MPa and possessed a diameter of 6mm and depth of 4mm, respectively. This was set in a pyrophylite-made highpressure cell assembly, after having been wrapped by a zirconium foil. Figure 2 illustrates the cross-section of the cell assembly. It was provided with a preformed gasket and



Fig. 1. A flow diagram of manufacturing process to prepare cBN sintered compacts.



Fig. 2. A cross section of a high pressure cell assembly.



was thermally treated at 700°C for 1h, in order to remove water of hydration from the pyrophylite. Each sample was dried under a vacuum at 150°C for 24h, while being set in the cell assembly, then set in a cubic type pressure generator provided with a 15mm long anvil and sintered at a very-high pressure (5.26GPa) and at 1500°C for 30min. These sintering conditions are in a region in which cBN is thermodynamically stable, according to the phase diagram of BN, proposed by Bundy et al.<sup>21</sup> Pressure was corrected by using gold with the established relationship between its melting point and phase. The sintering temperature was measured by Pt-PtRh(13%) thermocouples inserted right under the samples.

On completing the sintering process, each sample was withdrawn from the cell assembly, in order to identify the crystalline phases by the X-ray diffraction analysis, to measure microhardness and to observe the microstuctures by SEM analysis.

## 3. Results and Discussion

The X-ray diffraction analysis of each sintered sample detected no special reaction products other than the diffraction peaks relevant to cBN, hBN and PSZ. It was therefore considered that cBN and PSZ present in each sinter kept their original properties.

**Figure 3** plots the X-ray diffraction peak intensity ratios of  $I_{hBN}$  (002)/ $I_{cBN}$  (111) and  $I_{mZrO2}$  (111)/ $I_{iZrO2}$  (111) against amounts of PSZ in the sample (vol%).

The PSZ-free sample possessed the highest proportion of cBN partially transformed into the graphite type phase hBN. PSZ prevented the phase transformation, almost completely when added to 30vol%. The cBN particles were considered to be too hard to be deformed during the sintering process. It is conceived that in the absence of a sintering aid, the sufficiently high pressure was not applied on some parts of the cBN particle surfaces, which caused the transformation of the cBN phase into hBN. PSZ becomes deformed under pressure to serve as a medium to transmit pressure, hence, allowing pressure to act widely on the cBN particle surfaces, as its proportion is increased, with the result that the phase transformation into hBN is controlled efficiently.

For the crystalline structures of PSZ in the cBN sinter, the crystal phase changes more at a lower proportion of PSZ, and m-ZrO<sub>2</sub> tends to increase in quantity than partially stabilized t-ZrO<sub>2</sub> as the high-temperature phase. The t $ZrO_2/m$ - $ZrO_2$  ratio in the cBN sinter containing 30vol% of PSZ was almost the same as that in the starting powder, but t- $ZrO_2$  was transformed into m- $ZrO_2$  to a notable extent in the sinter containing 5vol% of PSZ. It was not clearly understood why partially stabilized t- $ZrO_2$  was transformed into m- $ZrO_2$ .

It was anticipated that the PSZ particles were scattered and surrounded by cBN particles almost completely in the sinter containing only 5vol% of PSZ. Consequently, the difference in thermal expansion coefficient between cBN and PSZ would produce a stress, unless the phase transformation proceeded significantly, on the assumption that the system was sintered sufficiently. The difference between cBN and PSZ in volumetric shrinkage was estimated, as produced by the difference in thermal expansion coefficient when the sinter was cooled from a sintering temperature of 1500°C to room temperature. Thermal expansion coefficient of PSZ used in this study was αPSZ≈10.5×10<sup>-6</sup>KM^-1 (40° to 1000°C).3) That of cBN has not been studied extensively, partly because of difficulty in producing large single crystals. In this study, the value of  $\alpha_{cBN} \approx 4$  to  $5 \times 10^{-6} \text{K}^{-1}$ (room temperature to 1000K) was used, which was estimated from the lattice energy.4) Assuming that these values were applicable in a temperature range from room temperature to 1500°C, the difference between cBN and PSZ in volumetric shrinkage was estimated at  $3 \times (\alpha_{CBN} - \alpha_{CBN} - \alpha_{C$  $_{PSZ}$ )×(1500–RT)≈ -2.5 to -2.9(%). On the other hand, the difference in the volumetric shrinkage associated with the phase transformation from the t-ZrO<sub>2</sub> to m-ZrO<sub>2</sub> phase was known to be around 4%. Based on these estimates, approximately 34% of t-ZrO<sub>2</sub> present in the cBN sinter containing 5vol% of PSZ was transformed into m-ZrO<sub>2</sub>, on the assumption that each of the intensity ratios of the diffraction peaks of m-ZrO2 and t-ZrO2 at the (111) plane was approximately proportional to the weight ratio. This transformation would be accompanied by a volumetric shrinkage of around  $4 \times (0.34) = 1.4(\%)$ , which was approximately half that of the absolute value of the shrinkage associated with the difference in thermal expansion coefficient. The t-ZrO<sub>2</sub> to m-ZrO<sub>2</sub> phase transformation worked to relax stresses generated by a temperature change from sintering to room temperature.

Figure 4 shows the effects of PSZ content on the microhardness H<sub>v</sub> of the cBN composites, where hardness of the HIP-treated, highly densified sinter having the theoretical density of the monolithic PSZ is shown, for comparison. The cBN sample was not sufficiently sintered in the absence of PSZ and its H<sub>v</sub> was less than 1000. Increasing PSZ content increased hardness gradually, to a peak



Fig. 4. Hardness of cBN sintered compacts versus amount of PSZ additive. (\*: manufactured by HIP)



Fig. 5. Schematic description of hardness of cBN sintered compacts with PSZ additive.

level of 2300 or more (which is about the dame hardness as that of sintered cBN on the market) at a PSZ content of 12vol%. However, increasing the content further decreased hardness, back to the level equivalent to that of the monolithic PSZ at a content of 30vol%. It was interesting to note that the properties of the cBN composite containing approximately 30vol% of PSZ reflected mainly those properties of PSZ.

The hardness characteristics of the cBN composite sinters may be explained schematically and qualitatively by considering the cBN and PSZ particles to be the spheres of approximately the same size, as shown in **Fig.5**.

First, on the assumption that the cBN particles were not deformed, but instead the PSZ particles were sufficiently deformed, during the very-high-pressure sintering process, and if the cBN particles had been closely packed; then increasing the PSZ content would be accompanied by the reduced formation of hBN, also would increase sinter hardness, as indicated by the arrow 1, to the peak level at a conteat around 26vol% (cross-hatched region a). Increasing the PSZ content beyond 26vol% would allow the PSZ particles to break into the joints between the cBN particles and separate them, hence, hardness would be reduced as indicated by arrow 2, Fig.5. The second assumption, which counters the first one, was that the PSZ particles became deformed in such a way that they almost kept their original shapes and hence, were unable to fill the spaces between the cBN particles. The cBN and PSZ particles would form, in general, topologically random lattices. Assuming that the lattices represented h.c.p., the PSZ particles would be mainly deformed proceeding the sintering process, while the lattices would be kept essentially intact after being exposed to the very-high-presure sintering conditions, in view of the second assumption. This becomes reduced to the problem of site percolation.5) The threshold level was known to be close to 15vol%.5) It should be noted that the threshold levels of s.c., b.c.c. and f.c.c. were around 14 to 17vol% in three-dimensional systems,<sup>5)</sup> hence, the three-dimensional, topologically random lattices would be not far from the above levels. Thus, increasing the PSZ content beyond the 15vol% region (cross-hatched region b) allowed the bonded cBN particles to be separated to large scales by the PSZ particle clusters and reduced hardness of the sintered samples as indicated by arrow 3.

These discussions led to the conclusion that hardness attained a maximum at a PSZ content of around 15vol%, as indicated by the broken line in Fig.5. The actual results should show a broader peak and the position thereof shifted from 15vol% to some extent, because of slight deviations from the assumptions of the same size spheres and uniform mixture. Hardness of the composite containing 12vol% of PSZ may be regarded as a representative value sufficiently close to the peak.

**Figure 6** presents the SEM photographs of the ground surfaces of the sintered cBN samples containing (A) 0, (B) 12 and (C) 30vol% of PSZ. The smooth and white portions in Figs.6 (B) and (C) represent PSZ.

The PSZ-free sample seemed to be rarely sintered. However, judging from its hardness of around 1000, the cBN particles were possibly sintered with point-contacted and were considered to be transformed into hBN phase in the other portions on the surfaces. The sintered composite containing 12vol% of PSZ was highly densified but not well densified in one part, conceivably resulting from uneven distribution of PSZ. A hardness  $H_v$  far beyond 2300 may be realized, if the cBN and PSZ particles are uniformly mixed. The composite containing 30vol% of PSZ was characterized by PSZ particles grown to large, network-like



1µm

Fig. 6. Scanning electron micrographs of cBN sintered compacts. (A) 0vol% PSZ, (B) 12vol% PSZ, (C) 30vol% PSZ

(represented by the black portions) into approximately primary particles sizes. Hardness of this composite suggested that its characteristics, though reflecting those of cBN, were mainly derived from those of PSZ.

# 4. Conclusions

The authors have attempted to improve toughness of cBN by the solid phasse sintering at a very-high pressure using PSZ as the sintering aid and have investigated its applicability and effectiveness as the sintering aid.

- The cBN and PSZ particles did not react with each other under the conditions of 5.2GPa and 1500°C to form any product detectable by X-ray diffraction analysis and their inherent characteristics were kept intact in the composite.
- Increasing PSZ content prevented cBN from being transformed into hBN.
- 3) When the PSZ content was decreased to around 12vol%, its crystalline phase started to change, accelerating to release partially stabilized t-ZrO<sub>2</sub> and to transform it into m-ZrO<sub>2</sub>.
- Hardness of the cBN composite, prepared by sintering the cBN and PSZ particles of approximately the same

primary particle size, changed with PSZ content, attaining a maximum at a PSZ content of 12vol%.

