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# Editorial



### **Even Margins**

W E are so accustomed to seeing the printed page with ev en margins on both right and left that any variation is annoying to the e yes. The printer can adjust his words or even letters with sufficient un equal spacing so that each line of type is exactly filled without too much use of the hyphen. He does have trouble with very short lines, as in ru nning text alongside a picture in a narrow column. The ordinary typewri ter of course cannot do such unequal spacing, and when typed pages are reproduced by a photographic process, for example in preparing our Divi sional Extended Abstract booklets, the right-hand margin must be left u neven, unless some special method is used in preparing copy for the pho tographer.

Special typewriting machines are available, such as the Vari-Typer, which can do adjustable spacing somewhat as the typesetter does; but e verything must be typed twice, or a counting procedure of some kind mus t be employed. Ordinarily the operator types a line, deciding how many characters are appropriate; then the machine is adjusted automatically to space this many characters evenly in the allotted line width. On rep eating the typing, the evenly spaced copy is obtained. The procedure is time consuming and expensive, but some method of the sort is necessary if photo-reproduced copy is to compare in appearance with material prin ted in the usual way. Such machines are extremely versatile since they can have easily interchangeable sets of type of any styles desired, and mathematical and scientific material can be copied as flexibly as by an y method.

One way to obtain even right margins is that adopted here: just typ e to the end of the line, and never use the margin release key. (A surp rising number of spaces between words come at the end of the line). Thi s page is an experiment, no doubt not an original one at all; the style is certainly not a popular one. Splitting words in this way does not ma ke comprehension difficult, even if it is annoying at first. If it were widely used, we believe the style would soon be commonly accepted. To t he beginning student of a foreign language many characters, symbols, or different scripts are, for a time, disconcerting; to the native who has studied his language from childhood these things are familiar and obvio us, and have their own understandable history and background.

To our Division Committees in charge of preparing Extended Abstra cts, we commend thorough examination of this style, with the object of making the pages neat. If the reader is sufficiently interested, he wil l become accustomed or at least resigned to it. To the Printer of this JOURNAL (if we have not lost him already), we commend his usual style except for just this one page! — CVK

P.S. Suggestions are invited for the name of our new publication, whi ch was announced in the February JOURNAL. They should be received befo re the Los Angeles Meeting in May. Present suggestions are ELECTRO CHEMICAL TECHNOLOGY and ELECTROCHEMICAL ENGINEER ING.



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## Kinetics and Mechanism of Nickel-Sulfur Reaction

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#### ABSTRACT

Kinetics and mechanism of the reaction between nickel and sulfur vapors were investigated in the temperature range  $480^{\circ}-640^{\circ}C$  under atmospheric pressure. The sulfurization of nickel has been found to follow, under these conditions, the parabolic rate law. The activation energy of this process amounts to 22 kcal/mole. The examination of x-ray patterns of the scale formed on the surface of the metal has demonstrated that this scale layer is composed almost entirely of NiS. Morphologic investigations show that the scale is composed of two distinct layers. The outer layer, constituting the main part of the whole scale, is compact, polycrystalline, and exhibits an ordered growth texture. The inner layer is porous and does not exhibit any growth texture. The investigations carried out with the aid of the radioactive sulfur isotope <sup>\$SS</sup> have demonstrated that the sulfide scale on nickel is formed exclusively by the outward diffusion of the metal.

The confrontation of experimental data with the results obtained by Dravnieks (1) leads to the assumption that the mechanism of the sulfide scale formation on nickel does not depend on the state of aggregation of the oxidizing medium.

Dravnieks (1) and Wagner and Lichter (2) have demonstrated that the sulfurization of nickel in molten sulfur in the temperature range  $205^{\circ}-445^{\circ}$ follows the parabolic rate law. On the other hand Hauffe and Rahmel (3), as well as Pfeiffer (4), stated that if the reaction was carried out in sulfur vapor at  $630^{\circ}$  under a pressure not exceeding 1 mm Hg the course of the reaction could be described with a linear rate law.

It was thereby stated that the sulfide scale formed on nickel is composed exclusively of the NiS-phase independently of the state of aggregation of the oxidizing medium and of the temperature. The scale is built up of two distinct layers; the outer one is compact, and the other, inner layer, is porous. Arkharov and Blankova (5), Czerski (6), Mrowec and Werber (7), Pfeiffer (4), and Hauffe (3) suppose that the formation of these two layers of the same reaction product can be explained by assuming simultaneous diffusion of both reactants through the scale layer in two opposite directions.

However, according to the opinion of Pines and Tchaikowskij (8), the sulfide scale layer on nickel grows exclusively because of the inward diffusion of sulfur.

From the literature data given above it can be seen that the mechanism of sulfurization of nickel is not yet definitively cleared up and more experimental work must still be done. The aim of the present work was therefore to investigate the kinetics and mechanism of sulfurization of nickel in sulfur vapor under atmospheric pressure in the temperature range  $480^{\circ}-640^{\circ}$ C.

#### Experimental

The measurements were carried out on specimens containing 99.85% Ni. By means of spectral analysis the presence of the following impurities Fe, Mn, Cu, Mg, Si, Co, Al, and traces of Ag, Zn, Ca has been shown. The metal was melted in vacuo  $(10^{-4} \text{ mm Hg})$  and cold rolled to sheets 0.1 cm thick. The sheets were annealed for 100 hr at 750°C in helium atmosphere and subsequently cut into samples of dimensions 3 x 2 x 0.1 cm. The surface of the samples was polished with emery paper (including No. 4/O) and washed with water, acetone, and methanol. The process of sulfurization was carried out in a modified apparatus of Wagner (2) enabling continuous gravimetric measurements of the reactions kinetics (9) (Fig. 1). The apparatus (Fig. 1) consisted of two electrical furnaces into which a quartz tube containing molten sulfur was inserted. The lower furnace controlled the temperature of the molten sulfur at the bottom of the quartz tube and



Fig. 1. Apparatus for kinetic measurements of sulfurization of metals in sulfur vapor under atmospheric pressure by the continuous gravimetric method.

the upper furnace controlled the temperature of the sulfur vapor in the reaction chamber. The temperature of sulfur vapor in the reaction tube was controlled automatically by an electronic compensator with an accuracy of  $\pm 3^{\circ}$ C. The thermocouple was introduced into the reaction tube on the specimen level at a distance from the tube wall equal to that of the specimen. Purified nitrogen was introduced into the upper, nonheated part of the quartz tube in order to avoid penetration of oxygen into the reaction zone. Traces of sulfur escaping with nitrogen from the reaction tube were directed into a corresponding trap with the aid of an appropriate exhauster. The specimen suspended in the reaction tube was fastened with a nichrome wire to an arm of an analytical balance. The wire was preliminarily oxidized in air at 1000°C for 100 hr to protect it against the attack of sulfur. In order to eliminate the possibility of condensation of sulfur on the wire in the upper, nonheated part of the tube the wire itself was heated to 600°C with an additional heater which maintained its temperature above 450°C. Preliminary investigations have shown that the mass of the wire did not change much during the reaction (the variation amounted to  $\pm$  1.0 mg). These variations can be explained by the convection flow of air and sulfur vapor around the wire. The increase in weight of the sulfurized nickel specimens was of the order of 100 mg; the mass of the wire on which the specimen was suspended therefore could be considered to be practically constant. The sulfurization rate could be measured continuously by determining the weight increase of the sample. The investigations were carried out in the temperature range 480°-640°C. This restriction of the temperature range resulted from the necessity of investigating the process at temperatures above the boiling point of sulfur and below the melting point of the eutectic Ni-NiS (645°C). The results of the sulfurization rate measurements are given in Fig. 2 and 3. The figures show the  $(\Delta m/q)^2$  values plotted against t where  $\Delta m$  is the weight gain of the sample, q the surface area of the sample, and tthe reaction time. Surface area q was assumed to be constant during the sulfurization process and equal to the initial surface area of the metal speci-



Fig. 2. Weight gain plot for the temperature range 480°-560°C



Fig. 3. Weight gain plot for the temperature range 560°-640°C

men. It is clear that this surface decreases during the process, but owing to the particular geometric form of specimens used the maximum changes in the surface area of metal did not exceed 2-3% of the initial value in the investigated ranges of temperature and reaction time.

As can be seen, the experimental data in these coordinates fit a straight line independent of the reaction temperature. This means that in our experimental conditions the scale formation process follows the parabolic rate law:

$$\left(\frac{\Delta m}{q}\right)^2 = k'' \cdot t \qquad [1]$$

where k'' is the parabolic rate constant of the sulfurization process. Measurements of the sulfurization rate could be reproduced with an accuracy of  $\pm 5\%$ . Table I contains the parabolic rate constants calculated from our data. The relation between the rate of sulfurization and the reaction temperature is illustrated by Fig. 4 in which log k'' is plotted vs. 1/T. As can be seen from the figure this relation is linear. Activation energy for the sulfurization of nickel as calculated from these figures amounts to 22 kcal.



Fig. 4. Change of the parabolic rate constant for the NiS formation with temperature.

Table I. Parabolic rate constants

No.	Temp, °C	k" (g² cm-4 sec-1)
1	480	1.05 • 10-7
2	500	$1.65 \cdot 10^{-7}$
3	520	$2.60 \cdot 10^{-7}$
4	540	3.50 · 10-7
5	560	$4.65 \cdot 10^{-7}$
6	580	$5.92 \cdot 10^{-7}$
7	600	8.75 . 10-7
8	620	11.2.10-7
9	640	15.7.10-7

Morphologic investigations have demonstrated that, independent of the reaction temperature, the sulfide scale growing on nickel is composed of two layers. The outer layer, constituting the main part of the scale, is compact, polycrystalline, and exhibits an ordered growth texture (5). The thinner, inner layer is porous and composed of very small crystals of sulfide. In this layer no growth texture could be detected. According to the results of the x-ray analysis both scale layers are built up of the same phase of the reaction product which was identified as the high-temperature form of NiS (stable above 300°C) (10). The mean chemical composition of the scale corresponded to the nonstoichiometric formula Ni0.01-0.02S and was practically independent of the temperature of the reaction.

As proved by detailed microscopic observations the ratio of the thicknesses of the two scale layers depends on the temperature of the sulfurization process and the time of the reaction. The relative mass of the porous inner layer has been found to decrease with increasing reaction temperature. On the other hand, the ratio of thicknesses of both scale layers observed on various samples at the same temperature has been found not to be constant, but to vary with increasing duration of the experiment (the porous inner layer is growing faster). Corresponding photomicrographs of the cross sections through the scale formed at 600°C are shown in Fig. 5. The boundary between the layers of the scale can be seen easily on these micrographs; the



Fig. 5. Cross section through specimens sulfurized at 600°C: a, 1 hr; b, 4 hr. I. The outer layer is compact. The dark regions result from the mechanical process of the metallographic preparation of the scale. II. The inner layer is porous. The platinum wire marker was artificially retouched for greater clarity of the micrograph.

growth of the scale is accompanied by a distinct growth of the relative thickness of the porous inner layer. On the micrographs one can also see a thin platinum wire marker wrapped primarily around the metal sample and situated nearly at the boundary between both layers of the scale.

According to the conventional interpretation such position of the marker (11, 12) is taken as proof that the scale grew because of the diffusion of both reactants, nickel and sulfur, migrating simultaneously in two opposite directions. The compact outer layer formed because of the outward diffusion of the metal; the thinner, porous inner layer formed because of the inward diffusion of sulfur.

Recent investigations by two of the present authors (13-15) and Rickert (16) on Cu-S and Ag-S systems have shown however that the position of the marker in the scale does not definitively explain the mechanism of observed double-layer scale formation. Thus, contrary to the results obtained by the marker method, the formation of a double-layer sulfide scale on copper and silver was found not to depend on the diffusion of both reactants in the opposite directions. The scale was formed exclusively because of the outward diffusion of the metal (15, 17). The formation of the porous inner layer is bound up, in this case, with secondary processes occurring within the scale during its growth (17, 18). From the morphologic point of view the structure of the two-layer sulfide scale on nickel is analogous to the structure of the sulfide scale formed on copper and silver. Therefore it can be supposed that the mechanism of both sulfurization processes is also analogous, and the process develops exclusively owing to the outward diffusion of nickel. In order to verify this assumption Brückman, Mrowec, and Werber carried out a new series of measurements (19) using the isotopic method described in previous papers (13, 15). These investigations were carried out at 600°C in an apparatus shown in Fig. 1. Nickel plates of the same dimensions as those in the kinetic investigations were preliminarily sulfurized in a medium not containing the radioactive sulfur isotope until a scale layer was formed thick enough to absorb fully the radiation emitted by the isotope <sup>35</sup>S. The radioactive sulfur isotope in the form of a pellet was then introduced into the reaction chamber and the sulfurization was continued. After various periods of time the process was stopped by removing the specimens from the sulfurizing medium and by cooling them in air. The scale layer was separated from the metal and the activity of both scale surfaces was measured with the aid of a G.M. counter.