- 5) Hardness of the composite could be increased to over 2300.
- 6) Hardness of the composite containing 30vol% or more of PSZ suggested that its characteristics, though reflecting those of cBN, mainly should be derived from those of PSZ.
- 7) It has been thus demonstrated that PSZ is a good sintering aid for cBN.

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# Oxygen Diffusion in Y<sub>2</sub>O<sub>3</sub>-Containing Tetragonal Zirconia Polycrystals with Different Grain Sizes

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The oxygen diffusion coefficient in Y<sub>2</sub>O<sub>3</sub>-containing tetragonal ZrO<sub>2</sub> polycrystals (Y-TZP, 2.75mol% Y<sub>2</sub>O<sub>3</sub>) was determined over the temperature range (600 to 800°C) by monitoring diffusion process with a microbalance. Oxygen isotope (180) was used as a tracer. The same diffusion coefficient was obtained for specimens with different grain sizes, indicating that there was no fast diffusion along the grain boundaries in Y-TZP. The oxygen lattice diffusion was faster in Y-TZP than t-ZrO<sub>2</sub> doped with 14% CeO<sub>2</sub>. This suggested that most cerium atoms in t-ZrO<sub>2</sub> doped with CeO<sub>2</sub> were in 4+ rather than 3+. The oxygen lattice diffusion coefficient in Y-TZP was almost the same as that in Ca-stabilized cubic ZrO<sub>2</sub>, but was several orders of magnitude higher than that in m-ZrO<sub>2</sub> doped with 1-2% Y<sub>2</sub>O<sub>3</sub>. [Received June 26, 1990; Accepted October 26, 1990]

**Key-words:** Oxygen lattice diffusion, Tracer diffusion, Tetragonal  $ZrO_2$ 

#### 1. Introduction

Oxygen diffusion in ceramic oxides is frequently dependent on the presence of grain boundaries and it is known that diffusion in the grain boundaries proceeds faster than the lattice diffusion in Al<sub>2</sub>O<sub>3</sub> and MgO.<sup>1,2)</sup> There are however some exceptions; e.g., oxygen diffusion in tetragonal ZrO<sub>2</sub> seems to be unaffected by the grain boundaries,<sup>3)</sup> and diffusion in the grain boundaries is not promoted in this system.

Zirconium oxide, though widely used as oxygen ion conductors (or oxygen sensors),4) has not been intensively studied for the relationships between the crystalline structures and oxygen diffusion<sup>5,6)</sup> and between dopant concentrations and diffusion coefficient. In particular, studies on diffusion in tetragonal ZrO<sub>2</sub> (t-ZrO<sub>2</sub>) seem to be limited to those on oxygen diffusion in Ce-doped ZrO<sub>2</sub>.<sup>7)</sup> Tetragonal ZrO<sub>2</sub> is unstable at room temperature and is frequently present in cubic ZrO<sub>2</sub>(c-ZrO<sub>2</sub>) or monoclinic ZrO<sub>2</sub> (m-ZrO<sub>2</sub>) as the secondary phase and these are some of the reason for retarded diffusion studies. More recently, highly densified t-ZrO<sub>2</sub> of single phase has been prepared as a Y-doped tetragonal zirconia polycrystal (Y-TZP) and the oxygen lattice diffusion coefficient in Y-TZP was measured in this study. The measurement was done for the tetragonal ZrO<sub>2</sub> samples of different grain sizes, in order to observe whether oxygen diffusion in the grain boundaries was promoted or not in these systems.

### 2. Experimental Procedure

Y-doped zirconia ( $Y_2O_3$ : 2.75mol%) was sintered at 1400°C for 2h and then HIP-treated at 1400°C and 200MPa for 1.5h in an argon atmosphere containing 4% of oxygen in order to prepare the test samples. Some of the samples were further treated in air in order to prepare samples of different grain sizes. **Table 1** summarizes the sample preparation conditions. Each sample was cut into a spherical sample (approximately 2mm in diameter), which was polished by #1200 diamond. It was then treated at 600 to 800°C for 8h in an  $^{16}O_2$  atmosphere, while set on a microbalance placed in a vacuum system, cooled, and then again treated for measurement of diffusion coefficient in an oxygen gas atmosphere containing 52% of  $^{18}O$ . Changes in sample weight were monitored to follow the diffusional process, in particular for the exchange reaction

and the subsequent diffusion. The detailed diffusional test apparatus and procedure are described elsewhere.<sup>8,9)</sup>

The test sample possessed a density of  $6.08g/cm^3$  and bending strength of 1450MPa at room temperature. The tested sample was broken and the fracture surfaces were analyzed by a scanning electron microscope (JAX8600), in order to determine the grain sizes. The HIP treated sample was too fine with respect to grain size to be analyzed satisfactorily by a scanning electron microscope and was analyzed by a transmission electron microscope (2000EX) after having been formed into a thin film by an ion beam thinning apparatus (JIT-100). The results are given in Table 1. the HIP treated sample possessed an average grain size of 0.35µm, but the size was increased by approximately one magnitude to 2.6µm, when the sample was further treated at 1600°C in air.

X-ray diffraction analysis was performed for each sample in order to determine its crystalline structure. Compositions (tetragonal phase %) from the X-ray intensities were determined by using the following equation proposed by Toraya et al.:<sup>(0)</sup>

$$v_{\rm m} = 1.34 X_{\rm m} / (1 + 0.34 X_{\rm m}) \ldots \ldots \ldots \ldots (2)$$

where,  $X_m$  was fraction of the monoclinic phase, determined by the X-ray diffraction peaks and  $V_m$  was volume fraction

Table 1. Grain sizes and tetragonal phase % of  $ZrO_2$  doped with 2.75mol%  $Y_2O_3.$ 

Fabrication Process	Grain size/µm	Tetragonal /%
HIP	0.35	100
HIP + 1500°C, 3h 1400°C, 3h in air	0.42	89.3
HIP + 1600°C, 8h in air	2.6	86.4

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of the monoclinic phase. It was found that the HIP treated sample consisted of tetragonal zirconia and transferred itself into the mixed phase containing 10.7vol% of the monoclinic phase, when treated at 1500°C for 3h and at 1400°C for 3h, as shown in Table 1.

#### 3. Results and Discussion

The relationship between weight change  $\Delta w$  and time t was established using the diffusional test results, based on which the weight change in infinite time  $\Delta w_{\infty}$  was calculated, to determine  $\Delta w / \Delta w_{\infty}$  ratio. The ratio was then translated into the ratio M<sub>1</sub>/M<sub>∞</sub>, which was plotted against t<sup>0.5</sup> for the HIP treated sample, as shown in Fig.1. The curve was concave in the vicinity of t=0. This similar trend was observed when the sample was annealed at 1500°C. The curve will become linear, when diffusion proceeds and the effects of other parameters are negligible,<sup>11,12)</sup> The shape of the curve in Fig.1 suggested that the exchange reaction between <sup>18</sup>O and <sup>16</sup>O was sufficiently slow to affect the diffusion in the solid phase. The test results were analyzed using the equation developed for the case where diffusion in a spherical sample was affected by the surface exchange reaction.<sup>11)</sup> The solid lines shown in Fig.1 represented the calculated results, which were in good agreement with the experimental results. The sample possessing an average grain size of 2.6mm, after having been treated under HIP conditions and then at 1600°C, possessed similar diffusional test results; there occurred no significant difference in diffusion behavior between the HIP treated sample and that heat-treated later, as shown in Fig.1.

Figure 2 shows the oxygen lattice diffusion coefficient data, calculated from the test results. Some samples contained m-ZrO<sub>2</sub> to a small extent, in addition to t-ZrO<sub>2</sub> (Table 1). According to the phase diagram proposed by Scott for the Y2O3-ZrO2 system,13) the compositions prepared in this study consisted of c-ZrO2 and t-ZrO2, when treated at 1500 to 1600°C. Part of c-ZrO2 might have been transformed into m-ZrO2 at room temperature and the remainder was possibly present in too small a quantity to be detected by X-ray diffraction analysis. Furthermore, the monoclinic phase might also have been transformed into the tetragonal and cubic phases at the diffusional test temperature level (600 to 800°C).<sup>13)</sup> In any case, the diffused quantity  $M_{\star}/M_{\infty}$  was much larger relative to the fraction of m-ZrO<sub>2</sub> (or c-ZrO<sub>2</sub> at a test temperature) present in the system and therefore, it was considered that oxygen diffusion coefficient of the tetragonal system had been measured in the tests. At the same time, a non-equilibrium phase may have been present in some samples, according to the phase diagram.

It was observed that the annealing treatment of the sample increased its grain size from 0.35 to 2.6 $\mu$ m, but



Fig. 1. Plots of  $M_t/M_{**}$  for Y-TZP at two grain sizes. The curves are calculated with appropriate equation.

oxygen diffusion coefficient hardly changed as shown in Fig.2. Oxygen diffusion along the grain boundaries was promoted in an Al<sub>2</sub>O<sub>3</sub> system, as suggested by different diffusion coefficient levels in the polycrystalline and singlecrystalline phase<sup>1)</sup> and similar trends have been found in a MgO system by Hashimoto et al.<sup>2)</sup> If oxygen diffusion in the grain boundaries proceeds faster than the lattice diffusion in t-ZrO<sub>2</sub>, there should be some difference in oxygen diffusion coefficient between the samples possessing clearly different grain sizes (0.35 and 2.6µm, for example), but the test results showed no significant difference, which led to the concept that oxygen diffusion along the grain boundaries was not enhanced in t-ZrO<sub>2</sub>. Similar trends were observed with a c-ZrO<sub>2</sub> system.<sup>3)</sup> It may be concluded, therefore, that oxygen diffusion observed in this study was the lattice diffusion.

Thickness of the surface film, as predicted by Ikuma et al.,<sup>9)</sup> was 5.3nm at 700°C. Assuming this represents thickness of the grain boundary layer (w), the diffusion test results would not be affected by oxygen diffusion in the grain boundaries, when

$$wD_{b,o} \le dD_{1,o} \quad \dots \quad (3)$$

knowing that the diffused quantity is determined by diffusion coefficient (Db.0: grain boundary diffusion coefficient, D<sub>1.0</sub>: lattice diffusion coefficient) and magnitude of diffusional field, where d is the grain size. Equation (3) be- $D_{b,0} \le 5.6 \times 10^{-6} \text{ cm}^2/\text{s}$ , comes when d=3µm and  $D_{1,0}=10\times10^{-8}$  cm<sup>2</sup>/s. Therefore, the presence of  $D_{b,0}$  will not be recognized in this study, when  $D_{b,0}/D_{1,0} \le 560$ . Similarly, if the grain size is 0.4µm, it will not be recognized, when  $D_{b,0}/D_{1,0} \leq 75$ . Assuming that the experimental error was negligible, the  $D_{b,0}/D_{1,0}$  ratio in the systems of this study were below 75. The test results shown in Fig.2 are represented by a linear line for the oxygen lattice diffusion coefficient of Y-doped tetragonal ZrO<sub>2</sub> (Y-TZP) and the least-square method was used to establish the relationship:



Fig. 2. Oxygen lattice diffusion coefficients of Y-TZP at three grain sizes.

Figure 3 plots oxygen lattice diffusion coefficients measured in this study, together with literature results, for Ca-doped tetragonal  $ZrO_2$ , <sup>3,6,14</sup> Ce-doped tetragonal  $ZrO_2$ , <sup>7)</sup> undoped, monoclinic  $ZrO_2$ , <sup>9,15,16)</sup> and Y-doped monoclinic ZrO<sub>2</sub>.<sup>9,17)</sup> Diffusion coefficient of Y-doped tetragonal ZrO<sub>2</sub> was the highest among those shown in Fig.3 and that of undoped, monoclinic ZrO<sub>2</sub> was he lowest at 600°C. For the tetragonal systems, though the data was limited, the oxgen diffusion of Y-doped ZrO2 (Y2O3: 2.75mol%, prepared in this study) is different from that of Ce-doped ZrO<sub>2</sub> (Ce: 14mol%).<sup>7)</sup> These samples, however, cannot be compared directly, because they contained different quantities of the dopants and the fraction of Ce<sup>3+</sup> in the total quantity of Ce was not known, though it was considered that Y was totally present in the form of Y<sup>3+</sup>. Addition of Y<sub>2</sub>O<sub>3</sub> increased  $V_0^{\circ}$  quantity by the following reaction in order to speed up oxygen diffusion:

The similar effects as represented by Equation (5) will be produced, when  $Ce^{3+}$  is present. The results shown in Fig.3, therefore, suggest that Ce in the Ce-doped t-ZrO<sub>2</sub> sample<sup>7)</sup> consisted of mostly Ce<sup>4+</sup> and a very small quantity of Ce.<sup>3+</sup>

The Y-doped t-ZrO<sub>2</sub> sample possessed a higher D<sub>1,0</sub> value than the undoped m-ZrO<sub>2</sub> sample and the Y-doped m-ZrO<sub>2</sub> sample containing a similar quantity of Y (Y<sub>2</sub>O<sub>3</sub>: 1 to 2mol%). It was therefore considered that oxygen diffusion in ZrO<sub>2</sub> was affected by the difference in crystalline structures, tetragonal or monoclinic, but this point should be further elucidated in the future, because different temperature dependences were involved in this comparison. However, the Y-doped t-ZrO<sub>2</sub> sample prepared in this study possessed almost the same diffusion coefficient as the Cadoped c-ZrO<sub>2</sub> sample. The same was true for the activation energy in the same temperature range; 134kJ/mol for the former versus 118 to 131kJ/mol for the latter.<sup>3,14)</sup> It was therefore considered that oxygen diffusion in these samples became saturated in this temperature range, because the same saturated in this temperature range.



Fig. 3. Oxygen lattice diffusion coefficients in ZrO<sub>2</sub> reported in the literature. Cubic-ZrO<sub>2</sub>: Oishi and Ando,<sup>6</sup> Simpson and Carter,<sup>3</sup> and Kingery et al.<sup>14</sup>; tetragonal ZrO<sub>2</sub>: Ando et al.<sup>71</sup> and this study; monoclinic ZrO<sub>2</sub>: Keneshea and Douglass,<sup>15</sup> Madeyski and Smeltzer,<sup>16</sup> Ikuma, Komatsu and Komatsu,<sup>91</sup> and Ikuma et al.<sup>171</sup>

samples of different crystalline structures and dopant quantities possessed almost the same diffusion coefficient and activation energy. Further studies in the future are needed for the additional discussion.

#### 4. Conclusions

Oxygen diffusion coefficients of the Y-doped tetragonal zirconia polycrystals were measured at 600 to 800°C, using the oxygen isotope exchange reaction. The sample of 0.35µm in grain size possessed almost the same diffusion coefficient as that of 2.6µm grain size indicating that the ratio of oxygen grain boundary diffusion coefficient to oxygen lattice diffusion coefficient was below 75. In other words, oxygen diffusion was not promoted in the grain boundaries in tetragonal ZrO<sub>2</sub>. The same phenomenon was observed with cubic ZrO2. Y-TZP possessed a higher oxygen diffusion coefficient than Ce-doped (CeO2: 14mol%) tetragonal ZrO2, which meant that Ce in the Cedoped t-ZrO<sub>2</sub> sample consisted of mostly Ce<sup>4+</sup> rather than Ce.3+ It was also observed that the Y-TZP sample possessed almost the same oxygen lattice diffusion coefficient as that in the Ca-stabilized tetragonal ZrO2 sample, but higher than that in the Y-doped monoclinic ZrO<sub>2</sub> sample.

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# Information & Communications

# News

# Selective Growth of Silicon Carbide Uniform Film

A group under Research Associate Kohta Sato, Faculty of Engineering, Chiba University, has developed film making technology to selectively grow high-quality silicon carbide films by the plasma CVD (Chemical Vapor Deposition) process. The plasma reaction process can make high-quality film, but it lacks uniformity. Chiba University has adopted very commonly used high-frequency plasma equipment. It has prepared the silicon carbide film on quartz substrate at a power of 2W by blowing in vinyl silane of raw material gas. It is important to control the accelerating voltage by controlling the power and the gas blowing pressure. Sato and others optimized the reaction conditions and raw material gas and succeeded in preparing the uniform films, solving the energy created at the reaction of only carbon and silicon by quantum chemical calculation which is called the ab initio (nonexperience molecular orbit) method. The bandcap of the prepared silicon carbide film is 2.83 electron voltage and exceeds the 2.1 electron voltage of the previously recorded maximum. It is expected to be applied for the development of blue color LED (Light Emitting Diode), and broad bandcap semiconductor elements operated at a high temperature.

## Ceramic Thin Film Using Carbonic Acid Gas Laser

Mitsubishi Electric Corporation has developed technology to make ceramic thin films which are hard to tear off at high speed using a carbonic acid gas laser. It is a process to vaporize ceramics by laser light for deposition on substrates such as semiconductors and metals. Thin films which are more than ten times as strong as conventional ones have been obtained by placing substrates and ceramics in vacuum equipment. In the experiments, quartz (silicon oxide) was deposited on substrates of stainless steel and silicon. By supplying oxygen at the rate of 0.16 micro cubic meters per second, strong thin films which do not tear off even at a substrate temperature of 200°C have been obtained. Due to improvements in the deposition speed, their preparation at the speed of 1 micron for approx. one minute have also been made possible. That preparation speed is more than 10 times as fast as conventional processes. The above company plans to establish the technology by solving questions such as "Why can strong thin films be made quickly by supplying optimal oxygen?" and "Can the same results be obtained for any kind of ceramics?".

# Synthesis of Titanium Nitride by Spark Process

A group under Assistant Prof. Yasunari Kaneko, Faculty of Science and Engineering, Ritsumeikan University has synthesized titanium nitride powders by a spark discharge (spark) process using titanium electrodes in liquid nitrogen. Powders are prepared by rotating the disc of electrode in liquid nitrogen by motor and by generating arc by switching on and off line materials. Powders comprised of irregular grains of more than 100 microns in size, spherical grains of less than 100 microns, and ultra fine grains of less than 100 nanometers were found. Two experiments have been done with the electrodes of the experimental equipment: one was to use the same metals of aluminum, tungsten, niobium, zirconium and iron in addition to titanium, and the other was to use foreign metals of titanium and aluminum, and titanium and tungsten. According to the experiment results, nitride compounds were obtained by the spark process between the same metals when electrodes of titanium, aluminum, zirconium and niobium were used, but not in the case of tungsten and iron. When the fusion of metals and the dissolution of nitrogen occurred at the spark discharging point, nitride compounds are prepared if the melting points of nitride compounds are higher than those of metals. And in the reverse case, metals themselves are obtained

## Making an Aluminum Fluoride-Type Glass Fiber

Hoya Corporation has succeeded for the first time in making fibers from aluminum fluoride-type glass. Since fluoride-type fibers can reduce transmission loss, they are expected to be next-generation optical fibers, following the quartz-type. As the YAG laser used as an operative scalpel cannot use quartz type fibers, a multi-joint transmission system by mirror reflection is adopted substituting aluminum fluoride-type glass. The above company makes discs of 35mm in diameter and 15mm in thickness from aluminum fluoride-type glass for clads and cores. They are set to the extruder and heated to 402°C. Then the preforms of 8mm in diameter are obtained at the speed of 7mm per hour. They have succeeded in developing single mode fibers whose core diameter is 520 microns by extruding the preforms as materials together with clad glass. So far, fluoride type-glass has been not easily machinable. But by overcoming its defects, promotion of its applications can be accelerated.

# Receiving Light Emission from Silica Glass

A group under Assistant Prof. Nagasawa, Faculty of Engineering, Shonan Engineering University has confirmed a new light emitting phenomena. The group has thus developed light sources used for glass lasers which continuously oscillate light of visible wavelength. It confirmed the new light-emitting phenomena by irradiating krypton-fluorine exima laser light to high purity silica glass. There exist positive holes (electrically positive portions caused by the lack of electrons placed on the circumferences of atomic nuclei) coming from crystalline defects of internal portions of silica glass, and the electrons excited by the energy of light move. The transition energy for the light emission ranges from approx. 2 electron volts to 4 electron volts and the emittied light has the bandwidth of 450 to 650 nanometers. When it comes to direct applications for the laser, there are many problems to be solved; but it can be said that a new material for laser light sources has been introduced.