The inner surface of the scale (which had been in contact with the metal during the sulfurization) was found to be practically inactive independent of the time of the sulfurization carried out in the radioactive medium. The results obtained for different reaction times are given in Table II. It can be seen that the radioactivity at the inner surface does not exceed 2% of the activity measured at the outer surface of the scale. The activity at the inner surface of the scale has been shown not to increase with increasing time of sulfurization in the active

Table II. Radioactivity at the surfaces

No.	tı, min	t2, min	t2/t1	A <sub>1</sub> , imp. min <sup>_1</sup>	A2, imp. min-1	$\frac{A_2}{A_1}100$
1	15	15	1	3080	20	0.6
2	15	45	3	4500	90	2.0
3	15	75	5	3270	31	0.9
4	15	105	7	4620	60	1.3
5	15	135	9	6220	82	1.3

 $t_1$ , time of sulfurization in the nonactive medium;  $t_2$ , time of sulfurization in the medium containing the radioactive sulfur isotope;  $A_1$ , activity of the outer scale surface (which was in contact with the oxidizing agent); and  $A_2$ , activity of the inner scale surface (which was in contact with the metal).

medium containing the <sup>35</sup>S-isotope. If the inward diffusion of sulfur were to participate in the growth of the scale, an appreciable radioactivity could be expected to appear at the inner scale surface after relatively short periods of sulfurization carried out in the radioactive medium. The results described above can then be considered to prove that the inward diffusion of sulfur does not practically participate in the formation of the sulfide scale on nickel. The insignificant activity revealed at the inner surface of the scale can be explained probably by the inevitable contamination of this surface with traces of the sulfide formed primarily on the outer surface of the scale. The inner surface becomes contaminated during the operations of cutting the fragile scale layer and separating it from the metal.

#### Discussion

The sulfurization of nickel in the temperature range 480°-640° under atmospheric pressure has been shown to follow the parabolic law. With the aid of the radioactive sulfur isotope it could be found that sulfurization occurs in these conditions exclusively owing to the outward diffusion of the metal. This conclusion concerning the mechanism of nickel sulfurization has been fully confirmed by the recent investigations carried out by Mrowec and Rickert (28) with aid of the well-known Wagner pellet method. On the basis of obtained results it can be stated that the outward diffusion of the metal being the slowest partial process determines the rate of sulfurization of nickel. Taking into account the deviation from the stoichiometric composition in the case of NiS (metal deficit) (10, 20) it can be assumed that the metal, in conformity with the theory given by Wagner (21), diffuses in the form of ions and electrons through the cation vacancies and electron holes in the crystal lattice of NiS.

From the considerations given above it follows that the sulfide scale formed on nickel ought to be compact and composed of a single layer only. It has been found, however, that the scale is built up of two layers of the same reaction product. The formation of the porous inner layer can be explained on the basis of the following assumptions concerning the mechanism of the reaction: during the initial stage of the reaction a thin, compact, and adherent scale layer is formed. Since the scale is formed owing to the outward diffusion of the metal, *i.e.*, at the phase boundary scale/sulfur, the contact between the growing layer of the reaction product and sulfurized metal could be easily cut off if the plastic flow of the scale toward the surface of the metal would not take place. The extent of this plastic flow is limited by the dimensions and the size of the specimen. For geometrical reasons the deformations of the scale are not observed at edges and curved parts of the sample (2, 15, 22, 23). At some critical scale thickness which depends on the temperature of the reaction, on the plasticity of the scale, and on the geometry of the sulfurized metal specimen the decrease in the volume of the metal cannot be further compensated by the plastic flow of the scale; the contact between the scale layer and the metal becomes partially broken and longitudinal cracks are formed. The formation of the cracks begins at the edges of the specimen where the plastic flow of the scale is limited in its extent by geometrical factors.

Before the crack has been formed the gradient of the chemical potential responsible for the outward diffusion of the substrate is distributed in the scale in the following manner.

The chemical potential of the metal attains its highest value at the phase boundary scale/metal. This value is approximately equal to the value calculated for virtual thermodynamic equilibrium between the metal and the scale.

Conditions at the phase boundary scale/sulfur do not deviate very much from the conditions of the thermodynamic equilibrium between NiS and sulfur; in the vicinity of this phase boundary the chemical potential of the metal attains its minimal value.

When the contact between the metal and the scale gets partially broken the chemical potential of the metal in the scale tends to attain at the phase boundary scale/crack a value corresponding to the equilibrium state between sulfur and nickel sulfide. Correspondingly, the sulfur vapor pressure in the void space must increase. At the metal surface the process of secondary NiS formation begins: the pressure of dissociation of the nickel sulfide remaining in contact with the metal is lower than the dissociation pressure of the detached scale consisting of the same phase. The secondary process of the sulfide layer formation at the metal surface results in decreasing the vapor pressure within the crack and in shifting the equilibrium of the system scale/ crack: the scale dissociates in order to replace the sulfur deficit in the crack. Nickel ions and electrons formed in this process migrate through the NiS lattice vacancies toward the surface of the scale and recombine there with sulfur. The existing gradient of the sulfur vapor pressure enables the migration of the sulfur molecules toward the surface of the metal or NiS grains adjacent to the metal and participate there in the formation of the porous inner layer of the scale. Owing to this process the contact between the scale and the metal is partially maintained. In accordance with the mechanism described above, formation of the two-layer scale does not involve the diffusion of both reactants through the layer of the reaction product in two opposite directions, but is conditioned by secondary processes which depend on the conditions of the experimentlimited size of sulfurized specimens.

Such a mechanism of the two-layer scale formation was first proposed by Dravnieks and McDonald (24). It was proved experimentally in a recent investigation of Mrowec and Werber who had used the radioactive sulfur isotope in investigations of the mechanism of two-layer scale formation on copper (13, 15, 17) and silver (15, 25).

Rickert, who investigated the mechanism of the sulfurization of copper and silver using a modified Wagner-Tubandt pellet method, came to analogous results (16). An analogous mechanism of the two-layer scale formation on Fe has also been proposed by Birchenall (26).

The rate of sulfurization is considerably influenced by the formation of the porous inner layer. In view of the fact that nickel can be transported only through the volume of the sulfide, the cross section available for diffusion in the porous inner laver is smaller than in the case of the compact outer layer. The fact that the process of sulfurization of nickel can be described in the initial stage of reaction with the parabolic law indicates that, in this case, the porosity of the inner layer is small and remains practically constant in the course of the reaction. This means that the secondary processes mentioned above and resulting in filling the longitudinal cracks between the metal and the compact scale layer occur sufficiently fast to compensate to a considerable degree the loss of the metal. The absolute values of the parabolic rate constants given in Table I must be considered, therefore, regarding the formation of the porous inner layer, to be only approximate values and to characterize the formation of NiS in given conditions only in a rough manner. These values cannot therefore be used for the evaluation of the selfdiffusion coefficients with the aid of the well-known Wagner relation (27). Much more reliable results may be obtained with the help of the pellet method (15) enabling the elimination of all secondary processes resulting in the formation of the inner porous laver of the scale (16, 28).

The investigations carried out by Dravnieks (1) have demonstrated that the sulfurization of nickel in molten sulfur can be described also with the parabolic law. The energy of activation calculated for this process from data obtained in the temperature range  $324^{\circ}-444^{\circ}$  (when the high-temperature modification of NiS is formed) amounts to 20 kcal. Considering the analogy between processes of sulfurization in molten sulfur and in sulfur vapor and taking into account the equality of energies of activation it can be assumed that the mechanism of this reaction does not depend on the state of aggregation of the oxidizing medium.

On the other hand, investigations carried out by Hauffe and Rahmel (3) and by Pfeiffer (4) proved that the sulfurization of nickel in sulfur vapor at low pressures (<1 mm Hg) and at  $600^{\circ}-630^{\circ}\text{C}$  can be described with the linear rate law. This shows that it is not the outward diffusion of the metal but the chemical reaction occurring at the phase boundary scale/metal or scale/sulfur which must be considered as a rate-determining step. According to Pfeiffer the transition of nickel in form of ions and electrons through the phase boundary scale/metal is the slowest partial process which determines the rate of sulfurization.

The investigations carried out by the present authors have demonstrated, however, that the sulfurization of nickel carried out at the same temperature but under a higher sulfur vapor pressure can be described with the parabolic rate law. These results indicate that the mechanism of the sulfurization is influenced by the pressure of sulfur vapor.

If the rate of sulfurization were controlled, as postulated by Pfeiffer, by the transition of nickel atoms from the metal in to the scale, this rate should not be dependent on the pressure of sulfur vapor. Such dependence is, however, strongly suggested from the comparison of Hauffe's and Pfeiffer's lowpressure experiments with our high-pressure experiments. According to our opinion it is rather the chemical reaction at the phase boundary scale/sulfur that is the rate-controlling process. Evidently it must be preceded by chemisorption of sulfur at the outer surface at the scale. At low pressures of sulfur and correspondingly low surface concentration of S-atoms or molecules chemical reaction may be slow even in comparison with the solid-state diffusion; at higher pressures of sulfur vapor and higher surface concentrations of adsorbed sulfur the chemical reaction may become faster than the diffusion of nickel.

#### Summary

The sulfurization of nickel in sulfur vapor under normal pressure at temperatures between  $480^{\circ}$ - $640^{\circ}$ C has been found to follow the parabolic law. In the sulfide scale layer formed in these conditions and built up of NiS (with stoichiometric deficiency of the metal) two different sublayers can be clearly distinguished: the outer compact sublayer and the inner porous one.

With the aid of the radioactive tracer method it has been demonstrated that sulfurization can proceed exclusively owing to the outward diffusion of nickel. The porous sublayer, therefore, can be formed exclusively as the result of secondary processes occurring within the layer of the reaction product and consisting of the formation of a "crack" between the scale and the metal in the course of the reaction. This crack becomes filled with fine-crystalline nickel sulfide formed as a result of interaction between the metal and the sulfur supplied to the metal surface by the dissociation of the compact scale layer. Relative thicknesses of these two sublayers depend on the temperature of sulfurization, on the duration of this process, and on the geometry of specimens under investigation.

In view of formation of the porous sublayer, the rate constants, which can be determined experimentally, must be considered to characterize the reaction rate in the Ni-S system in given conditions only in an approximate manner.

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# **Oxidation of Iron-Nickel Alloys**

#### V. Influence of H<sub>0</sub>O in Oxidizing Gas

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#### ABSTRACT

The oxidation of three iron-nickel alloys nominally 30%, 41%, and 78% Ni was investigated over the temperature range of  $600^{\circ}$ -1000°C in controlled  $O_z/N_a$  atmospheres with partial pressures of H<sub>2</sub>O of 0.32 mm, 5.81 mm, and 26.3 mm. The gross effect of H<sub>2</sub>O in the oxidizing atmosphere is to increase the oxidation rate (up to 13-fold for the 30% alloy at 1000°C). In addition, at higher temperatures and higher  $p_{\pi_0}$ , the rate-determining diffusion process changes from the first half to the second half of the 60-min reaction. The observed rates for the 30% and 41% alloy during the second phase are higher, while the second-phase rate for the 78% alloy is lower. The Arrhenius plots for these alloys are not linear over the 600°-1000°C range. Below 800°C a low apparent activation energy, 30-40 kcal, is calculated, while above 800° a value in the 60 kcal range is obtained.

The results are interpreted in terms of changes in the physical condition of the oxide film as caused by  $H_2O$  which enhances surface migration of ions and promotes solid-state reactions.

Several previous reports from this laboratory have dealt with the oxidation of iron-nickel alloys (1-4). Alloys of these two elements have found many engineering applications because of their magnetic properties, their ability to participate in glass-to-metal seals, and their thermal expansion characteristics. Therefore, it is important to know quite completely the behavior of these alloys in various environments such as oxidizing atmospheres at high temperature.

The present investigation is concerned with the oxidation of alloys, nominally 30, 41, and 78% Ni, in the range  $600^{\circ}-1000^{\circ}$ C. In an earlier report (3) the kinetics of oxidation in two atmospheres, laboratory air and a 21.7% O<sub>2</sub>-78.3% N<sub>2</sub> mixture, was established. An inspection of the rates in the two

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atmospheres does not allow any good generalization to be made relative to the oxidizing potential of these two atmospheres. The observed reaction rate in the laboratory air was greater, less, or equal to that in the controlled atmosphere depending on the alloy and the reaction temperature. Certain conclusions could be drawn from the rate data however. The first had to do with the precision of the measurements. While two runs made during the same day in laboratory air were quite precise (within 3% of an average value) runs made several weeks or months apart might vary by 60%. The second conclusion was that, while the reaction rate for oxidation in the controlled atmosphere followed the parabolic law quite well, in laboratory air there were real deviations. Moreover, the deviation was not always in the same direction.

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While not the only "contaminant" in the atmosphere it is highly probable that water vapor is the significant one. The k<sup>1</sup> laboratory air is free of exhaust fumes, sulfur oxide gases, and such compounds that have been demonstrated to have an accelerating effect on the corrosion of metals. Thus, to explain these results it was necessary to learn the role of H<sub>2</sub>O on the mechanism and kinetics of oxidation.

The role of  $H_2O$  in high-temperature oxidation is an extremely important item despite the fact that it has been often overlooked. The development of general principles which would define its part in the oxidation process would be a significant contribution to oxidation theory. Further, knowing the role of  $H_2O$  in the oxidation process would help to interpret much of the "practical" oxidation data in the literature in comparison with well-controlled experiments. A final contribution to basic oxidation theory is the over-all objective of this series of papers, the complete description of the kinetics and mechanism of oxidation of iron-nickel alloys.

#### Experimental

Alloys.—The composition of the alloys, the heat treatment prior to oxidation, and the technique of surface preparation have already been described (2, 3). It has been pointed out that the preferred method of surface preparation involves chemical etching because, following proper etching, electron diffraction patterns of the alloy itself were obtained whereas abrasion and polishing techniques sometimes gave patterns difficult to interpret.