## Super High-Pressure Slip Casting System for Ceramics

In co-operation with Shinei Kiko Co., Ltd., Kawasaki Steel Corporation Ltd. has developed a super high-pressure slip casting system which greatly shortens the molding time of ceramics. Instead of a gypsum mold, the new equipment uses a boron nitride mold of porous ceramics which is highly durable. The ceramics mold can apply pressure of 100 to 300kg/cm<sup>2</sup> and thereby shorten the molding time of one cycle to 20 seconds, which is equivalent to that of the injection mold. It can make parts of complex shapes and about 50 to 100mm in thickness which are hard to obtain by injection molding. The degreasing time is reduced to one twentieth that of the injection mold. The mold has uniform pore diameter and porosity, and can be freely designed (in the range of 0.1 to 2 microns for pore diameter and 10 to 50% for porosity) by calibrating the weight percentage of boron nitride and its grain size. Both companies plan to produce it as a mass production manufacturing machine for engineering ceramics.

# Growth of Single Crystal of Bismuth Titanate

The LSI Laboratories of Nippon Telegraph and Telephone Corporation and Prof. Tsuguo Fukuda of the Research Institute for Iron, Steel and Other Materials of Tohoku University have succeeded in preparing a single crystal of BTO (Bismuth Titanium Oxide) to be used for optical memory materials. They obtained a crystal of shrenite structure by



slightly increasing the proportion of the raw material bismuth oxide to titanium oxide. A platinum crucible of 5cm in diameter and height is placed in a high-frequency induction heating CZ (Czochralski) furnace having an output power of 15 kilowatts. By using platinum wire as the seed crystal and rotating it, the single crystal is pulled up at the speed of 0.5mm per hour. The maximum size of the single crystal is 2cm in diameter. BTO is a photorefractive crystal whose refractive index changes with the irradiation of light. The change of refractive index can be applied to the recording media of holograms and phase conjugate mirrors, which correct the shear of an image.

## Preparation of Uniformly Ultra-Fine Grains of Inorganic Materials

Suzuki Oil and Fat Co., Ltd., the Osaka Government Industrial Research Institute of the Agency of Industrial Science and Technology, and the Miyazaki Prefectural Industrial Research Institute have established for the first time in history a technique for preparing uniformly ultra-fine grains of inor-



Photo Conventional uneven ceramic fine powder



SPG composed of uniform grains of 2 microns

ganic materials which had been hard to achieve so far. The technique is based on the "surface reaction method" of the Osaka Government Industrial Research Institute and membrane emulsification "SPG the technique" which is the patent of Miyazaki Prefectural Industrial Research Institute. Fine grains of uniform size were prepared from inorganic emulsion solutions by using SPG-made high-function separating membrane. Within the range of 0.1 to 10µm, it is possible to accurately design uniform grain sizes, and to make cavities and micro beads. Suzuki Oil and Fat Co., Ltd. has already succeeded in manufacturing uniform products of up to 2m in diameter for the silica fine grains which are about to be commercialized. Their cost is low, and their applications are expected to be as materials for fine ceramics, medical drugs and paint. The company has applied for a patent used and will continue research to make ultra-fine grains of up to 100

#### Wide Temperature Range Acoustic Emission (AE) Sensor

Hitachi, Ltd. has developed a heat resistant AE sensor capable of equipment diagnosis in a wide temperature environment of from -269° to 250 °C. The sensor will serve to detect anomalies and monitor quench (a phenomenon in which a state of superconductivity is broken) in the superconductive equipment of high temperature facilities such as power plants and ironworks. An AE sensor is a unit which detects an elastic wave (generated when a material is deformed or broken) by a ceramic piezo-electric device and converts it into voltage output. It comprises a conductive case with a piezo-electric device covered with a metallic plate and electrically insulated by an alumina plate. Organic adhesives used for bonding ceramic

# Lubrication Effect of Soot for Combustion Engines

Soot contained in the exhaust gas of engines, etc. is carbon containing oxygen and hydrogen. It is said that soot is troublesome because when soot in oil sticks to sliding parts, it causes them to seize up. However, Toyota Kogyo University has discovered that soot has a highly lubricating effect at high temperatures. This phenomenon could be applied to ceramic engines and ceramic bearings and put to practical use in the very near future. In an experiment, a collar manufactured by boring a cylinder and a rectangular flat plate were rotated and rubbed in the smoke of burning benzene, and frictional characteristics were measured on sliding parts. The collar and the flat plate were made of three kinds of fine ceramics, namely, those of alumina, silicon nitride and silicon carbide.

Experimental results showed that the friction coefficient of ceramic materials at 300 to 400°C in the atmosphere was 0.1 or less. In addition, ceramics materials showed good lubricating effects at higher temperatures in vacuum and the thin air atmospheres. The rubbed portion of the flat plate was smooth, and its irregularity was on a scale of 1 to 2 microns at about 300°C.

# Quantum Magnetic Flux Dynamics of High Tempprature Superconductors

Hitachi Ltd. has developed a quantum magnetic flux dymanics analysis method.

Measurement of quantum magnetic flux is an important factor for determination of electric conductivity characteristics at the superconducting phase. As a result, analysis of quantum magnetic flux is indispensable for application of superconductors to superconducting magnets and superconducting devices. Hitachi has developed a molecular



dynamic analysis method which applies interactions of multi-quantum magnetic fluxes accurately. With this, analysis is carried out on superconductors. A quantum magnetic flux generally penetrates superconductors in the form of a string. In such cases, if the string bends while passing through a superconductor, its bending effect in a high-temperature oxide superconductor is 10 to 100 times larger compared to a conventional metallic superconductor. This is because oxide superconductors have a laminated layer structure. Figure shows results of analysis with the new method, in which quantum magnetic fluxes through an oxide superconductor display bending forms.

# Two-Step Annealing Process Effective for Preparation of T<sub>c</sub> Bi-Pb-Sr-Ca-Cu-O Superconductor

Tsukamoto et al. of Nippon Cement Co., Ltd. have reported that the 2-stage annealing process, consisting of preannealing at 720° to 810C for a short time (2Hr) and annealing at 850C for 15Hrs was found effective in pre-



Fig. 1. (A) XRD patterns, and (B) temperature dependence of the resistance of the film annealed at 850°C for 15h without preannealing.



Fig. 2. Temperature dependence of the resistance the annealed film.

paring a Bi-Pb-Sr-Ca-Cu-O system superconductor. With this process, they succeeded in stable preparation of the superconductor with good repeatability. T<sub>c</sub> was found to be over 100K.

The superconducting film contains a small amount ( $\leq$ 50%) of the high Tc phase. The long preannealing duration helped to increase the amount of the high Tc phase, but the temperature dependence of resistance shows a double step superconducting transition and no zero resistivity at temperatures over 100K. They suppose this phenomenon was caused by the grain boundary insulator phase.

Figure 1 shows XRD patterns (A) and temperature dependence of resistance of the film without preannealing, while Fig. 2 shows temperature dependence of the resistance of the annealed film. (P1040-1042)

# Future Prospects for Machinable Ceramics

Machinable ceramics feature free-cutting with carbide tools and permit easy machining such as cutting, grooving, drilling and tapping. With their resistance to drugs, heat and corrosion, a wide range of applications are being promoted as a substitute material for teflon, bakelite, and metals such as stainless steel. While machined products including bolt and nuts have been produced, some enterprises have started production as part of their own ceramics business.

Mitsui Mining Co., Ltd. has assessed a new business field related to ceramic materials such as cement, building materials and tiles, in addition to its energy related business involving coal and oil. Mitsui Mining developed four years ago machinable ceramics capable of cutting using mica crystallized glass by the sol-gel method. With a view to offering convenience to its customers, the company has been expending energy into actively keeping a large assortment of goods in stock. At present, however, it is producing only about two tons annually for use in electric machinery and precision and medical instruments. The products are priced as high as 70,000 to 80,000yen/kg. As a result, most business inquiries are centered around prototypes, not necessarily leading to massive orders.

To cope with this, Mitsui Mining has developed mica machinable ceramics intended for mass production priced as low as onethird compared with conventional ones. Their manufacturing process has not been made clear, but the company claims that their mass production is possible by a new method totally different from the conventional sol-gel and melting methods. Their composition, structure and quality have not undergone major changes compared with their conventional counterparts. Their maximum working temperature and bending strength are 1000°C and 1100kg/cm<sup>2</sup>, respectively. Machinable ceramics produced by the new manufacturing process conduct near-net shape molding, sintering, and then precision machining such as grooving, drilling and tapping, with carbide and high-speed steel tools. With ease of machining, the ceramics can be applied to precision ceramics parts which require dimensional precision. The company will produce, for the time being, standard-shape plates of 300mm<sup>2</sup> and 210mm<sup>2</sup>, and plans to add cylindrical products in the future. The company is also planning to enhance production facilities in its central laboratory in Kokubumachi, Gunma-ken, thereby establishing a setup for monthly production of one ton

INAX has established a manufacturing process for high temperature-stabilized  $\beta$  wallastnite, a porous machinable ceramic. The product is produced by sintering
wallastnite at 1200°C without crystallizing it. 20 to 40% of it is fine pores which contribute to improved resistance against cracks during machining. Compared with mica machinable ceramics, it features higher porosity, fire resistance and lower thermal conductivity, and is presumably suitable for shapes, filters and building materials. The company has signed an agency agreement with Mitsui Mining Co. and Asahi Rika Glass Co. for selling its products. It is priced at 50,000 to 100,000 yen/kg.