Oxidation studies .- The Chevenard thermobalance employed in this work is capable of operation up to 1050°C. The instrument furnace has a quartz tube liner which allows the introduction of special atmospheres into the oxidation zone. The oxidizing atmospheres flowing at a rate of 263 ml/min consisted of a mixture of 21.7% oxygen and 78.3% nitrogen (by volume) with three different H<sub>2</sub>O contents. These atmospheres were: (a) the gas mixture without any intentional addition of H<sub>2</sub>O with a dewpoint of  $-20^{\circ}$ F [vapor pressure H<sub>2</sub>O = 0.32 mm (5)]; (b) the gas mixture to which H<sub>2</sub>O was added by passing the gas stream through a fritted glass plug and water held at about 0°C. The measured dewpoint of this gas was +38°F [vapor pressure  $H_2O = 5.81 \text{ mm} (5)$ ; (c) the gas mixture to which H<sub>2</sub>O was added by passing the gas stream through a fritted glass plug and water held at room temperature. The measured dewpoint of this gas was  $+80^{\circ}$ F [vapor pressure  $H_2O = 26.3$ mm (5)].

In each case the dewpoint of the gas was measured with a General Electric Dew Point potentiometer with a precision of  $\pm 3^{\circ}$ F. At least duplicate experiments were run at 600°, 700°, 800°, 900°, and 1000°C in each atmosphere, each run being of 60 min duration.

Treatment of data.—The oxidation rate for these iron-nickel alloys may be represented by a parabolic rate equation.

where  $\Delta m$  is gain in weight in g/cm<sup>2</sup> of a sample oxidized for t seconds;  $k_p$  is the parabolic rate constant (g<sup>2</sup> cm<sup>-4</sup> sec<sup>-1</sup>); b is a constant (g<sup>2</sup>cm<sup>-4</sup>). The data for certain experiments were represented over the entire run by a linear plot, Eq. [1]. In other cases, notably those at higher temperatures and higher H<sub>2</sub>O vapor pressure, the plot was not linear over the whole 60 min duration. These data could be represented in either of two ways. The first would be by using two parabolic equations, one for the early part of the run and a second for the later part of the run. Alternatively the data could be represented over the entire time interval by using an equation wherein the  $(\Delta m)$  exponent fell somewhere between 1.5 and 2.5. On theoretical grounds the use of two parabolic equations for separate time intervals seems more justified.

The temperature dependence for reactions of this type is usually described by an Arrhenius type equation:

$$k_p = Ae \frac{-\Delta E^*}{RT}$$
 [2]

in which  $\Delta E^*$  is termed the apparent energy of activation and A the frequency factor. The exact significance of  $\Delta E^*$  has not been satisfactorily established insofar as high-temperature oxidation is concerned and can only be considered a guide to the type of oxidation process. Some of the difficulties in the interpretation of  $\Delta E^*$  have been discussed (3). Further, where the reaction product film is composed of more than one species it would be suspected that  $\Delta E^*$  would not be constant over an extended temperature range. This was the situation encountered in this study.

Electron diffraction examination of oxide films.— Electron diffraction analyses by the reflection technique were made of the oxide films with a General Electric electron diffraction instrument. This instrument is equipped with a furnace attachment enabling one to study the oxidation products at the temperature of reaction. The detailed description and interpretation of the patterns obtained in these special atmospheres have been reported (4).

#### Results

The parabolic rate constants,  $k_n$  in Eq. [1], for the 30% Ni alloy are listed in Table I. Only average values for the several runs are given, the precision of these data having been discussed (3). The values given for the  $p_{\rm H_{20}} = 0.32$  mm run were taken from this earlier paper. These data are plotted in Fig. 1. At 600° there is a moderate increase in rate while at 700° the rate constant is insensitive to H<sub>2</sub>O additions to the gas stream; at 800° the rate doubles over the  $p_{H_{20}}$  range investigated here; at 900° and 1000° the rate increases by a factor of 5 and 14, respectively, the "initial" rate being compared in the last two cases. The influence of water vapor in the oxidizing gas has a second effect at 900° and 1000°. At these temperatures it is necessary to use two parabolic equations to represent the experimental data. The first equation holds for the mittal 30 min, the second (solid circles on Fig. 1) for the 30-60 min part of the reaction. This in-

 $(\Delta m)^2 = b + k_p t$ 

[1]

Table I. Parabolic rate constants for 30% Ni alloy

		k	₽ (g <sup>2</sup> cm <sup>-4</sup> sec <sup>-1</sup> )	
t °C	$p_{\rm H_{2}0} = 0.32 \rm mm$		$p_{\rm H_{2}0} = 5.81~{\rm mm}$	$p_{\rm H_{2}0} = 26.3  \rm mm$
600	$1.27  imes 10^{-12}$		$1.74 imes10^{-12}$	$2.14  imes 10^{-12}$
700	$1.46  imes 10^{-11}$		$1.65 imes10^{-11}$	$1.50 imes10^{-11}$
800	$8.5 imes10^{-11}$		$1.24 imes10^{_{-10}}$	$1.85  imes 10^{_{-10}}$
900	$5.2 imes10^{ ext{-10}}$	(a)	1.42 × 10 <sup>-9</sup> (0-30 min)	2.73 × 10 <sup>-</sup> ° (0-30 min)
		(b)	$1.75  imes 10^{-9}$ (30-60 min)	4.28 × 10 <sup>-</sup> (30-60 min)
1000	$3.3 imes10^{-9}$	(a)	$1.10  imes 10^{-8}$ (0-36 min)	$4.48  imes 10^{-8}$ (0-30 min)
		(b)	$1.53  imes 10^{-8}$ (36-60 min)	$10.8  imes 10^{-8}$ (30-60 min)

crease in rate for the second part of the reaction itself increases with  $p_{\text{H}_20}$ . At  $p_{\text{H}_20} = 5.81$  the second parabolic reaction rate constant increases by about 30% over the first, while at  $p_{\text{H}_20} = 26.3$  mm the rate during the second half of the reaction approximately doubles.

The temperature dependence of the reaction is given by the Eq. [2] type of plot in Fig. 2.<sup> $\circ$ </sup> The curves labeled A and D, B and E, and C and F represent data at 0.32 mm, 5.81 mm, and 26.3 mm vapor pressure H<sub>2</sub>O, respectively. The apparent activation energies derived from the slopes of these lines are:

$$A = 41.2 \text{ kcal} B = 41.2 C = 41.5 D = 55.2 E = 60.6 F = 73.7$$

It is very obvious that a single linear plot does not represent the data over the entire temperature range. Above 800° the slope increases to yield activation energies considerably higher than the "normal" 41,200 cal.

The parabolic rate constants representing the

<sup>2</sup> Note that in Fig. 2, 4, and 6, decreasing rate constants are plotted in the vertical direction.







Fig. 2. Temperature dependence of oxidation rate for 30% Ni alloy; A, D,  $p_{\rm H_{2}0}=0.32$  mm; B, E,  $p_{\rm H_{2}0}=5.81$  mm; C, F,  $p_{\rm H_{2}0}=26.3$  mm.



Fig. 3. Oxidation rate of 41% alloy as a function of vapor pressure  $H_{\rm z}O.$  O, 0-30 min kinetics;  $\bullet$ , 30-60 min kinetics.

oxidation kinetics of the 41% alloy in the three different atmospheres are listed in Table II and plotted in Fig. 3. In the oxidation of the 41% Ni alloy the effect of H<sub>2</sub>O is evidenced at 600° and 700° with increased rates; at 800° there is practically no effect, and at 900° and 1000° the rates are increased approximately threefold over the  $p_{\rm H2}$ o range studied. The necessity to represent the data by two

Table II. Parabolic rate constants for 41% Ni alloy

			k <sub>p</sub> (g <sup>2</sup> cm <sup>-4</sup> sec <sup>-1</sup> )		
t °C	$p_{\rm H_{20}} = 0.32 \rm{mm}$		$p_{\rm H_20} = 5.81 \text{ mm}$		$p_{\rm H_20} = 26.3 \rm mm$
600	$1.27 imes10^{-12}$		$2.20  imes 10^{-12}$		$2.88  imes 10^{-12}$
700	$9.8 imes10^{ ext{-12}}$		$1.37  imes 10^{-11}$		
800	$9.3 imes10^{-11}$ *		$8.33 imes10^{-11}$		$1.18 imes10^{-10}$
900	$4.05\times10^{{\scriptscriptstyle-10}}$		$8.92  imes 10^{-10}$	(a)	1.10 × 10- <sup>®</sup> (0-30 min)
				(b)	1.58 × 10 <sup>-*</sup> (30-60 min)
1000	$3.51 imes10^{-9}$	(a)	6.90 × 10 <sup>-9</sup> (0-30 min)	(a)	1.20 × 10 <sup>-s</sup> (0-30 min)
		(b)	8.00 × 10 <sup>-</sup> (30-60 min)	(b)	$1.71  imes 10^{-8}$ (30-60 min)

\* Corrected from typographic error in (3).



Fig. 4. Temperature dependence of oxidation rate for 41% alloy; A, D,  $p_{\rm H_2O}=0.32$  mm; B, E,  $p_{\rm H_2O}=5.81$  mm; C, F,  $p_{\rm H_2O}=26.3$  mm.

parabolic equations rather than one is observed at 900° in the 26.3 mm  $p_{\rm H_{20}}$  atmosphere and at 1000° in both the 5.81 mm and the 26.3 mm  $p_{\rm H_{20}}$ atmospheres. The rate during the second phase of the reaction increases by about 43% over the first half of the reaction.

The temperature dependence of the reaction is given in Fig. 4. Again, the Arrhenius plot is not linear, but deviates because of higher reaction rates above  $800^{\circ}$ . In each of the three atmospheres, a low apparent activation energy is observed in the  $600^{\circ}-800^{\circ}$  range and a high value in the  $800^{\circ}-1000^{\circ}$  range. The activation energies corresponding to the slopes are as follows:

A	40.8 kcal
в	33.9
С	32.7
D	59.3
$\mathbf{E}$	58.3
$\mathbf{F}$	61.3

The parabolic rate constants which describe the oxidation behavior of the 78% alloy in the three

Table III. Parabolic rate constants for 78% Ni alloy

		k <sub>p</sub> (g <sup>2</sup> cm <sup>-4</sup> sec <sup>-1</sup> )	
t °C	$p_{\rm H_20} = 0.32 \mathrm{mm}$	$p_{\rm H_20} = 5.81 \rm{mm}$	$p_{\rm H_20} = 26.3 \rm mm$
600	$7.2 imes10^{-13}$		$2.13 imes10^{-12}$
700	$3.01\times10^{\scriptscriptstyle-12}$	$6.56 imes10^{-12}$	$8.59\times10^{\text{-12}}$
800	$1.70  imes 10^{-11}$	$3.34 imes10^{ ext{-11}}$ (a)	$3.65  imes 10^{-11}$ (0-36 min)
		(b)	$2.47  imes 10^{-11}$ (36-60 min)
900	$7.5 imes10^{-11}$	$1.16  imes 10^{-10}$ (a)	$1.69  imes 10^{-10}$ (0-30 min)
		(b)	$1.08 \times 10^{-10}$ (30-60 min)
1000	(a) $6.4 \times 10^{-10}$ (0-30 min)	$7.85  imes 10^{-10}$ (a)	$1.49 \times 10^{-9}$ (0-30 min)
	(b) $5.5 \times 10^{-10}$ (30-60 min)		$1.16  imes 10^{-9}$ (30-60 min)



Fig. 5. Oxidation rate of 78% alloy as a function of vapor pressure H<sub>2</sub>O. O, 0-30 min kinetics; •, 30-60 min kinetics.

atmospheres are given in Table III and the log  $k_p - \log p_{H_{20}}$  plot in Fig. 5. Here the over-all effect of increased H<sub>2</sub>O vapor pressure is one of increased rate. The effect is not as pronounced as is the case with the 30% and 41% alloy, but rather a consistent doubling or tripling over the whole  $p_{H_{20}}$  range. The other effect observed was seen in the high  $p_{H_{20}}$  run and in the temperature range of 800°-1000°. Under these experimental conditions the oxidation kinetics is represented by two parabolic rate constants, the second  $k_p$  less than the first.