Sumitomo Metal Industries, Itd. has established Jukin Photon Ceramics Co., a venture business in which it had invested. Photon Ceramics was established to commercialize an oxide ceramics burner utilizing a far infrared radiation for charcoal-fire burning. The company has been doing business in far infrared radiated ceramics material and free-cutting mica ceramics. Free-cutting mica ceramics have been put to practical use in materials for electronic parts under the guidance of the Ishikawa Prefectural Industrial Research Institute. Sumitomo Metal Industries is planning to stimulate stagnant sales of Photon Ceramics by taking over the management. The company will further improve properties of free-cutting mica ceramics, deterioration at high temperature, and precision workability to extend their market for use in vacuum equipment, medical instruments and heat resistant parts.

Amid the successive advent of new materials such as fine ceramics, composite materials, functionally gradient materials, etc., proposals and devices for new machinability, processing methods and devices have also appeared for structural ceramics. The furture will tell how wide the range of applications will be.

#### Quantum Flux Parameter

The Research Development Corporation of Japan has been working (under the guidance of E. Goto, project leader) on the development of a quantum flux parametron (QFP; an original Japanese circuit element) by combining technology related to parametrons with that related to Josephson circuits. The corporation has recently developed a logic circuit system as a fundamental technique for making the original circuit element practical, and succeeded in applying it to superhighspeed operation of 8GHz. In addition, the corporation has experimentally manufactured and operated a high-density 3-dimensional packaging model of this circuit element. The results of a series of tests show that the element excels in logical operation.

QFP is a device prepared using Josephson junctions in which the minimum logical unit is quantum flux. As it is applicable to superhigh-speed operations, it is expected to be employed in future supercomputers.

The element features: (1) less power consumption than any other elements available by present-day techniques, i.e., 1nW per operation, since the logical unit is quantum flux, (2) faster switching speed by approximately two orders than in conventional semiconductor devices, i.e., less than 10 picoseconds, since it applies the reversal development of quantum flux, and (3) suitability for 3-dimensional packaging, since it can transmit signals by means of inductance connection instead of direct electrical connections. Using this QFP, therefore, it will become possible to develop a superhigh-speed computer that can be housed in a small cube several centimeters high.

The project team of the corporation has been pursuing studies with the view to inspecting the operating state of a fundamental QFP device; examining a computer system provided with the features of the device; creating an inframicro-magnetic field helpful in making the detection of quantum flux practical; and realizing a cryogenic condition practically.

#### Wide-Margin Logic Circuit

#### Highly-Functional

Figure 1 shows the QFP logic circuit system, known as a D-gate, while Figure 2 shows the basic circuit of the QFP. This circuit is activated synchronously with the exciting magnetic flux supplied externally to the excitation line. The magnetic flux signals ap-



Fig. 1. D-Gate



Fig. 2. Basic OFP circuit



Fig. 3. Operational waveforms of the circuit

plied to the input line before excitation are taken out of the output line after being amplified by the effect of the physical properties of the superconductive loop, including the above-mentioned Josephson junctions. This loop functions in the same way as a transistor, and when combined a logical arithmetic circuit is formed. For the D-gate circuit, x and y input signals are applied to the input line of each QFP, while s and t input signals are used through a transformer to excite 2 QFPs. In other words, the D-gate circuit features a structure in which QFPs are excited by the signals (to be specific, the output signals of different QFPs). To make this excitation system practical, a partial circuit has been provided for stabilizing and amplifying the exciting magnetic flux.

Figure 3 shows the operational waveform of the circuit. According to the figure, the y input is fixed at 1 while s and t undergo change when output is directed to the B points. Then QFP(b) is excited by the s and t input signals.

This circuit shows irregularities in the Josephson junctions but is provided with a wide operational margin and excels in logical operation. Accordingly, it can be used to improve the efficiency of adders widely used in computers.

#### Demonstration of High-speed Operation

Efforts made to demonstrate high-speed QFP operation have resulted in the detection of feeble signals whose intensity is 1/2 that of 5-GHz excitation signals. This is due to



Photo 1. Package for high-frequency measurement



Fig. 4. Frequency analysis of high-frequency operation

defects not in the circuit itself but in the packaging technique used to make the related circuits excite synchronously with each other, and also in the measuring system used to abate noises and remove feeble signals to a room temperature condition. To obviate these defects, a standing-wave method capable of receiving signals simultaneously at all points on the same wiring system has been developed as follows. By making use of phase differences produced when signals are transmitted in a chip (at the velocity of light between circuits several mm apart) and the



Photo 2. Fundamental demonstration model for 3-dimensional packaging





reflection of the signals, reversed excitation signals on the wiring system are superimposed; a packaged circuit as shown in **Photo** I has been developed to abate crosstalk noise induced on the output line by external noise and input excitation signals. The outer dimensions of this package are 6cm<sup>2</sup>, and the circuit element attached to the center is 2.7cm<sup>2</sup>.

A performance test with a 1/2 frequency divider has proved (see Fig.4) that the QFP thus obtained can be applied to high-speed operation of 8 GHz (4-phase), which is faster by approximately two orders in switching speed than devices employed in the fastest computers currently available.

#### 3-Dimensional Packaging

As the QFP transmits information using magnetic flux, signals can be transmitted between stacked IC substrates according to a non-contact system without connectors. As the QFP needs only 1/100 as much power as semiconductors, the temperature rise due to heat generated by a number of circuit substrates placed in contact with one another can be disregarded. This means that a CPU in a large computer can be housed in small cube several centimeters high.

To prove the feasibility of the above 3-dimensional packaging, an experimental model (see **Photo 2**) has been manufactured with circuit substrates to which chips are attached. For this demonstration model, a QFP is provided on each chip, while an excitation line to excite the QFP and a signal line to connect chips are provided on each wiring substrate.

Between wiring substrates, a transformer connection is established according to a noncontact system (see Fig.5). The wiring substrates and chips must be bonded together with high accuracy (within approximately  $3\mu$ m), so a specially designed chip-positioning device is used. Using the basic demonstration model, the corporation succeeded in activating the QFP on a chip by input signals from a wiring substrate.

The project team is planning to reconfirm the characteristics of the D-gate in the widemargin highly-functional logical circuit during high-speed operation, examine the superhigh-speed operating limits of the QFP element, and develop a move advanced noncontact-type signal transmission system for 3-dimensional packaging.

# Abstracts of Articles on Ceramics from the Selected Journals of the Academic Societies

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## Hydrogenation Mechanism of Coal Tar Pitch for Carbon Fiber (Part 2) Hydrogen Transfer Mechanism from Tetralin to Coal Tar Pitch for High Performance Carbon Fiber Using Tritium Tracer Method

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Behavior of hydrogen in hydrogenation of the coal tar pitch for high performance carbon fiber with tetralin was investigated in temperature range of 410 to 470°C for 60 min using tritium tracer technique to elucidate the mechanism of hydrogen transfer. The amount of tritium transferred from tetralin to the pitch increased with rise in reaction temperature while the amount of hydrogen added from tetralin to the pitch was kept at almost constant value in temperature range of 410 to 470°C. At 410°C, the THFIS fraction decreased from 13.6 wt% to 5 wt% of the raw pitch, which was kept constant independent of the reaction temperature. HIS-BS fraction, increasing with rise in temperature from 410 to 450°C, was the main product at 450°C. Tetralin solvent began to decompose at 470°C and substantial hydrogen exchange reaction proceeded between pitch and tetralin.

Chemical modification of the surface of ceramic hydroxyapatite for HPLC packing. Kanako SUZUN<sup>†</sup>, Moriaki TacAva, Takashi Oboavasu, Toshihiro IsuKawa, Naoki KANEYAMA<sup>\*\*</sup>, Tsuneyoshi HORICOME and Hiroshi SUCANO<sup>\*</sup> (\*Department of Biochemistry, Faculty of Science, Niigata University, 2-Igarashi 8050, Niigata-shi, Niigata 950-21; \*\*Corporate Research and Development Laboratory, Tonen Corporation, 1-3-1, Nishi-Tsurugaoka, Ohi-machi, Truma-gun, Saitama 354)

Reactions of ceramic hydroxyapatite beads with organic silanes, organic titanates, sodium dodecylphosphate, and other reagents were studied to develop new column packings for HPLC. Epoxy, pyridyldithio and amino groups of 40~80 µm0/g were introduced on the surface of the apatite beads by reactions with organic silane compounds at 140°C for 30 h. Dodecyl groups were also introduced by incubation with sodium dodecylphosphate at room temperature for 2 h. Modification methods using silanes and dodecylphosphate were applicable to titanium dioxide and zirconium oxide. The apatite, titanium dioxide and zirconium oxide medified with silanes and dodecylphosphate were stable in aqueous solvents. Reversed-phase HPLC using a column of the dodecylapatite gave high-resolution and reproducible elution patterns. These modified patites will be of use for HPLC columns packings.

#### Keyword phrases

chemically modified hydroxyapatite; HPLC packings; reversed phase HPLC.

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#### Ceramic Membranes for Bioprocesses

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Ceramic micro- and ultrafiltration membranes suitable for use in bioprocesses can now be made from a wide range of inorganic materials. This article describes the membrane properties attributable to manufacturing procedure. The studies concerning the filtration of bacterial cells by ceramic membranes are also reviewed. Since ceramic membranes have a potential to vary the properties such as pore size, membrane resistance, zeta potential and surface free energy, the examinations to clarify the relationship between membrane properties and filtration characteristics were carried out. And concept for the designing of membranes using filtration of methanogenic cells was proposed. To apply the ceramic membranes for bioprocesses widely, the investigations to establish the concept for the optimum designing of membranes, and also to estimate the influence of shear induced by filtration operations on lysis of cells will be needed.

Key words : Membrane, Ceramic membrane, Microfiltration, Ultrafiltration

#### Bunseki Kagaku Vol.39, 1990 p.487–492

Kei Kin Zoku Vol.40, No.8, 1990 p.587-592

#### Taikabutsu Vol.42, No.9, 1990 p.478–483

Fabrication and mechanical properties of SiC whisker · Al<sub>2</sub>O<sub>3</sub> particle/6061 cmposite materials\*

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6061 aluminum alloy matrix composites were fabricated by a squeeze-exhaust casting method and their mechanical properties were investigated. The present composites were reinforced with 20 vol.% duplex materials consisting of various ratio of SiC whisker and Al<sub>2</sub>O<sub>3</sub> particles. In the extruded composites containing small amount of whisker, most whiskers were arranged in one direction and few of the whiskers were broken. The composites containing 2 portion of whisker and 8 of particles showed maximum tensile strength of 51.7 kgf/mm<sup>2</sup> at room temparature and 15.8 kgf/mm<sup>2</sup> at 300°C. The work hardening exponent of the duplex reinforced composites was higher than that of composites simply reinforced with whisker or particles.