Figure 6 gives the temperature dependence of the rate. The apparent activation energies corresponding to the slopes are as follows:

A =	35.5
B =	33.6
C =	33.4
D =	66.0
D = E =	66.0 60.4

#### Discussion

Experimental observations indicate that certain broad conclusions may be drawn as to the influence of moisture in the oxidizing gas on the oxidation kinetics of these alloys. The most conspicuous effect



Fig. 6. Temperature dependence of oxidation rate for 78% alloy; A, D,  $p_{\rm H_{2}0}=0.32$  mm; B, E,  $p_{\rm H_{2}0}=5.81$  mm; C, F,  $p_{\rm H_{2}0}=26.3$  mm.

is to increase the rate as expressed by the parabolic rate constants. This holds with few exceptions (700°C with the 30% alloy, 800° with the 41%alloy). With respect to the 30% alloy this increase is considerable, over 13-fold over the  $p_{H_{20}}$  range considered. The second effect is demonstrated at the higher temperatures and higher partial pressure of H<sub>2</sub>O. Under these conditions the oxidation reaction over the 60-min duration must be represented by two parabolic equations rather than a single one. The inference is that different processes operate during different phases of the reaction. In the case of the 30% and 41% alloys the reaction rate accelerates during the second half of the reaction, whereas with the 78% alloy the parabolic rate constant is less. For each of the three systems it is quite obvious that the conventional "Arrhenius" plot is not linear over the entire 600°-1000°C range. This nonlinearity is emphasized with the increase in  $p_{H_{2}0}$ . Recognizing this nonlinearity over the whole temperature range it is still possible to calculate two values of apparent activation energy for each alloy. One value would hold below 800°, and this would be a low activation energy process, 30-40 kcal. A second would hold for experiments above 800°, a high activation energy, of the order of 60 kcal. A final effect of moisture in the oxidizing gas, namely, the production of an enlarged lattice parameter in the oxide product, has already been discussed in connection with the electron diffraction examination (4) of the films formed under these experimental conditions. A major reaction product on alloys containing 30% and 41% Ni is a spinel of the  $Ni_xFe_{(3-x)}O_4$  type in which the Ni and Fe content can vary with distance from the metaloxide interface. NiFe<sub>2</sub>O<sub>4</sub> has an  $a_{\bullet}$  value of 8.33Å; and usually the  $a_o$  value for the spinel formed on this type of alloy falls in the range 8.33-8.40 depending on the Ni content (6). The spinel formed in the higher  $p_{\rm H_{20}}$  atmospheres had observed  $a_o$ values of 8.60Å and 8.58Å for the 30% and 41% alloy, respectively. The structure of the oxide film formed on the 78% alloy apparently was not influenced by H<sub>2</sub>O vapor in the oxidizing gas within the limitations of the electron diffraction technique.

Thus the influence of moisture is revealed in both reaction kinetics and oxide film structure with the 30% and 41% alloy and in reaction kinetics with the 78% alloy.

With few exceptions, these occurring at  $600^{\circ}$  and  $700^{\circ}$ C, the oxidation rates observed previously in laboratory air (3) can be explained on the basis that the oxidizing atmosphere contained moisture equivalent to a few millimeter partial pressure which varied from day to day. The few exceptions to this semiquantitative explanation are rates that were lower in laboratory air than in the controlled atmosphere. These deviations at the lower temperatures fall almost within experimental error and, as discussed below, the influence of moisture should be more pronounced at the higher temperatures. The present results also explain the need to use two parabolic plots to represent data for the 30% alloy and the 78% alloy in laboratory air at

 $1000^{\circ}$ , accounting for the higher later phase kinetics of the 30% and the lower later phase kinetics of the 78% alloy.

In attempting to explain the observed results the first consideration should be one of the thermodynamics involved. From free energy calculations on Fe-Ni alloys of these compositions it would be concluded that Fe would react with H2O vapor at these temperatures while Ni would not. Experimentally this appears valid as discussed by Kubaschewski and von Goldbeck (7) who found the Fe-Ni system to be almost ideal. Thus at the start it would be expected that the reactions that take place by moisture additions to the oxidizing atmosphere would involve mainly Fe and the oxides of Fe rather than Ni and NiO. This was confirmed by the only structural changes observed. The 78% alloy contained 3.8% Mo which would be expected to react with H<sub>2</sub>O and lead to a higher rate.

Considering the reaction product formed on the 30% and 41% Ni alloy, the interpretation of the enlarged lattice parameter constitutes a critical point as the rate-determining step for oxidation of these alloys is most likely the diffusion of cations through a spinel of variable nickel content. The possibility of this parameter being due to the incorporation of Mn in the lattice was discussed (4). and it was pointed out that Mn in the amount present in our alloys had been observed to have a profound effect on the oxidation rate of heater alloys by Gulbransen et al. (8, 9) and actually detected by Yearian and co-workers on chrome steels (10). However, the possibility also exists that the lattice parameter is a measure of the physical condition of the film. Spinels with lattice parameters in the 8.5-8.7Å range were observed by Hickman and Gulbransen (11) in their early oxidation studies, for example, a spinel of  $a_{\circ} = 8.66$ Å was observed on an 18-8 stainless steel after oxidation at 700°C. These investigators considered this high value as being associated with a stressed condition which in time could lead to cracking. Pande also observed oxide lattice parameters during electron diffraction studies that were 0.60% higher than x-ray measurements and discusses these in terms of the particle size of crystals (12). That water vapor can have a profound effect on nucleation, lateral growth, and morphology of oxide films was clearly demonstrated by Gulbransen and Copan (13) in experiments carried out with pure Fe at 450°C for 48 hr. Fine oxide whiskers grew in a dry O2 atmosphere (dewpoint  $-79^{\circ}$ C) as contrasted with blades grown in a 10% H<sub>2</sub>O-90% argon atmosphere. Their experiments led to the conclusion that H<sub>2</sub>O facilitates nucleation, promotes surface diffusion, and expands reaction sites. This would imply that the general effect of moisture in the absence of specific reactions (e.g., hydroxide formation) would be to increase reaction rate, and this would explain the over-all general effect. Thus, while there may exist compositional variation in oxide films formed in atmospheres of varying dewpoint which have gone undetected it seems more logical that the kinetic changes observed reflect changes in the physical condition of the films.

The morphology of the oxide films which would normally be grown on the 30% and 41% alloys would be governed to a large extent by solid-state reactions that would occur as the component oxides attempt to achieve equilibrium structures as established by Brabers and Birchenall (14). These solidstate reactions would be enhanced by the presence of moisture. Reported observations on the kinetics of such reactions and the influence of moisture on the kinetics leads one to conclude that such solidstate reactions must be given consideration in establishing the mechanism of oxidation of binary or ternary alloys that contain more than one oxidizable metal. The reaction between NiO and Fe<sub>2</sub>O<sub>3</sub> to form nickel ferrite commences at about 650°C and is rapid above 800°C (15, 16). For example, at 900°C the reaction is over 70% completed in 30 min as shown by Turnbull (16) in his review and interpretation of the kinetics of this reaction. Fe<sub>2</sub>O<sub>3</sub> is observed on the surface layers of oxides formed on the 30% and 41% alloys in low dewpoint atmospheres but not in the higher dewpoint runs, suggesting that under the latter conditions cation diffusion occurred to establish a spinel with lower nickel content (less protective). Water vapor has the effect of promoting such solid-state reactions. Wickert and Wiehr (17) observed that water vapor lowered the temperature at which solid-state reactions would occur between CuO and Fe<sub>3</sub>O<sub>4</sub> and increased the rate of reaction as compared to that in neutral atmosphere. Bénard (18) concludes from sintering experiments with oxides that in certain situations water vapor increases rate of reaction by promoting surface diffusion of ions. Certainly the possibility of these solid-state reactions occurring exists, and certainly such reactions would alter the morphology of the oxide films, but with the available experimental evidence one can only speculate as to whether these changes would account for the increased rate observed in the three systems.

The nonlinearity of the Arrhenius plot may be explained on the basis of different rate-determining mechanisms holding in the two temperature ranges. It seems reasonable that any change in the rate-determining mechanism would be gradual rather than abrupt, so any discussion of "low temperature activation energy" and "high temperature activation energy" is quite arbitrary. The activation energy value derived for the 30% and 41% alloys in the  $600^\circ$ - $800^\circ$  range is interpreted as representing diffusion through a spinel structure varying in composition from NiFe<sub>4</sub>O<sub>4</sub> (near the metal-oxide interface) to Fe<sub>5</sub>O<sub>4</sub>.

This diffusion process is considered to involve an activation energy of about 41.5 kcal, and lower values are interpreted in terms of this diffusion process being enhanced by surface migration as suggested by Bénard. Considering the way in which these activation energies are established, more precise interpretation would be questionable. In the  $800^{\circ}-1000^{\circ}$  range the rate is accelerated, but the slope of the Arrhenius plots would indicate a high activation energy, characteristic of some other

process. The higher activation energy was common with all three alloys and would support the hypothesis which explained the moisture influence in terms of the physical condition of the film.

There is evidence that would lead one to expect that, if one dealt with an oxidation involving a single diffusion process, and further, if the oxide film remained compact and continuous during the oxidation run, then a linear Arrhenius plot would indeed be observed. Obviously such conditions were not achieved in these experiments, but were by Paidassi (19) who obtained linear temperature dependence plots for the oxidation of iron over the range of 700°-1250°C. His micrographs show a uniform, compact, and continuous oxide film, and his kinetics indicate diffusion through an FeO layer. On the other hand if there was no change in reaction mechanism, but there was change in the physical condition of the film, a nonlinear Arrhenius plot would result. Thus the temperature dependence plots of Gulbransen and Andrew (20) on the oxidation of Ni over the 750°-1050°C range yielded a heat of activation of 41,200 cal below 900°C and 68,300 cal above, with the explanation probably lying in cracking and change in the physical condition of the film. Studies on film structure similar to those conducted by Brabers and Birchenall (14) would be very illuminating here.

Several investigators have employed models which utilize the defect structure of the oxide as altered by the moisture in the oxidizing atmosphere (21). Presumably the decomposition of water vapor at these elevated temperatures would supply hydrogen or oxygen to alter the concentration of defects. It would not appear that such models would apply in view of our experimental conditions. The percentage decomposition of  $H_3O$  is low and would alter in a negligible way the total oxidizing potential of the atmosphere.

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# Oxidation of Refractory Metals as a Function of Pressure, Temperature, and Time: Tungsten in Oxygen

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#### ABSTRACT

By regarding the kinetics of oxidation of tungsten as occurring by the consecutive reactions:  $W + O_2 \rightarrow WO_2$ ;  $WO_2 + \frac{1}{2}O_2 \rightarrow WO_{a(s)}$ ;  $WO_{a(s)} \rightarrow \frac{1}{n}(WO_s)_{n(x_2)}$  and by expressing the rate in terms of conventional chemical kinetic quantities, it is shown that the results of three investigations may be correlated in the temperature range 500°-1300°C and pressure range 0.0013-20.8 atm of oxygen. A good approximate form for the rate of attack of metallic tungsten above 700°C is shown to have the form: Rate  $= d(m/A)/dt = 5.89 \times 10^{6} \exp(-12,170/T) P^{1/2} mg_{W}/cm^{2}$  hr, where T is expressed in °K and P in atmospheres of oxygen.

Although there has been much work done on the kinetics of oxidation of tungsten as summarized recently (1), the basic understanding of the mechanism of oxidation has not as yet yielded to analysis. This is due in part to the complexity of the chemistry and in part to the fact that an entirely adequate theory for oxidation of metal oxygen systems has not heretofore been available. It has been fairly well established (2) that tungsten in the presence of oxygen reacts first to form a suboxide, which for present purposes may be assumed to be WO<sub>2</sub>, according to:  $W + O_2 \rightarrow WO_2$ , followed by subsequent reaction to form WO<sub>3</sub>: WO<sub>2</sub> +  $\frac{1}{2}O_2 \rightarrow$  $WO_{s(s)}$ . The WO<sub>3</sub> then sublimes according to:  $WO_3 \rightarrow$ 1/n (WO<sub>3</sub>)<sub>n(yap)</sub>. There are minor changes in the stoichiometry of these oxides with temperature and pressure, but these may be considered incidental to the kinetic problem.

It is the purpose of the present paper to demonstrate the utility of a method of treatment of reacting metal-oxygen systems recently developed (3). The method will (a) correlate the results of the three principal experimental investigations (2, 4-6), (b) introduce the effect of pressure on the rate of oxidation, and (c) present the results in a form having practical utility.

#### **Development** of Rate Equations

It has been shown (3) that all metal-oxygen reactions are first order complex chain reactions whose rate is described by an equation of the form:

$$\text{Rate} = \frac{d \, m_{o_b}/A}{dt} = k_r C_i = k_r \, f(P) \qquad [1]$$

where  $m_{0b}/A$  (g/cm<sup>2</sup>) is the weight change per unit area of a specimen caused by reaction with b atoms of oxygen, k, is the reaction rate constant,  $C_i$  is the concentration of intermediate species controlling the rate of reaction, and f(P) is a complex function \* of pressure relating pressure to the intermediate species concentration.

When the reaction rate is controlled at a phase boundary Eq. [1] can be written:

$$Rate = k_s C_{is}$$
 [2]

where  $C_{i}$  is the concentration of intermediate species at the phase boundary (g/cm<sup>2</sup>) and k, is the specific reaction rate constant (sec<sup>-1</sup>). This has been interpreted (7) as

$$k_s = \frac{kT}{h} \exp \left(\Delta S^{\ddagger}/R\right) \exp \left(-\Delta H^{\ddagger}/RT\right) \quad [3]$$

where k is Boltzmann's constant (ergs/°K), T is absolute temperature (°K), h is Planck's constant (erg-sec),  $\Delta S^{\pm}$  the entropy of activation (cal/g mole °K) and  $\Delta H^{\pm}$  the enthalpy of activation (cal/ g mole).

When the reaction is controlled by diffusion through an oxide phase, the rate equation may be written

$$\frac{d m_{0b}/A}{dt} = \left\{ \frac{D \Delta C \rho_{ox} M_{0b/M e_a 0_b}}{2} \right\}^{1/2} \frac{1}{t^{1/2}} \quad [4]$$

where  $\Delta C = C_{i o-p} - C_{i o-m}$ , which is the concentration difference of diffusing species at the oxide-oxygen and oxide-metal interfaces, respectively, (g/ cm<sup>3</sup>),  $\rho_{ox}$  is the density of the oxide film (g/cm<sup>3</sup>), D is the diffusion coefficient (cm<sup>2</sup>/sec), and  $M_{ob,Me_{0}o_{b}}$  is

weight of oxygen consumed  $(b/2 O_2)$ weight of oxide formed  $(Me_aO_b)$ . (g/g)

The diffusion coefficient may be written in its temperature dependent form:

$$D = D_a \exp\left(\frac{-\Delta H^{\pm_a}}{RT}\right)$$
 [5]

where  $D_a$  is the diffusion constant and  $\Delta H^{\pm}_{a}$  is the enthalpy of activation of a diffusion process.