Keywords: particle dispersed composite material, squeeze casting, composite material, SiC whisker

Effect of fluoride addition on the synthesis of spinel and its sinterability

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The aluminum magnesium spinel was obtained from Mg(OH)<sub>2</sub> and  $\gamma$  -Al<sub>2</sub>O<sub>3</sub>. Synthesis and sinterability of speinel doped with AlF<sub>3</sub> and MgF<sub>2</sub> have been studied by X-ray powder diffractometry and TEM observation. The fluorides were hydrolyzed by water from the decomposition of Mg(OH)<sub>2</sub>. HF gas was generated, which was absorbed on the surface of MgO and Al<sub>2</sub>O<sub>3</sub>. Addition of fluoride accelerated the synthesis of spinel above 850°C. The mechanism is suggested as follows. Departure of HF from the surface of MgO and Al<sub>2</sub>O<sub>3</sub> increases the surface energy. Then MgO evaporates and deposits instantly on the surface of Al<sub>2</sub>O<sub>3</sub>, and reacts. The synthesis of spinel proceeds rapidly.

The relative density of sintered spinel whose powder was doped with fluoride and calcined at 1000°C was higher than that of no-dopant which was fired above 1400°C. At 1500°C for 2 hours the relative density of the sintered spinel with AIF<sub>3</sub> addition and MgF<sub>2</sub> addition was 99% and 96%, respectively. The pores of sintered spinel with MgF<sub>2</sub> addition whose sizes were about 2  $\mu$ m were observed in the firing bodies. This suggests traces of decomposed MgF<sub>2</sub> because the sizes of pores were similar to those of added MgF<sub>2</sub>.

Key words : Spinel, Synthesis, Sintering, Fluoride addtion, Evaporation

Zairyo Vol.39, No.444, Sept., 1990 p.1260–1265

Zairyo Vol.39, No.444, Sept., 1990 p.1235–1242 X-Ray Study of Elastic Deformation of Zirconia-Alumina Composite

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The X-ray diffraction method was used to measure the phase stress in composite ceramics of zirconia mixed with 20 and 40 wt% alumina which were subjected to elastic bending. The phase stress in each phase was determined from the diffractions of Al<sub>1</sub>O<sub>1</sub> (146), Al<sub>1</sub>O<sub>1</sub> (1.0.10) and ZrO<sub>2</sub> (133). The phase stress increased in proportion to the applied stress; the proportional constant was larger for Al<sub>1</sub>O<sub>2</sub> than for ZrO<sub>2</sub>. The macrostress calculated from the phase stresses by using the rule of mixture was nearly equal to the applied stress. The theoretical calculation based on the self-consistent model of elastic deformation of composites gave a lower phase stress to Al<sub>1</sub>O<sub>2</sub> and a higher phase stress to ZrO<sub>2</sub>, when compared with the experimental results. The theoretical analysis should be elaborated to include the influences of the free surface and the third phase on phase stresses.

Key words : X-ray stress measurements, Composite ceramics, Zirconia, Alumina, Elastic deformation, X-ray elastic constant, Self-consistent model

Scratching Behavior of Ferrite under Applied Load

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Need for precise grooving and cutting of ferrite-based composite materials into magnetic heads is increasing recently in the field of electronic industry. As materials for magnetic heads have inherent internal stress, it influences the quality of the head processed by cutting and grooving. This study focuess its attention on the effect of internal stress on its cutting behavior. Indentation and scratching tests were carried out to know the cutting mechanism of the composite ferrite material. it was found that the crack length and chipping area increased with an increase in applied load during scratching. The mode of crack growth and chipping pattern also varied with tensile load. Especially, the chipping area was very sensitive to tensile load under small indentation load.

Key words : Magnetic head, Ferrite, Crack growth, Chipping, Indentation, Scratching

# Effects of Carbon Atoms on the Defects in Czochralski-Grown Silicon Formed by Annealing

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The effects of carbon atoms on defect formation in annealings were studied. The results suggest that a defect associated with the photoluminescence line at 0.767 eV (P-line) captures the carbon atom preferentially in the formation process. By assuming that the defect is  $C_{-}O_{-}(C_{1})$  interstitul carbon atom,  $C_{1}$  oxygen atom), the experimental results on the 0.767 eV line can be explained. It is reported that the new donor formation is suppressed in a sample that does not contain carbon atoms, but the obtained value for the new donor concentration is  $2 \times 10^{16}$ /cm<sup>3</sup> in carbon-lean Czochralski-grown sample (carbon concentration  $< 10^{16}$ /cm<sup>3</sup>)

KEYWORDS: silicon, defect, carbon atom, photoluminescence, thermal donor, new donor, annealing

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**Physics** 

p.L1600-L1603

#### Nonseeded Crystalline Orientation Control for Si-on-Insulator Laser Recrystallization

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The orientation control technique for Si-on-insulator fabrication by laser recrystallization with artificial seeds, called 2-step laser annealing, is demonstrated. In this technique, a crystalline substrate is not used as a seeding material. Where the controllability is defined as the probability of having the orientation within 20° from (100), 94% controllability was successfully achieved for artificial seeds, and at a distance of 50 µm from the sseds, controllability was 73%.

KEYWORDS: Si-on-insulator, laser recrystallization, nonseeded orientation control, artificial seed, electron channeling pattern

Localized Orientation Control in BiSrCaCuO Superconducting Film

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This letter reports on localized orientation control in BiSrCaCuO superconducting films. Uniformly oriented crystals, of which the c-axis exists in-plane, were grown on a MgO (110) plane by annealing them in contact with a MgO (100) plane. Thus, stripe patterns including oblique tapers in stripe edges were fabricated on MgO (100) crystals to produce locally appearing (110) planes. By annealing them in contact with a MgO (100) plane, the uniformly oriented crystals were confirmed to grow around oblique tapers in stripe edges fabricated on MgO (100) crystals.

KEYWORDS: localized orientation, BiSrCaCuO film, uniformly oriented crystals, stripe pattern, Josephson junction

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#### Correlation between $T_c$ and Eu Lattice Vibration in T'-Phase Superconductor $(La_{1-x}Eu_x)_{2-y}Ce_yCuO_{4-\delta}$ Observed by <sup>151</sup>Eu Mössbauer Effect

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The electronic state and lattice vibration of Eu in T'-phase  $(La_{1-x}Eu_{x})_{2-y}Ce_{y}O_{4-\delta}$  was studied by <sup>15</sup>Eu Mössbauer effect. The isomer shift and the Debye temperature of Eu,  $\Theta_{D_{y}}$  showed that Eu is trivalent, and the Eu-O distance is larger than those in the hole-doped superconductors. With increasing Eu concentration, in spite of the shortening of the lattice constants,  $\Theta_{D}$  in T'-phase decreased. This is probably caused by the increase in the Eu-O distance with the change of Eu-O-La bonding into Eu-O-Eu bonding. A tight correlation between  $T_{c}$  and  $\Theta_{D}$  was found and the relation,  $T_{c}=0.712\Theta_{D}$  exp( $-\Theta_{D}^{*}$ ) (1300), was derived.

KEYWORDS: high-T<sub>c</sub> superconductor, (La<sub>1-x</sub>Eu<sub>x</sub>)<sub>2-y</sub>Ce<sub>y</sub>CuO<sub>4-δ</sub>, T'-phase, lattice constant, <sup>151</sup>Eu Mössbauer effect, lattice vibration, isomer shift, T<sub>c</sub> enhancement, Debye temperature

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p.L1612-L1614

Japanese Journal of Applied Physics Vol.29, No.9, Sept., 1990 p.L1608–L1611

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#### Effect of Sulfur Doping on the Structure and Properties of La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> Superconductor

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Effects of the substitution of sulfur for oxygen on the structure and electrical properties of  $La_{1,4s}Sr_{0,16}CuO_4$  superconductor have been studied. It was found that the superconducting transition temperature decreases, the temperature dependence of electrical resistance at low temperatures becomes semiconducting and the electrical resistance increases with increasing sulfur content. The crystal structure at room temperature changed from tetragonal to orthorhombic, while the in-plane lattice constants *a* and *b* increased and the lattice constant *c* decreased with increasing sulfur content. **KEYWORDS:** La-Sr-Cu-O superconductor, substitution, sulfur, crystal structure, electrical resistance

ETWORDS. La-SI-Cu-O superconductor, substitution, sundr, crystal structure, electrical resistance

#### Transport Critical Current Density of Polycrystalline YBCO in Zero Field Cooled and Field Cooled States: A Comparison

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Magnetic field dependence of transport critical current density  $(J_2)$  of a polycrystalline YBCO superconductor in field cooled and zero field cooled cases have been studied experimentally. The measured  $J_c$  value when the sample was cooled in a field (FC) was always larger than that measured for a zero field cooled (ZFC) case in the same magnetic field. We also observe (i) a peak in the field dependence of the ratio of  $J_c$  in FC case to that of ZFC case and (ii) an anomalous rise in  $J_c$ in ZFC case with increasing field. These observations are explained as a signature of two types of regions (intergrain and intragrain) in sintered specimens.