D<sub>o</sub> may be further interpreted by the reaction rate theory of Evring as (8)

$$D_o = \alpha d^2 q \, rac{kT}{h} \cdot \exp\left(\Delta \, S^+_d/R
ight)$$
 [6]

where  $\alpha$  is a geometrical factor related to the arrangement of sites into which a diffusing species may jump, d is the lattice parameter, q is the number of equivalent diffusion paths and  $\Delta S^{\pm}_{d}$  is the entropy of activation of the diffusion step.

For purposes of further analysis the following assumptions are made: (A) For every chemical product formed an equation may be written for its rate of formation. (B) The rate of formation of the inner oxide (WO2) is diffusion controlled and Eq. [4] applies. (C) The rate of formation of the outer oxide (WO<sub>3</sub>) is phase boundary controlled and is given by Eq. [2]. (D) The rate of volatilization of  $(WO_a)$  is also phase boundary controlled. (E) The rate of consumption of tungsten metal is unaffected by the volatility rate of  $WO_3$ . (F) The functions relating concentration to pressure are of the form of the Langmuir isotherm involving dissociation of oxygen molecules to atoms

$$C_{ii} = C_{ii}^{\circ} \left\{ \frac{\exp\left(\Delta S_{ii}/R\right) \exp\left(-\Delta H_{ii}/RT\right) P^{1/2}}{1 + \exp\left(\Delta S_{ii}/R\right) \exp\left(-\Delta H_{ii}/RT\right) P^{1/2}} \right\}$$
[7]

where  $\Delta S_{is}$  and  $\Delta H_{is}$  are the entropy and enthalpy of adsorption of intermediate species at the phase boundary, and C<sup>o</sup><sub>is</sub> is a conversion factor relating mole fraction of adsorbed species to concentration of adsorbed species (g/cm<sup>2</sup>) and

$$\Delta C = \Delta C^{\circ}_{d} \left\{ \frac{\exp\left(\Delta S_{d}/R\right) \exp\left(-\Delta H_{d}/RT\right) P^{1/2}}{1 + \exp\left(\Delta S_{d}/R\right) \exp\left(-\Delta H_{d}/RT\right) P^{1/2}} \right\}$$
[8]

where  $\Delta S_d$ ,  $\Delta H_d$ , and  $\Delta C^{\circ}_d$  (g/cm<sup>3</sup>) are the corresponding quantities of Eq. [7] pertaining to the appropriate intermediate species in the diffusion process. Tentative evidence for this type of pressure dependency may be inferred from the low pressure work of Speiser and St. Pierre (9).

A great source of confusion, resulting in considerable misinterpretation of kinetic data, has arisen from failure to pay careful attention to the meaning of defined rate equations.

The defining equation is in terms of oxygen consumption, Eq. [1]. However, of greater importance in metal oxygen reactions is the rate of metal consumption, given by

$$-\frac{d(m_{M_e}/A)}{dt} = \frac{1}{M_{0_b/M_{e_a}}} \frac{d(m_{0_b}/A)}{dt} (g/cm^2 \sec) [9]$$

where  $M_{O_b/Me_a}$  is

$$\frac{\text{weight of oxygen consumed } (b/2 O_z)}{\text{weight of metal reacted } (aMe)} (g/g)$$
or
$$\frac{-dX_{Me}}{dt} = \frac{1}{M_{O_b/Me_g \rho_{Me}}} \frac{d(m_{O_b}/A)}{dt} (\text{cm/sec}) [10]$$

where  $X_{Me}$  and  $\rho_{Me}$  are, respectively, the thickness and density of the metal.

Where volatile species are formed during reaction, it is necessary that care be taken that thickness or weight change measurements are properly related to oxygen or metal consumption.

The derivations which follow will be on the basis of oxygen consumption and will be modified to other convenient forms as necessary.

The reaction of tungsten with oxygen has been identified as a consecutive reaction and analyzed by Loriers (10) and Webb, Norton, and Wagner (6).

Using the present formulation, it is found that the rate due to the formation of the first oxide (WO<sub>2</sub>) is given by:

$$\frac{d(m_{o_2}/A)}{dt} = \left\{\frac{D_b \,\Delta C_b \,\rho_b \,M_{o_2/wo_2}}{2}\right\}^{1/2} \frac{1}{t^{1/2}} \\ -\frac{1}{M_{o_3/o_2}} \,k_{s_e} \,C_{i_{s_e}} \quad [11]$$

where  $m_{0_2}$  is weight change due to formation of WO. and subscripts b and c pertain to the quantities governing the formation rate of the oxides WO<sub>2</sub> and WO<sub>3</sub>, respectively.

$$\frac{d(m_{o_2}/A)}{dt}$$
 becomes zero at

$$t_{m} = \frac{D_{b} \Delta C_{b} \rho_{b} (M_{0_{2}/W0_{2}}) (M_{0_{3}/0_{2}})^{2}}{2k^{2}_{s_{o}} C^{2}_{4s_{o}}} \qquad [12]$$

The total amount of WO<sub>2</sub> formed can be found by  $\frac{d(m_{0_2}/A)}{M}$  which has the value:

d.t.

$$(\Delta m_{0_2}/A)_{\max} = \frac{D_b \,\Delta C_b \,\rho_b}{2k_{s_c} \,C_{is_c}} \cdot M_{0_2/W 0_2} \,M_{0_3/0_2} \quad [13]$$

The rate of formation of the second oxide, WO<sub>3</sub>, is given by

$$\frac{d(m_{os}/A)}{dt} = k_{s_o} C_{is_o} \qquad [14]$$

where  $m_{0_3}$  is weight gain due to the formation of WO<sub>3</sub>.

In graphical form Eq. [11] and [14] appear as represented in Fig. 1. The two processes combined are designated as "sum" in the figure and the arrow designates the value of  $t_m$  and  $(\Delta m_{0_2}/A)_{max}$ .

When the volatility rate becomes appreciable, an appropriate term must be subtracted from the sum of Eq. [11] and [14]. This rate may be represented by

$$\frac{-d(m_{\text{wos}}/A)}{dt} = k_{s_v} C_{i_{s_v}}$$
[15]

where  $m_{WO_3}$  is the weight change due to WO<sub>3</sub> volatilization. The subscript v pertains to the quantities governing the weight loss due to the volatilization of WO<sub>3</sub>. As illustrated in Fig. 2, the sum of the three terms takes different forms depending on the magnitude of the volatility rate.

A third type of weight change curve is encountered under the conditions where the molar evaporation rate of WO<sub>3</sub> exceeds the molar consumption rate of metal. Under these conditions an experimental weight change measurement represents the sum of oxygen pickup due to the formation of WO<sub>2</sub> and the







Fig. 2. Experimental weight change due to  $WO_2$  and  $WO_3$  formation and  $WO_3$  volatilization, Eq. [11], [14], and [15].

metal loss due to volatilization of W in the form of  $1/n(WO_s)_n$  as shown in Fig. 3. All three types of curves were obtained by Gulbransen in his extensive study (4, 5).

#### Analysis of Data

Equations [12] and [13] may be solved simultaneously to give the following equations:

$$k_{s_c} C_{u_c} = \frac{(\Delta m o_2/A)_{\max}}{t_m} \cdot M o_{3/o_2} \qquad [16]$$

$$(D_b \Delta C_b \rho_b M_{o_2/Wo_2}) = \frac{(\Delta m_{o_2}/A)^2_{max}}{t_m} \cdot \frac{2}{M_{o_3/o_2}} [17]$$

An overlay of experimental points was made and compared with a master plot of Eq. [11] and [14].



Fig. 3. Experimental weight change due to  $WO_2$  formation and W metal loss, Eq. [11] and [20].

From this, values of  $t_m$  and  $(\Delta mo_2/A)_{max}$  could be obtained. From Eq. [16] and [17], values of k,  $C_i$ , and  $D_b \Delta C_b \rho_b Mo_{2/}wo_2$  could be directly calculated. The logarithm of these values were then plotted vs. 1/T to determine activation energies and  $vs. \log P$  to determine pressure sensitivities. The results are presented in Fig. 4 through 7. From these plots it was determined that Eq. [7] and [8] represented reasonable pressure functions for both the diffusion controlled and phase boundary controlled reactions. Overheating is obtained at higher rates which accounts for the deviations of experimental points from the theoretical curves.

The simplest form of the equations governing the oxidation rate of tungsten is also the most directly practical, namely, by expressing it in terms of metal consumption.



Fig. 4. Arrhenius plot of  $k_{s_o} C_{is_o}$  isobars. Deviations from slope of -  $\Delta H^{\ddagger}/R$  indicate pressure sensitivity.

or



Fig. 5. Plot of  $k_{s_c} C_{is_c}$  isotherms vs. pressure showing pressure dependency at high temperatures and low pressures.



Fig. 6. Arrhenius plot of  $\{D_b \ \Delta C_b \ \rho_b M_{0_2/W \sigma_2}\}^{1/2}$  isobars. Deviations from slope of  $-\Delta H^{\ddagger}/2R$  indicate pressure sensitivity.



Fig. 7. Plot of  $\{D_b \Delta C_b \rho_b M_{0_2/W0_2}\}^{1/2}$  isotherms vs. pressure for data of Gulbransen showing pressure dependency at high temperatures and low pressures.

The rate of metal loss due to the formation of  $WO_2$  is, from Eq. [11] and [9]

$$rac{-d(m_{
m w}/A)}{dt} = rac{1}{M_{
m o_{2/W}}} rac{d(m_{
m o_{2}}/A)}{dt} = rac{1}{M_{
m o_{2/W}}} \left[ \left\{ rac{D_{
m b} \Delta C_{
m b} \ 
ho_{
m b} \ M_{
m o_{2/Wo_{2}}}}{2} 
ight\}^{1/2} rac{1}{t^{1/2}}$$

$$-\frac{1}{M_{o_3/o_2}}k_{s_c}C_{s_c} \left[ (mg/cm^2 hr) \quad [18] \right]$$

$$\frac{-dX_{\rm w}}{dt} = \frac{1}{\rho_{\rm w} \, M_{\rm O_2/w}} \left[ \left\{ \frac{D_b \, \Delta C_b \, \rho_b \, M_{\rm O_2/w_2}}{2} \right\}^{1/2} \frac{1}{t^{1/2}} - \frac{1}{M_{\rm O_3/O_2}} \cdot k_{*e} \, C_{*e_e} \right] \, (\rm cm/hr) \quad [19]$$

where  $\rho_w$  is the density of tungsten (g/cm<sup>3</sup>).

Each equation is to be integrated over the limits 0 to  $t_m$  determined by Eq. [12], as before.

The metal consumption rate due to the formation rate of  $WO_s$  is given by

$$\frac{-d(m_w/A)}{dt} = \frac{1}{M_{o_{3/W}}} \frac{d(m_{o_3}/A)}{dt}$$
$$= \frac{1}{M_{o_{3/W}}} k_{s_c} C_{s_c} (mg/cm^2 hr) \quad [20]$$

or

$$\frac{-d X_w}{dt} = \frac{1}{\rho_w M_{o_{3/w}}} k_{s_c} C_{is_c} (\text{cm/hr}) \qquad [21]$$

Since the metal loss due to the formation of  $WO_z$  reaches a limiting value, Eq. [20] and [21] may be used as a satisfactory approximation to describe the oxidation rate.

The values obtained by the above analysis for the appropriate quantities are presented in Table I. When these values are substituted into the appropriate equations, the experimental curves of three investigations (2, 5, 6) are adequately reproduced in the temperature range  $500^{\circ}-1300^{\circ}C$  and pressure range 0.0013-20.8 atm.

For purposes of practical application, the rate of consumption of tungsten above 700°C may be expressed by the equations

$$\frac{-d(m_w/A)}{dt} = 5.89 \times 10^{6}$$

$$\exp(-12,170/T) P^{1/2} (mg/cm^2 hr) [22]$$
and

 $\frac{-d X_{\rm w}}{dt} = 3.05 \times 10^{\circ} \exp(-12,170/{\rm T}) \ {\rm P}^{1/2} \ ({\rm cm/hr})$ [23]

where T is to be expressed in  $^{\circ}K$  and P in atmospheres of oxygen.

#### Discussion

Two recent investigations have reported a decrease in rate with temperature above 2000°C (11, 12). Referring to Eq. [12] and [13] and noting that the quantity  $D_b \Delta C_b \rho_b M_{0_2/WO_2}$  increases more rapidly than  $k_{*c} C_{*c}$  with increasing temperature, it is seen that both  $t_m$  and  $(\Delta m_{0_2}/A)_{max}$ , or  $(\Delta X_{0_2})_{max}$  where  $X_{0_2}$  is the thickness increase due to WO<sub>2</sub> formation, will increase at higher temperatures and also at lower pressures. The resulting weight or thickness change measurements will then take the form of the curves of Fig. 3. Since the absolute weight change and zero time are not known experimentally, an arbitrary straight line through a series of points will give an

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Phase boundary process

$$(3.6 \times 10^{\circ}) \cdot \frac{kT}{h} \cdot \exp(\Delta S^{\ddagger}/R) C^{\circ}_{iic}$$
  
= 7 × 10<sup>10</sup> (mg/cm<sup>2</sup> hr)  
$$\Delta H^{\ddagger} = 45.9 (\text{kcal/mole})$$
  
exp ( $\Delta S_{ii}/R$ ) = 2.2 × 10<sup>-5</sup>  
 $\Delta H_{ii} = -21.7 (\text{kcal/mole})$ 

apparent rate which will always be lower than the rate of metal loss, and in general decrease with increasing temperature.

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Diffusion process

$$= 7.15 \times 10^{15} (mg^2/cm^4 hr)$$

 $\Delta H_a^{\dagger} = 68 (\text{kcal/mole})$   $\exp(\Delta S_d/R) = 1.133 \times 10^{-6}$  $\Delta H_a = -27.6 (\text{kcal/mole})$ 

 $(3.6 \times 10^9) D_b \rho_b M_{O_2/WO_2} \Delta C_b^{\circ}$ 

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# The Effect of Organic Compounds on the Codeposition of Hydrogen with Nickel

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#### ABSTRACT

A coulometric method of analyzing for hydrogen was used to study the effect of a group of organic additives on the amount of hydrogen codeposited with nickel from a Watts-type bath. This technique indicated the presence of one form of hydrogen at the electrodes, and this was indicated to be hydrogen codeposited in the nickel. There was marked correlation between the hydrogen content of the nickel deposits and the current efficiency for the deposition of hydrogen. It was also observed that, in general, the brightest deposits occurred at the minimum in the hydrogen content curves.

Thon (1) studied the codeposition of hydrogen and nickel, but did not study the effect of additives. Yeager and co-workers (2) have also carried out this type of study. Brenner and co-workers (3) studied the effect of additives on this process, but found no definite relationship; however, the technique used in their study analyzed for both free and combined hydrogen in the deposit. The purpose of the work reported in this paper was to reinvestigate the effect of additives on the amount of hydrogen codeposited with nickel using a technique which analyzed only for the free hydrogen to see if there was a systematic variation.

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At the same time, a study was made of the effect of the organic compounds on the current efficiency for nickel deposition.

#### **Experimental Materials and Methods**

Nickel wire electrodes were prepared by sealing 14 gauge nickel wire in glass tubing with 1.2-1.5 cm lengths exposed. The wire electrodes were mechanically polished and plated at a known current density for a definite time, usually 6.96 ma/cm<sup>2</sup> for 12 min. They were plated in a Watts-type plating bath consisting of NiSO<sub>4</sub> · 6H<sub>2</sub>O, 240 g/l; NiCl<sub>2</sub> · 6H<sub>2</sub>O, 45 g/l; and H<sub>2</sub>BO<sub>5</sub>, 30 g/l. After dissolving the components, nickel carbonate was added to raise the pH.

The solution was filtered and the pH lowered to 4.0 by adding dilute hydrochloric or sulfuric acid. Measured amounts of a solution of the organic additive in the Watts bath were added to the plating bath with a graduated pipette.

Hudrogen content studies.—After plating, the electrode was rinsed with distilled water, and the hydrogen was analyzed coulometrically by the procedure used by Franklin and Cooke (4). The electrode was oxidized polarographically in a cell filled with hydrogen-saturated 2N sodium hydroxide. The reference cell was mercury, mercuric oxide, 2N sodium hydroxide. A Sargent Model XXI polarograph was used to record the current-voltage curves. The area under the curves was used as a measure of the amount of hydrogen in the deposit. Most of the data recorded are differences between results obtained with and results obtained without additives present in the plating bath. Each of the hydrogen analyses was made at least in triplicate, and each complete curve reported was run at least twice. The ethanenitrile study (Fig. 3) was repeated by three different workers on a number of electrodes over a period of two years. Even though the total amount of hydrogen codeposited varied from one experiment to another, the differences using the same basic pretreatment method were the same within  $\pm 5\%$ . All connections were standard taper or ball and socket ground glass joints.

The appearance of the deposit was also noted as the additive concentration was varied.

Current efficiency studies.-The apparatus used to determine current efficiencies is shown in Fig. 1. The coil cathode of 14 gauge nickel wire was attached to the iron shaft of the mercury sealed rotating electrode designed after that of Kolthoff and Lingane (5). The length of wire extending into the solution was 28 cm. The iron shaft of the stirrer was coated with ceresin wax. The stirring motor was rotated at 600 rpm, and the anode was made of nickel wire.

In a typical run, 35 ml of the plating solution were placed in the cathode compartment, and enough plating solution was placed in the anode compartment to equalize the liquid levels. The entire apparatus was immersed in a water bath maintained at  $25^{\circ} \pm 0.1^{\circ}$ C. After making preliminary runs until the amount of hydrogen evolved in a run became constant, measured amounts of a solution of the organic additive in the plating solution were added to the cathode compartment. After each addition, the electrode was plated for 12 min at a current density of 6.96 ma/cm<sup>2</sup>. The amount of hydrogen evolved was indicated by the displacement of a drop of butyl phthalate along the capillary tube, the current was measured with a previously calibrated ammeter, and the time was measured with a timer. The current efficiency for nickel deposition or for hydrogen ion discharge was obtained from the number of coulombs passed and the volume of hydrogen evolved. All curves are the average of at least two runs. The same pretreatment technique was used in all experiments. The volumes of hydrogen were reproducible within  $\pm 3\%$ .

In all experiments the inorganic chemicals were reagent grade, the water was triply distilled, and the organic chemicals were the purest grades available commercially. (In all cases except one this was either Spectrograde or Eastman White Label. The disodium 2,7-naphthalene disulfonate was technical grade. At a later date this chemical was purified somewhat, but the purification did not alter the general shape of the curve.)

#### Data and Results

Effect of organic compounds on the hydrogen content of electrodeposited nickel.-Along with this study of Watts nickel an investigation was made of the polarographic oxidation of palladium, black nickel, and iron electrodes. With all of these metals three peaks were observed that could be interpreted as being due to the oxidation of three forms of hydrogen. In the cases of palladium and platinum black all three forms could be observed by bubbling hydrogen over the electrode. However, it was necessary to generate hydrogen electrolytically or codeposit hydrogen with the metal in order to observe all three forms with black nickel and iron. These peaks were not observed unless hydrogen was generated, indicating that they were caused by the oxidation of hydrogen at the electrode. Hydrogen



Fig. 1. Apparatus for measuring the hydrogen evolved during the plating process.



Fig. 2. Current-voltage curve for the oxidation of the hydrogen codeposited with Watts nickel.

was placed on the electrodes in one bath and then the polarograms were run in a hydrogen-free sodium hydroxide solution. This would make it unlikely that solution hydrogen was being oxidized.

Figure 2 shows a typical current voltage curve for the oxidation of the hydrogen present at a nickel electrode which has been plated in a Watts bath.2 The peak is the middle peak observed in the oxidation of hydrogen on black nickel. Since hydrogen was not appreciably absorbed from solution into nickel it was not possible to make a study similar to that made of platinum (4). However, the hydrogen oxidized to cause this peak was concluded to be hydrogen in the interior of the nickel deposit. This was shown by dipping the freshly plated electrode in 1N potassium permanganate in 1N sulfuric acid. There was no change in the area under the oxidation curve. With black nickel the two other peaks decreased markedly. In addition when the electrode was plated, mechanically polished, then replated before oxidizing, the area under the curve

<sup>2</sup> The areas recorded in the figures correspond to the shaded area in Fig. 2. This is not the total hydrogen content since the residual current lies lower than the level portion of the curve. However, it was found that the residual was constant for each electrode; therefore, the total amount of hydrogen would be different, but the shape of the curve would be the same.





Fig. 4. Amount of codeposited hydrogen as a function of nitrile concentration. ○—○— Pentanenitrile; ●—● butanenitrile; A,A', dark streaked; B,B', dull; C,C', semi-bright; D,D', bright.

was higher than the area obtained when the electrode was plated only one time. Both of these experiments indicate that the hydrogen being oxidized is in the interior of the nickel and not on the surface.

Figures 3 and 4 show the variation of the hydrogen content for ethanenitrile, propanenitrile, butanenitrile, and pentanenitrile. The visual appearance of the deposits is also indicated in these figures. Curves similar in shape were obtained for hexanenitrile, 3 hydroxypropanenitrile, butanedinitrile, m-aminophenol, 1 ethylquinolium iodide, and disodium 2,7 naphthalenedisulfonate. As will be noted in the curves there was considerable variation in the initial point. This was probably caused by differences in pretreatment of the electrode. Using the same pretreatment, one obtains results that agree within  $\pm 5\%$ . For all of these compounds there was the same marked correlation between the hydrogen content and the appearance of the deposits that is seen in Fig. 3 and 4. The best deposits were always obtained at the minimum in the curve. However, in the cases of m-aminophenol and butanedinitrile the minimum hydrogen content did not correspond to the minimum in the curve as seen, for example, in Fig. 5. Of the compounds investigated only thiourea (Fig. 6) did not give a curve similar to those above. But, even here it can be seen that there



Fig. 5. Amount of codeposited hydrogen as a function of butanedinitrile concentration; B, dull; C, semi-bright.



Fig. 6. Amount of codeposited hydrogen as a function of thiourea concentration; B, dull; C, semi-bright.



Fig. 7. Effect of stirring on the hydrogen content curves obtained with disodium 2,7-naphthalenedisulfonate; (a) stationary electrode, —\_\_\_\_\_\_\_; (b) rotating electrode, \_\_\_\_\_\_\_, \_\_\_\_; B,B', dull; D,D', bright.

is the same correlation between the appearance of the plate and the hydrogen content.

Effect of pressure on hydrogen content.—In a further investigation of the correlation between the appearance of the deposit and the amount of co-deposited hydrogen, a study was made of the effect of pressure on the codeposition of hydrogen and nickel. It was noted that there was a decrease in hydrogen content with a decrease in pressure and that the plates became smoother and more even, but not bright. In addition, it required only a concentration of  $3.2 \times 10^{-3}$ M propanenitrile to obtain the brightest deposits at 70 mm pressure compared to  $4.5 \times 10^{-3}$ M propanenitrile at atmospheric pressure.

Effect of stirring on hydrogen content curves.— Since some of the experiments were run in stirred solutions and some in nonstirred solutions, a study was made of the effect of stirring on the hydrogen content of the deposits. In the case of the nitriles, stirring had no effect on the hydrogen content curves. Figure 7 shows the effect of stirring on the hydrogen content curves for disodium 2,7 naphthalenedisulfonate. As can be seen, stirring causes a



Fig. 8. Comparison of results for propanenitrile; (a) hydrogen content, \_\_\_\_\_\_, \_\_\_\_, (b) current efficiency, •\_\_\_\_\_, •\_\_\_\_, •\_\_\_\_, •\_\_\_.



Fig. 9. Comparison of results for pentanenitrile; (a) hydrogen content, \_\_\_\_\_; (b) current efficiency,

shift in the curve, but does not change the general shape of the curve.

Effect of organic compounds on the current efficiency of hydrogen deposition.—The observed variation of the hydrogen content could be due to variations in the current efficiency of the deposition process or it could be due to variations in the amount of hydrogen adsorbed at the surface of the electrode. In order to distinguish between these two possibilities the current efficiency in the Watts bath for the deposition of hydrogen was measured as a function of the concentration of the organic additive.

Figures 8, 9, and 10 show a definite correlation between the current efficiency for the deposition of hydrogen and of hydrogen content curves for propanenitrile, pentanenitrile, and disodium 2,7 napthalene disulfonate, indicating that the cause of the variation in hydrogen content is a change in the current efficiency for the deposition process.

In summary, it has been shown that there is a marked correlation between the amount of hydrogen codeposited with nickel from a Watts bath containing various organic additives, the current efficiency for hydrogen deposition, and the appear-



Fig. 10. Comparison of results for disodium 2,7-naphthalenedisulfonate; (a) hydrogen content, \_\_\_\_\_\_\_\_, \_\_\_\_\_, (b) current efficiency, ●\_\_\_\_\_\_\_, ●\_\_\_\_\_, \_\_\_\_,

ance of the deposit. All of these quantities vary in the same manner as a function of the concentration of the additive.

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# Simultaneous Cataphoretic and Electrolytic Deposition of Nickel for Cathode Bases of Reliable Electron Tubes

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#### ABSTRACT

The combination of electrolysis and cataphoretic deposition of metal particles was used in the development of a porous nickel matrix layer for electron tube extended interface cathodes. The codeposition phenomenon was studied and the influence of the various parameters (time, temperature, concentration) on the deposited layer structure was shown. The technique may be used for preparing porous layers from metal mixtures and alloys.

The extended interface (matrix) cathode used in high voltage or high power electron tubes was described by Fisk *et al.* (1) and by Field (2). This cathode consists of a nickel base metal, which is coated by a porous nickel layer. This nickel layer is sintered to the base and thereafter the voids are filled with the standard emissive (BaSrCa)CO<sub>a</sub> coating material. The main advantages of the use of a porous nickel matrix layer as the base for oxide coated cathodes are: good heat and electrical conductivity, increase in the adherence of the emissive coating to the base metal, decrease in the interface resistance, and finally minimization of the detrimental effect of the high voltage sparking.