KEYWORDS: superconductivity, critical current, intragrain magnetisation

Japanese Journal of Applied Physics Vol.29, No.9, Sept., 1990 p.L1615–L1617

#### Property and Structure of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub>-Ag Composites Prepared from Nitrate Solutions

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Mixtures of Y, Ba, Cu, and Ag nitrate aqueous solutions (nominal molten ratio of Y:Ba:Cu = 1:2:3) were evaporated to dryness. The dried powders were codecomposed at 850°C in air, and sintered at 920°C for 20 h in O<sub>2</sub>. The phases were only orthorhombic YBa;CuO<sub>2</sub> and Ag. The bulk density, grain size, and critical current density ( $\lambda_2$ ) increased with increasing amount of Ag  $\leq$  5 wt%; for instance, up to 5.65 g/cm<sup>3</sup>, 30  $\mu$ m, and 215 A/cm<sup>2</sup>, respectively. The critical remperature (7, (zero)) was about 91 K (with a width of 1-2 K) and insensitive to the amount of Ag  $\leq$  5%. With addition of Ag, the degradation in moisture was improved.

KEYWORDS: superconductor, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>4</sub>, Ag addition, grain growth, critical temperature, critical current density, nitrate solutions, degradation in moisture, homogeneity of structure

Japanese Journal of Applied Physics Vol.29, No.9, Sept., 1990 p.L1618–L1620

#### Estimation of Respective Volume Fractions of High- and Low-T<sub>c</sub> Phases in Inhomogeneous Oxide Superconductors

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For Bi- or Tl-based oxide superconductors, several different phases usually coexist in a sample. We propose here a new way of quantitative estimation of the volume fraction of each phase. It is based on the fact that the ratio of the reversible magnetization of each phase varies with temperature and magnetic field. In this estimation, fundamental parameters such as penetration depth or upper critical field of each phase should be specified beforehand, and the sample is required to be roughly c-axis oriented.

KEYWORDS: high-T<sub>c</sub> superconductor, Bi-Sr-Ca-Cu-O system, magnetic properties, reversible magnetization, volume fraction, anisotropy

Journal of the Ceramic Society of Japan, Int. Edition Improvement of Critical Current Density

Japanese Journal of Applied Physics Vol.29, No.9, Sept., 1990 p.L1621–1623

#### in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+r</sub> Superconductor by Sn Addition

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When SnO<sub>2</sub> was added to Y-123 (YBa<sub>2</sub>Cu<sub>2</sub>O<sub>6+2</sub>) powder and sintered at 1223 K for 86.4 ks, the densification was enhanced remarkably, and the density reached 99% of the theoretical value for the 2-mol%-SnO<sub>2</sub>-added specimen, while the average grain size became smaller with Sn addition. Fine spherical BaSnO<sub>3</sub> precipitates were observed to be distributed in the grains and at grain boundaries. The AC magnetization measurements indicated that Sn addition causes intragrain  $J_c^{m}$  to increase at 77 K in the magnetic field between 0.02 and 0.12 T. The  $J_c^{m}$  exceeded 10° A/cm<sup>2</sup> at 0.04 T for the 3-mol%-SnO<sub>2</sub>-added specimen.

KEYWORDS: YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub>, Sn addition, critical current density, flux pinning, densification, BaSnO<sub>3</sub> precipitates

#### Japanese Journal of Applied Physics Vol.29, No.9, Sept., 1990 p.L1624–L1627

#### Substituting Effect of Bi on Superconductor YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-v</sub>

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Substitution of a small amount of bismuth for yttrium in  $Y_{1-x}$ Bi<sub>x</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7-y</sub> leads to a decomposition into more than two phases even at a low bismuth content of x=0.02. Experimental results of resistivity measurements and X-ray powder diffraction analysis are reported with emphasis on the low bismuth content. The resistivity exhibits rather complicated sample-dependent behavior for x larger than 0.02, reflecting the decomposition due to the substitution of bismuth.

KEYWORDS: Y-Ba-Cu-O superconductor, substitution effect of Bi, decomposition, resistivity measurement, X-ray powder diffraction

Japanese Journal of Applied Physics Vol.29, No.9, Sept., 1990 p.L1628–L1631

#### Preparation of Superconducting 1201 Phase in the $(Pb_{1-y}Cu_y)Sr_{2-x}La_xCuO_z$ System

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An almost-single-1201-phase sample has been synthesized in the  $(Pb_{1-y}Cu_y)Sr_{2-x}La_xCuO_x$  system. The sample showed the superconducting transition with the onset temperature of about 36.5 K and a zero resistivity temperature of about 31.5 K. These values were about 7 K higher than those reported by Adachi *et al.* The X-ray powder diffraction study showed that the almost-single phase was attained at the nominal composition of x=0.9 and y=0.5, and the crystal structure had a tetragonal symmetry with a=0.3769 nm and c=0.8697 nm.

KEYWORDS: superconductor, Pb-based copper oxide, (Pb<sub>1-y</sub>Cu<sub>y</sub>)Sr<sub>2-x</sub>La<sub>x</sub>CuO<sub>z</sub> system, 1201 phase, transition temperature, X-ray diffraction

Japanese Journal of Applied Physics Vol.29, No.9, Sept., 1990 p.L1632–L1634

Preparation and Superconducting Properties of

 $La_{2-x}(Ca_{1-y}Sr_y)_{1+x}Cu_2O_{6-x/2+\delta}$ 

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Superconductivity has been detected in the Ca-based 2-1-2-6 compound  $La_{2-y}(Ca_{1-y}Sr_y)_{+y}Cu_2O_{4-y/2+y}$  and the relationship between crystal structure and superconducting properties is investigated by varying x, y, and O<sub>2</sub> pressure during synthesis. It is shown that the lattice parameter a is restricted to between 3.823 and 3.826 Å for the superconducting material, irrespective of x, y, and O<sub>2</sub> pressure. For a fixed Sr content y, the smaller a is, the higher the  $T_c$  is obtained. On the other hand, lattice parameter c has no clear correlation with superconductivity.

**KEYWORDS:**  $La_{2-x}(Ca_{1-y}Sr_y)_{1+x}Cu_2O_{6-x/2+\delta}$ , superconductivity, high pressure synthesis, crystal structure

#### Japanese Journal of Applied Physics Vol.29, No.9, Sept., 1990, p.L1638–L1641

#### Work Function of a High-T<sub>c</sub> Superconductor, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>

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To characterize the electronic properties of superconducting YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, its work function  $\Phi$  has been measured by two different methods. From the photoelectric and electrical determinations, it is shown that  $\Phi$  of polycrystalline YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> is close to 4.0 eV. The relatively high work function of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> for its low electron density implies that a strong exchange-correlation potential exists in the bulk. Systematic studies are necessary in order to determine whether or not the work function is a useful parameter for the new high- $T_c$  superconductors as well as for the conventional ones.

KEYWORDS: superconductivity, high-T<sub>c</sub> superconductor, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, work function, electronic properties, surfaces, photoelectric effect, contact potential difference

#### Superstructure in Thin Films of Bi-Based Compounds on MgO

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In situ epitaxial growth of BiSrCaCuO films by three target sputtering was performed on MgO substrates at a temperature of 650°C. From high resolution transmission electron microscopy, the film showed a superstructure consisting of the alternate stacking of the low- $T_c$  and high- $T_c$  phases with a c-axis of 34 Å. The film in the [110] or [110] directions was parallel to (100)MgO, and the transient layers between the substrate and the film were less than a few atomic layers thick. X-ray diffraction simulations indicated that the films contained random layer ordering of 34 Å bi-layers (low- $T_c$  and high- $T_c$  +how- $T_c$ ) and random layer ordering of low- $T_c$  and high- $T_c$  phase layers.

KEYWORDS: superconductor, thin film, BiSrCaCuO, sputtering, superlattice, transmission electron microscopy

Japanese Journal of Applied Physics Vol.29, No.9, Sept., 1990 p.L1642–L1644

#### Fluorine Doping and Superconductivity of Nd<sub>2</sub>CuO<sub>4</sub> Thin Films

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Fluorine was doped into sputter-deposited Nd<sub>2</sub>CuO<sub>4</sub> films to induce superconductivity in the films. The films annealed in the presence of NF<sub>7</sub> gas were observed to show remarkable resistivity change which was in parallel with the change of *a*-axis length. Fluorine incorporation in the films was verified by the X-ray photoelectron spectroscopy analysis. The specimen annealed at 800°C in 0.1 Torr NF<sub>7</sub> (1%)/Ar gas under UV light irradiation exhibited the onset of superconductivity at 27 K after a reducing procedure at 700°C in Ar.

KEYWORDS: Nd<sub>2</sub>CuO<sub>4</sub>, fluorine doping, NF<sub>3</sub>, superconductivity, thin film, sputtering

Japanese Journal of Applied Physics Vol.29, No.9, Sept., 1990 p.L1645–L1647 Suspension-Spun Tl-Ba-Ca-Cu Oxide Filament with High Critical Current Density

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High  $T_c$  TI-(Ba, Sr)-Ca-Cu-O superconducting filaments were successfully prepared using a technique in which suspension-spun and pyrolyzed filaments were densified by pressing and sintering. A high  $J_c$  at 77 K, 0 T of 12000 A/cm<sup>2</sup> was attained for the filament sintered at 840°C for 1200 s with a zero resistance state of 102 K. Although the starting powder had a high  $T_c$  phase of TI<sub>1</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>2</sub>O<sub>4</sub>, the structure of the filament. We are of the voltility of TI oxide from the large surface area of the filament.

KEYWORDS: TI-(Ba, Sr)-Ca-Cu-O superconducting filament, high critical current density, suspension spinning

Japanese Journal of Applied Physics Vol.29, No.9, Sept., 1990 p.L1648–L1651

#### Thin Film Structure of $YBa_2Cu_3O_{7-\delta}$ on (001) MgO Substrate Studied by TEM

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A plan-view TEM observation was made for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-6</sub> (YBCO) thin films prepared by MOCVD on (001) MgO substrates. For the TEM observation, the MgO substrate plates were ion-thinned before the YBCO deposition. The YB-CO thin films were found to be polycrystalline with a grain size of about 0.5  $\mu$ m. Most of the YBCO grains are grown with their [001] axes nearly normal to the MgO substrate plane. Between the neighboring YBCO grains, a small-angle misorientation was observed quite frequently. Most of the misorientation angles measured by selected-area electron diffraction were less than about 5 degrees. At the small-angle grain boundaries, a nearly periodic array of dislocations was observed in the high-resolution lattice images. The AC and DC Josephson effects of YBCO thin film bridges reported previously are discussed in relation to the small-angle grain boundaries.

KEYWORDS: grain-boundary junction, TEM observation, small-angle grain boundary, MOCVD, YBCO thin film, AC Josephson effect, DC Josephson effect, lattice imaging

Japanese Journal of Applied Physics Vol.29, No.9, Sept., 1990 p.L1652–L1654

#### Influence of the Flux Creep on the Critical Current Density in Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> and Y(Ho)Ba<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> Superconductors

Hiroaki Kumakura, Kazumasa Togano, Eiji Yanagisawa<sup>†</sup>, Jun-ichiro Kase<sup>†</sup> and Hiroshi Maeda

National Research Institute for Metals, 1-2-1, Sengen, Tsukuba-City, Ibaraki 305 'Research Center, Asahi Glass Co., LTD, Hazawa-cho, Kanagawa-ku, Yokohama 221

Intragrain  $J_c$  values of the textured Bi- and Y-based oxides were obtained at 4.2 K-77 K by the D.C. magnetization measurements with various sweep rates of the magnetic field. The  $J_c$ 's at 4.2 K were comparable for both oxides. However, with increasing temperature, the  $J_c$  of the Bi-based oxide became much more sensitive to the electric field criterion  $E_c$  related to the sweep rate of the magnetic field than that of the Y-based oxide. As a result,  $J_c$  at 77 K of the Bibased oxide was significantly decreased in magnetic fields for small  $E_c$ . The dependence of  $J_c$  on  $E_c$  for both oxides can be well understood using the flux creep model.

KEYWORDS: Bi-Sr-Ca-Cu-O, Y(Ho)-Ba-Cu-O, D.C. magnetization, critical current density, criterion for J<sub>c</sub> definition, flux creep

Japanese Journal of Applied Physics Vol.29, No.9, Sept., 1990 p.L1655–L1658

#### Fabrication of Y-Ba-Cu-O Superconducting Films on Cu Substrates by an Electrophoretic Deposition Technique

Direct formation of  $Y_1Ba_2Cu_3O_{7-r}$  films on Cu substrates by electrophoretic deposition is studied. Electrophoretic deposition was carried out using presintered  $Y_1Ba_2Cu_3O_{7-r}$  powder dispersed in distilled acetone. The deposited films were annealed in air at 900°C. We succeeded in obtaining superconducting  $Y_1Ba_2Cu_3O_{7-r}$  films on Cu substrates. The films on Cu plates and Cu film/YSZ exhibited the zero-resistance state at 66 K and 76 K, respectively. Interfacial chemical reactions at the  $Y_1Ba_2Cu_3O_{7-r}/Cu$  interface are discussed. The achievement of the zero-resistance state is considered to be due to the reduction of the interfacial reactions.

KEYWORDS: electrophoretic deposition, high T<sub>c</sub> oxide superconductor, Y<sub>1</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>, Cu substrate, interfacial reaction

Japanese Journal of Applied Physics Vol.29, No.9, Sept., 1990 p.L1659–L1662

#### Experimental Analysis of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub>/Ag Proximity Interfaces

Akira FUJIMAKI, Tomohiro TAMAOKI, Tetsuya HIDAKA, Masashi YANAGASE, Tetsuyoshi SHIOTA, Yoshiaki TAKAI and Hisao HAYAKAWA

Department of Electronics, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01

We have fabricated SNS (superconductor-normal metal-superconductor) junctions consisting of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>4</sub>(YBCO) /Ag/Nb trilayers in order to probe surface properties of the YBCO films. The trilayers are *in situ* deposited, and patterned by a photolithographic technique. These junctions exhibit Josephson-like behavior. The contact resistivity and its temperature dependence suggest that the weaklinks are formed inside YBCO and that the junction properties depend on the area of surface non-superconducting phases consisting of the YBCO components.

KEYWORDS: SNS junction, high-temperature superconductor, Josephson effect, surface of YBa2Cu3Ox

Materials Transactions, JIM Vol.31, No.9, 1990 p.755–758

## Superconducting Behavior in the Bi-In-Sr-Ca-Cu-Pb-O System

By D. Matsuoka\*, M. Okada\*\*, T. Murakami\*\*\*, K. Cross\* and M. Homma\*\*

The superconducting behavior of the nominal composition of  $(Bi_{1-,}In_{2})_{S}r_{2}Ca_{2}Cu_{3}Pb_{0,6}O_{y}$  was studied. It was found that the samples with  $x \le 0.90$  fired at 850°C for 50 h in air showed zero resistance above 60 K. The sample with x=0.25 showed the highest zero resistance above 60 K. The sample with x=0.25 showed the highest zero resistance above 60 K. The sample with x=0.25 showed the highest zero resistance above 60 K. The sample with x=0.25 contained % In for the amount of Bi. The surface of the sample with x=0.90, which showed zero resistance above 60 K, was covered with  $Bi_{0}Sr_{2}Ca_{1}Cu_{2}O_{2}$  because the In oxide is volatile from its surface over 850°C. The addition of In to the system has no effect on the critical temperatures, but is effective in increasing the volume fraction of the  $Bi_{0}Sr_{2}Ca_{2}Cu_{2}O_{10}$  compound.

Keywords: bismuth superconductors, indium addition, magnetic susceptibility, microstructure

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Materials Transactions, JIM Vol.31, No.9, 1990 p.772–777

## AE Signals and Fracture in SiC-Fiber Reinforced Aluminum after Applying Cyclic Deformation

#### By Akira Okada\* and Shin-ichi Kitagawa\*\*

The correlation between the mechanical property change and the AE signal emitted during the 3-point bending deformation was investigated for the SiC-fiber reinforced aluminum after applying cyclic deformation. AE signals reflect the change in bonding between SiC and the Al matrix, and the introduction of defects, by cyclic deformation. The spectrum at a higher frequency became stronger in the specimens degraded by applying the fatigue history and in these specimens preformed SiC-Al wires were observed with SEM to split into several thin-rebunches. Almost the whole number of AE events was observed just before the occurrence of rupture in the specimens without cyclic deformation, while in the specimens with cyclic deformation, the number of the AE signals increased continuously over a wide stress range with increasing applied stress from a relatively smaller applied stress until the specimen

Keywords: SiC-fiber, composite materials, acoustic emission, fast Fourier transform, fractography, FRM, acoustic emission-spectrum

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Materials Transactions, JIM Vol.31, No.9, 1990 p.793-801

## Equilibria between Liquid Tin and FeO<sub>x</sub>-CaO-SiO<sub>2</sub> Slag

By Yoichi Takeda\*, Akira Yazawa\*\*, Po Po Chit\*\*\* and Hayao Ujiie\*\*\*\*

To clarify the effects of oxygen potential, temperature and slag composition on the solubility of tin in slag, liquid tin or tin-iron alloy was brought into equilibrium with various slags of the FeO<sub>x</sub>-CaO-SiO<sub>x</sub> system mostly at 1573 K. The experiments were carried out by measuring oxygen potentials by use of oxygen concentration cells. Increasing oxygen potential resulted in increasing in content in slag and decreasing iron content in metal. Tin in slag was estimated as being divalent. And the contents of tin were generally similar for both binary fayalite (FeO<sub>x</sub>-SiO<sub>x</sub>) and ferrite (FeO<sub>x</sub>-CaO) type slags, and much higher than those in terrany FeO<sub>x</sub>-CaO-SiO<sub>x</sub> slag. The minimum solubility of tin in slag may be observed at the molar ratio of CaO/SiO<sub>x</sub> which is near 2 if the slag is in the molten state. Increasing iron oxide content results in increasing tin content in slag. The activity coefficient of SnO(1) in binary fayalite (FeO<sub>x</sub>-SiO<sub>x</sub>) and ferrite (FeO<sub>x</sub>-CaO) slag is 1 to 2 and the maximum activity coefficient is around 7 in the ternary FeO<sub>x</sub>-CaO-SiO<sub>x</sub> slag whose composition is close to saturation with solid dicalcium silicate and 25 mass% iron oxide. For practical purposes, tin content in slag is shown as a function of iron content in metal to know how much tin from slag can be reduced with desirable metal composition. Based upon the experimental results, the tin smelting process reasonably explained.

Keywords: tin smelting, tin refining, tin solubility in slag, slag loss, activity of tin oxide, activity coefficient of tin oxide, silicate slag, fayalite slag, ferrite slag, equilibrium between slag and tin

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# CURRENT TOPICS IN MARINE BIOTECHNOLOGY



This is a collection of papers presented at the First International Conference on Marine Biotechnology held in Tokyo from September 3 through 6, 1989. About 400 scientists from 23 different countries conferred about developments in marine biology, meeting in six sections: microorganisms, microalgae, macroalgae, fish, shellfish and other marine animals, and supporting technology and interfacial subjects. There were many very lively discussions and reports of exciting new findings in every area.

Many participants agreed that marine biology can develop only through multidiscriplinary and international cooperation, and a committee meeting was held during the Conference' to plan for future International Conferences. Considering the rapid progress in this field, it was unanimously decided that one should be held every two years. By vote, Washington, D.C., U.S.A. was chosen as the place for the second conference, as proposed by Dr. O.R. Ząborsky of National Research Council, National Academy of Sciences, U.S.A. The third meeting will be held in Norway, and the fourth in France. The organizers are happy that meeting sites have been fixed so long in advance, since we observe that marine biotechnology is growing so rapidly in many parts of the world.

This Conference was made possible by the advice, help and cooperation of many people, both in scientific and governmental organizations and in private companies. I would like to express our special thanks for the cooperation of government agencies including the Ministry of Agriculture, Forestry and Fisheries, the Ministry of Education, Science and Culture, the Ministry of Health and Welfare, the Ministry of International Trade and Industry, the Science and Technology Agency and the Ministry of Foreign Affairs. There was financial support from the Commemorative Association for the World Exposition (1970) and ninety private companies listed in the proceedings. Special thanks should be extended to the staff of Marine Biotechnology Institute Co., Ltd., for their devoted help in the organization of this Conference.

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