On considering the working mechanism of such a nickel matrix cathode, it is evident that the porous nickel matrix must have the following properties: (A) Adherence: A very good adherence to the base metal after sintering, to avoid peeling off of the matrix. (B) Pore size: The size of the voids must be several times larger than those of the carbonate grains. This means that the pores should be filled easily by the emissive materials. It is recommended, assuming a carbonate size of  $2-5\mu$ , to have a pore size of  $25-50\mu$ . (C) Reproducibility: Height, density, surface properties of the porous layer, and the dimensions and shape of the voids must be reproducible from sample to sample and lot to lot in mass production.

The most important part of this type of electron emitter is the uniformly porous nickel matrix layer. This layer can be prepared as described, utilizing painting (3, 4), spraying (4, 5), or press technique (3). The disadvantages of these methods are: it is difficult to get uniformly porous and reproducible structures, and the layer obtained might readily peel.

In order to develop a method to produce reproducible and reliable porous nickel matrix layers suitable for electron tube cathode purposes, we made experiments with a new process: simultaneous electrolytic and cataphoretic deposition. The two types of deposition can be performed from the same solution simultaneously, resulting in a porous nickel matrix deposit. In the following method, the influence of the various parameters on the layer structure and the mechanism of deposition are described.

#### **Experimental Method**

The experimental arrangement is shown in Fig. 1. The glass beaker (B) contained the plating solution with the added nickel metal powder. The



Fig. 1. Schematic drawing of the experimental setup

plating solution was a "hard nickel plating bath" containing 5% NiSO<sub>4</sub> and 2.3% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in deionized water. Carbonyl nickel powder of 325 mesh was mixed into the solution, and the mixture was agitated thoroughly by a Teflon stirrer ( $M_1$ ). The sample to be coated (C) was mounted on a holder and was rotated by a slow (10 rpm) motor ( $M_2$ ), and except for the round flat (0.5 cm<sup>3</sup>) target surface, it was protected by a Teflon shield (T). The sample was attached to the negative side of a d-c power supply, while the positive side was attached to a flat nickel anode (A) spaced approximately 8-15 mm from the sample. The temperature of the slurry was maintained by a hot-plate (H) and was controlled in the solution.

The nickel samples to be coated were cleaned carefully before using. The samples were degreased in ether and rinsed in acetone and boiling water. Finally they were rinsed again in acetone and dried in air. After mounting the samples on the holder, the sample was immersed in the slurry, and a voltage of 25v d.c. was switched on. After the time required for obtaining the proper coating thickness had passed, the voltage was switched off, and the sample was removed from the solution and from its holder. It was rinsed in distilled water, then in acetone, and after drying it was examined.

#### Appearance and Characteristics Data of a Nickel Matrix

The general appearance of a nickel matrix cathode suitable for electron tube application is shown in a schematic drawing, Fig. 2. The drawing shows a cross section of the porous layer. The characteristic data of such a matrix can be defined by the height of the porous layer and by its roughness. The porous nickel layer was scratched with a pin across the center of the coated surface (before sintering). The height of the matrix is defined as the depth of this scratched groove from the bottom (base metal) to the top of the nickel peaks (see Fig. 2A). The roughness of the coating denotes the distance between the peaks and valleys of the matrix (see Fig. 2B). The height and roughness measurements were made with a Zeiss light section



Fig. 2. Schematic drawing of the cross section of a deposited layer

microscope. Another characteristic datum of the porous layer is the weight of the deposited nickel. The apparent density of the layer can be calculated from the above data and also the ratio of height/ roughness. The ratio of height/roughness is most characteristic on the structure of the matrix layer, and it is affected by the different parameters as described below.

#### Influence of Several Parameters on the Matrix Surface Structure

The characteristic data of a porous matrix, height, roughness, height/roughness ratio, depend on the following parameters: nickel powder concentration, temperature of the plating solution, coating time. Experiments were made on the influence of these parameters on the structure of a porous matrix layer. The voltage was kept constant at 25v.

Effect of the nickel powder concentration.—The effect of the nickel powder concentration of the solution on the porous layer structure is shown in Fig. 3. The data were taken at  $70^{\circ}$ C bath temperature and with 12 sec coating time. Two conclusions can be drawn from the experiment: (a) Height and roughness values increase with increasing amount of nickel powder and finally they reach a saturation; and (b) the ratio of height/roughness decreases considerably with increasing nickel powder concentration. The roughness increases much faster at higher nickel concentration than the height, which





Fig. 3. Effect of the nickel powder concentration on the layer structure.

Fig. 4. Effect of the temperature on the layer structure



Fig. 5. Effect of the plating time on the layer structure (30 g/1000 ml nickel powder concentration in the solution).

means that the structure of the porous matrix layer changed considerably at higher nickel powder concentration.

Effect of bath temperature.—Figure 4 shows the effect of temperature on the structure of a matrix applying 30 g/1000 ml nickel powder concentration and 12 sec coating time. As can be seen (A) the height and roughness values increase with increasing temperature and tend to reach saturation above 75°C; (B) the ratio of height/roughness is not much affected by the temperature and it decreases only very slightly with increasing temperature.

Effect of coating time.—Figure 5 shows the effect of the coating time on the characteristic data of the matrix at 30 g/1000 ml nickel concentration and 70°C bath temperature. The results show that: (a) the height and roughness data increase with increasing coating time; (b) the ratio of height/ roughness remains practically constant, *e.g.*, the structure of the layer does not change by increasing the coating time.

#### Simultaneous Electrolytic and Cataphoretic Deposition

The preceding experiments show that the structure of the porous layer is affected considerably only by the change in the nickel powder concentration in the plating solution. It is evident that a combined deposition process takes place: an electrolytic deposition process of nickel on the cathode from the plating solution, and simultaneously a cataphoretic deposition of the nickel particles from the slurry. The nickel quantity deposited purely by electrolysis, having no nickel particles in the solution, was measured, as was also the deposition from the combined process, having 30 g/1000 ml nickel powder concentration in the slurry. We made experiments varying the coating time but keeping the temperature constant at 75°C (Fig. 6). The addition of the nickel powder to the solution causes a considerable increase in the deposited amount indicating that the cataphoretic process also takes place. The deviation from the pure electroplating caused by the addition of nickel powder is indicated also in the figure denoted as  $\Delta$ .



Fig. 6. Effect of the plating time on the deposited nickel quantity

The current density during our measurements was approximately 4 amp/cm<sup>2</sup>; it remained the same when nickel powder was added. There was a slight but definite trend of current increase over the plating period if nickel powder was present, which is normal for cataphoretic depositions. The current, however, remained constant during the plating experiments having no nickel powder in the solution.

From the above experiments we can conclude that by adding nickel powder to a regular nickel plating solution a combined electrolysis-cataphoresis process takes place. The cataphoretically deposited nickel powder is incorporated in the electrolytically deposited layer forming a very rough and highly porous nickel layer which is suitable for the extended interface (matrix) cathode purposes. This procedure can be used for deposition of a rough layer of any metal mixtures.

#### **Deposition of Metal Mixtures**

In certain types of electron tubes the emitter contains known amounts of additives in the nickel. This is necessary also for certain types of matrix cathodes. The technique described above is also useful in producing porous nickel matrixes with known amount of additives as magnesium, titanium, tungsten, aluminum, etc.

Metal powder mixtures.—We made experiments on depositing a mixture of nickel and titanium powder. The coating procedure described above was followed, except that a mixture of nickel and titanium (0.5%) powder was used. The resulting layer had the same structure as one without the titanium additive.

Chemical analyses were made on the original nickel and titanium metal powder mixture; the deposited coating was also analyzed. The original metal powder mixture contained 0.5% titanium, and the deposited porous coating contained only 0.26% titanium. These results were reproducible and indicate that metal particles different from nickel also can be deposited this way cataphoret-

ically. The chemical determination of titanium besides excess amount of nickel was performed by a modification of the colorimetric method described in Snell's book (6).

Nickel alloys.—Nickel alloy powder containing 3.6% tungsten was prepared. This powder was used in our experiments. The original powder and also the deposited layer were chemically analyzed. There was 3.5% tungsten in the original, while the tungsten content of the deposited layer was found to be 2.5%. The analysis of the tungsten content of the nickel was performed colorimetrically as described in Snell's book (6).

#### Sintering

The appearance of the resulting matrix layer, after deposition, is black, and it becomes metallically bright after sintering. The sintering was made in wet hydrogen at  $1000^{\circ}$ C for 10 min. The adherence of the sintered layer is excellent. Its removal from the base nickel after sintering is not possible.

#### Reproducibility

The reproducibility of the method (height, roughness values of the matrix layer) depends on how well the different parameters are kept constant during the preparation. With the simple equipment shown in Fig. 1 the values may be kept within  $\pm 4\%$  deviation from the mean. By introducing a more advanced setup, this reproducibility can be improved greatly.

Experiments in Electron Tubes

Spraying.—The voids of the porous matrix body are filled with the standard emissive spray material by a "wet" spraying. The void structure of the codeposited layer is such that no special solution or technique is required to fill the pores with the emissive material.

Electron tubes.—These were prepared utilizing this co-precipitated nickel matrix base cathode procedure. The pumping and processing of tubes with this type of cathode is similar to the standard sprayed oxide coated cathodes. Life and high voltage stability tests of electron tubes in which this type of matrix cathode was incorporated (under the trade name "Phormat cathodes") indicated high reliability and several thousand hour life. These experiments were made (7) in ML-7698 and ML-7815 tubes, tested in a grid-modulated amplifier circuit with a plate voltage of 3000v d.c. In the ML-7815 tube type in a hard tube modulator circuit, the Phormat cathode tubes withstood a field strength of 135 kv/ cm. At this field strength standard sprayed cathodes were almost completely destroyed, while the Phormat type cathodes showed only a few arc marks.

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# Electron-Microscopic Observations of the Structure of Electroplated Nickel

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#### ABSTRACT

Nickel electrodeposits, of various thicknesses, were prepared from Watts' baths containing several addition agents to study the development of the surface structure. By electron-microscopic examinations of replicas, thin films, and electrolytically thinned bulk metal the reasons for the formation of several structural features, previously observed, were found. Selected-area diffraction was found to be the best method of measuring the grain size of the electrodeposits studied. Markings believed to be sites of lattice-included foreign substances were observed.

An earlier paper (1) dealt with the use of electron microscopy in the elucidation of certain structural phenomena observed in nickel electrodeposits from Watts' baths containing a variety of addition agents. The work described below is a continuation of this study. The purposes of the present work are to investigate the causes for the formation of the various structural features, the reasons for the fiber axes observed under certain plating conditions, and the location of the foreign substances known to exist in plated nickel. In order to accomplish these objectives, the growth of different structures was observed with electron microscopy using replicas as well as thin metal films.

#### **Experimental Procedure**

To study the effect of addition agents on the growth of electrodeposited nickel as independently



Fig. 1. Negative parlodion replicas of surface structures of nickel from plain Watts' bath plated for (a) 20 sec, (b) 40 sec, (c) 1 min 20 sec, (d) 2 min 40 sec, (e) 5 min 20 sec, (f) 10 min 40 sec.

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#### Table I. Plating conditions and addition agents

Bath compositions: 400 g/l NiSO<sub>4</sub>  $\times$  6H<sub>2</sub>O, 45 g/l  $NiCl_2 \times 6H_2O$ , 45 g/l  $H_3BO_3$ . Plating conditions: pH: 4.0; temperature: 50°C  $\pm$  2°C; current density: 5 amp/dm<sup>2</sup>. Addition agents in baths where nickel was plated for 5 sec to 42 min, 40 sec.

> 1. None

- 2. 0.03 g/l Coumarin
- 3. 0.05 g/l Coumarin
- 4. 0.1 g/l Coumarin
- 0.15 g/l Coumarin 5
- 6. 0.02 g/l Thiourea 7.
- 0.07 g/l Thiourea
- 8. 0.2 g/l Thiourea 9. 0.3 g/l Thiourea
- 10. 0.25 g/l Aniline
- 11.
- 0.6 g/l 1-5 Naphthalene disulfonic acid + 0.2 g/l chloral hydrate

as possible of the substrate, special copper basis metal had to be prepared. This was done by vapor depositing copper on specular nickel or polished glass and then electroforming a piece of sufficient thickness to handle. After stripping, the copper surface which faced the nickel or the glass was specular and consisted of extremely fine, randomly oriented grains. Nickel was deposited on the specular copper from Watts' baths; the composition and plating conditions are listed in Table I. To study the growth, the plating time was increased in a geometric series from 5 sec to 42 min, 40 sec. The area deposited was 0.25 dm<sup>2</sup>, while that of the anode was 0.4 dm<sup>2</sup>. Otherwise the experimental apparatus was as previously (1) described. Thin nickel films were plated over thin copper on half the originally deposited area as in the earlier work.

The surfaces of the deposits were examined electron microscopically with negative parlodion replicas as before. When greater resolution was required, carbon replicas were made by first shadowing the specimen with palladium and then evaporating carbon. The replicas were removed by scoring the specimen to produce squares to fit the electronmicroscope holder and then making the specimen anodic in an aqueous solution of 25% by volume  $H_2SO_4$  with a stainless steel cathode. The current was slowly increased until the replica floated off. Thin films were also prepared by electropolishing. First the surface of the nickel was coated with an adherent plastic film. Then the copper basis metal was dissolved. The electropolishing method used was that described by Kelly and Nutting (2). Because of the plastic coating, the thin film came from a region near the surface.

#### **Results and Discussion**

The surface structures of the deposits from a plain Watts' bath plated for various times are shown in Fig. 1. Figure 1a shows that after 20 sec of plating a few grains grow faster than the others. There is some evidence from selected-area-diffraction studies of such grains in thin films that they have a (100) plane parallel to the surface. With increasing deposition time, these preferentially oriented grains grow over other grains and some new ones form



Fig. 2. Thin film of nickel deposit from plain Watts' bath



Fig. 3. Negative parlodion replica of 40µ-thick deposit from bath containing 0.03 g/l coumarin.

and start to develop until they occupy almost the entire surface. The growth layers become discernible at an early stage in the deposition and tend to become coarser probably by a bunching mechanism. The layers are not parallel, but inclined to the surface frequently resulting in a pyramid structure. In the thin nickel film, shown in Fig. 2, the growth steps and their orientations can be readily seen. An area such as that marked 'A' has a (100) direction perpendicular to the surface and a single-crystal pattern as determined by selected-area diffraction. It is thus possible to measure the grain size of the film by this method. Similar measurements using electrolytically thinned bulk material showed that the film is representative of the surface of the electrodeposit on which it was plated.

Some addition agents in Watts' baths do not change the fiber axis or decrease the grain size. An example of such a material is coumarin. Figures 3-5 show the effect of increasing coumarin concentrations in the bath on the structure of samples plated for 42 min 40 sec and which were about  $40\mu$  thick. Figure 3 represents the surface of a deposit from a solution containing 0.03 g/l coumarin. The difference between this deposit and one from a plain Watts' bath is that the height and distance between successive growth layers has decreased resulting in a flatter surface. The deposit from a bath with 0.05 g/l coumarin shown in Fig. 4 has more platelets growing parallel to each other, resulting in still larger areas which are flat. The degree of preferred

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Fig. 4. Negative parlodion replica of  $40\mu$ -thick deposit from bath containing 0.05 g/l coumarin.



Fig. 5. Negative parlodion replica of  $40\mu$ -thick deposit from bath containing 0.15 g/l coumarin.

orientation as determined by x-ray diffraction in the way previously (1) described did not change with the concentration of coumarin in the plating bath. The crevices between growth in different directions also have become shallower. It is also noticed that growth occurs simultaneously along two intersecting planes, probably of the same family in the areas marked 'C'. With a concentration of 0.15 g/l coumarin in the plating bath the deposit was quite bright. The reason for this is evident in Fig. 5 which shows very large areas of parallelgrowing platelets with a few, relatively shallow crevices. It can thus be seen that one way of getting brighter nickel deposits is to cause growth to proceed along the same directions and to decrease the step height. The same features as were observed in the examination of the replicas were seen in thin films. Selected-area diffraction again showed that almost all grains large enough to give single-crystal patterns had a [100] direction perpendicular to the surface.

Almost specular deposits are obtained in a bath containing 0.6 g/l naphthalene disulfonic acid and 0.2 g/l chloral hydrate because the platelets are fine and only very few crevices or ridges form. As the development of the structure of deposits from such a bath with increasing time is followed, there is practically no coarsening of the platelet size with deposit thickness. The crevices which are present



Fig. 6. Negative parlodion replica of  $40\mu$ -thick deposit from bath containing 0.02 g/l thiourea.



Fig. 7. Negative carbon replica of  $40\mu$ -thick deposit from bath containing 0.07 g/l thiourea.

are chiefly due to stacking irregularities of the growth layers. In thin films from these samples, where such irregularities caused the stacking of the platelets to be somewhat coarser than average, the edges of the steps could be seen and were found to be along [100] directions.

An interesting feature observed in many structures is the formation of colonies, *i.e.*, a series of grains surrounded by a relatively deep crevice, which often resembles a grain boundary. Samples from baths containing thiourea and aniline exhibited this structural feature. With a concentration of 0.02 g/l thiourea very large colonies formed as seen in Fig. 6. With increasing thiourea concentrations, the colonies become smaller as do the growth steps. Figure 7 is a photograph of the surface of a deposit from a bath containing 0.07 g/l thiourea. Deposits from a bath containing 0.3 g/l thiourea have no crevices deeper than  $0.4\mu$  and are bright.

Examination of the surface structures at various stages in the growth of a deposit from a bath containing 0.07 g/l thiourea showed that they begin as very fine grains which tend to form groups with crevices between them. With increasing thickness, the crevices become deeper, but are not yet continuous as seen in Fig. 8. The actual grain size of the samples, even the one from the bath with 0.02 g/lthiourea, is quite small. This can be seen in Fig. 9 which is a transmission electron micrograph of a





Fig. 8. Negative carbon replica of  $1\mu$ -thick deposit from bath containing 0.07 g/l thiourea.



Fig. 9. Transmission micrograph of electrolytically thinned deposit from bath containing 0.02 g/l thiourea.

40µ-thick deposit from this bath. The sample was thinned by electropolishing.

The colony size in samples from baths containing other addition agents can be quite small as shown in Fig. 10, an electron micrograph of a replica from a deposit plated for 5 min, 20 sec in bath containing 0.25 g/l aniline. The extremely fine grain size of this sample can be seen from Fig. 11, a photograph of the corresponding thin film. Also with a selected-area-diffraction aperture of  $\mu$  square, the pattern consisted of complete rings. This, plus the presence of all diffraction rings in what appeared to be normal intensities also indicates random orientation, a fact which the very irregularly oriented growth layers corroborates.

The location of codeposited material in electrolytically thinned films of copper deposits has recently been observed by Steinemann and Hintemann (3). Similar structural features were observed in nickel films. In Fig. 12 which represents a thin film from a  $2\mu$ -thick deposit from a bath containing 0.10 g/l coumarin, a large number of light markings are seen. These tend to be aligned along definite crystallographic directions. In a fully bright deposit from a proprietory bath shown in Fig. 13 they are more randomly distributed. To determine if these are the sites of codeposited foreign materials, the findings of Beacom and Riley (4) that foreign substances are preferentially codeposited at



Fig. 10. Negative parlodion replica from 5µ-thick deposit from bath containing 0.25 g/l aniline.



Fig. 11. Thin film of surface shown in Fig. 10



Fig. 12. Thin film showing markings in sample from bath containing 0.10 g/l coumarin.

protrusions in high-levelling baths, were utilized. Copper basis metal was prepared by vapor depositing on bright nickel having fine buffing scratches. The copper, copying the surface, therefore had tiny ridges. A photograph of the thin film plated on this surface and then stripped is shown in Fig. 14. A concentration of the light markings can be seen along the ridge. The plating bath, No. 11 in Table I was of the levelling type because the ridges could no longer be seen in a deposit  $0.5\mu$  thick. There is some evidence that the light markings represent sites where material has evaporated, as they tend

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Fig. 13. Thin film showing markings in bright nickel deposit



Fig. 14. Thin film showing markings lined up along ridges

to develop as a result of exposure to the electron beam. It is possible that some of the markings are due to electron bombardment. Such markings, however, tend to be randomly distributed and not lined up along certain directions. A few markings may be dislocations. However, in thin films, dislocations tend to extend from the top to the bottom surfaces. Most of the markings shown in the previous figures appear to be in a plane parallel to the surface. None of the markings were observed to move under the electron beam; dislocations often do. In a photograph taken as soon as an area is exposed to the electron beam there are dark markings and black areas lined up along the ridge.

The reasons for the formation of crevices, which have previously (1) been shown to be responsible for haziness in very fine-grained deposits and, depending on their size, can be a cause of dullness in general, have not yet been determined. On the basis of this study it is possible to make some suggestions. As previously indicated, irregularities in the height or spacing of the growth steps can cause crevices when the steps are inclined to the surface. A change in the growth direction of the platelet can result in a ridge or a valley. The crevices surrounding colonies may be caused, at least in part, by surface tension as suggested by the angles at their intersections. No crystallographic reasons have been found for their existence. The same diffraction patterns are observed on either side or on a crevice. Stresses may also cause regions to separate. There is a

marked similarity between the dark areas seen on a ridge and crevices in fine-grained deposits which are hazy. This suggests that there may be some local adsorption of foreign material which hinders deposition and thereby causes a crevice. It is noteworthy that Watson and Edwards (5) observed negative levelling at the same concentration of thiourea where the deep crevices were formed. It is quite possible that crevice formation is a normal phenomenon in electroplating. Only under the right conditions for levelling are these crevices prevented from forming to noticeable depths so that a specular deposit results. These optimum conditions need not be the same as those which give best results with the relatively larger crevices used in levelling experiments. It has been shown by Garmon and Leidheiser (6), for example, that levelling is a function of the size and shape of the crevice.

The results of this study also permit further discussions about preferred orientations. Strong fiber axes were observed in samples showing relatively large grains and extended growth layers. It has been found by Pick, Storey, and Vaughan (7) that the surfaces of growth steps are usually low-index crystallographic planes. As the conditions which favor extended growth layers also favor continuation of the substrate orientation, layers will be formed nearly parallel to each other, resulting in large grains. As these grains grow from preferentially oriented nuclei, they tend to be aligned with a common direction of low indices perpendicular to the surface. Under conditions of growth inhibition. the layers are small and tend to be more randomly oriented with respect to one another because there is only a weak tendency to continue the immediate substrate orientation. Thus, fine-grained structures show generally only weak fiber axes or are randomly oriented.

The relative merits of using thin films plated on copper and stripped by removing the latter and those prepared by thinning bulk material became evident from this study. As the measurements of grain size and orientation obtained from both methods were the same, either is suitable for this purpose. For the examination of growth layers, crevices, and surface contours, the as-plated thin films are best suited as these features are no longer visible after electropolishing. Etching effects from the electropolishing solutions often occur in complicated structures. This again favors the first method. A slight etching effect has also been observed in the thin films due to the solution which dissolves the copper. The as-plated films can be made thinner, and they are more uniform in thickness than the thinned films. On the other hand, to study dislocations, subgrain formations, and annealing behavior, the thinned films are preferable. Dislocations are probably introduced in the as-plated thin films. Small changes in the lattice spacing, as occur in going from copper to nickel, can be easily accommodated under conditions of epitaxy by the introduction of dislocations.

#### Conclusions

Electron microscopy, especially using thin films in conjunction with replicas, has been usefully applied to the study of the very fine structure of electroplated nickel. Selected-area diffraction appears to be the only satisfactory method of measuring grain size of electrodeposits of the type used in this study as other means do not differentiate between colonies and grains or between microstress and microcrystals. An investigation of the interaction of dislocations with the sites of lattice-included, foreign material should be very helpful in elucidating the reason for the wide range of mechanical properties, as should also be a study of the effect of crevices acting as possible stress raisers.

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## Aging of Electrodeposited Chromium

#### I. Deposits from Chromic/Chromous Plating Baths

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#### ABSTRACT

Deposits from the chromic/chromous plating baths used for the commercial electrowinning process lose about half their hydrogen and gain about 0.06 weight per cent (w/o) oxygen during about 100 days aging. The hydrogen loss does not occur in vacuum and is probably due to oxidation of elementary dissolved hydrogen. The remaining hydrogen is probably in hydrous oxide inclusions. The oxygen gain may be due to absorption in chromous oxide inclusions.

During studies of the nature and behavior of impurities in electrodeposited chromium, we have found that many deposits show pronounced aging effects during storage at room temperature. In this paper we report the results obtained with specimens deposited from chromic/chromous plating baths by the electrowinning process developed by the U.S. Bureau of Mines and the Union Carbide Metals Company (1). Studies of the aging of deposits from chromic acid plating baths are in progress (2) and will be reported later.

#### **Materials and Procedures**

Six deposit samples were used in this work. Deposits 1-5 were received from Union Carbide Metals Company in November 1959, and deposit 6 was received from the same source in March 1959. For these deposits, the usual heat-treatment in the plating plant to dry and dehydrogenate the material was omitted. The experimental specimens were given numbers which include the number of the deposit of which they were a portion, and a letter to distinguish between different specimens from the same deposit, e.g., 1A, 1B, 2A, etc.

Dilatometric work was done with a Leitz Type HTV Universal Dilatometer, which produces a photographic curve representing specimen length vs. temperature. The slope of this curve, minus the slope of a curve on the same film made with the same specimen after complete annealing, multiplied

<sup>1</sup>Present address: Research Department, Gillette Safety Razor Company, Boston 6, Mass. by the appropriate calibration factors, gives the rate of shrinkage. The dilatometer furnace heating rate was  $3^{\circ}$ C/min, and the specimens were in an atmosphere of about 1 cm pure hydrogen gas up to about  $550^{\circ}$ C, and in vacuum thereafter. The purpose of the hydrogen gas was to increase heat transfer.

Hydrogen analyses were performed with a glass vacuum system in which the specimen was heated at 3°/min and the hydrogen evolved was collected in a known volume. Pressure of the hydrogen was measured with an oil manometer containing Dow Corning DC 703 silicone oil, and a Gaertner Scientific Corp. Model M300 cathetometer. To facilitate rate of evolution measurements, which require rapid manipulation, no Toepler pump was used, and the upper boundary of the known volume was the mercury vapor stream in the collector diffusion pump. Since this vapor stream retreats further into the pump as the pressure builds up, the known volume (511-561 cc) had to be calibrated as a function of pressure. It was established experimentally that loss of hydrogen by permeation through the silicone oil or by oxidation by mercury oxide in the pump was negligible, and also that no measurable hydrogen was evolved during the period of pumping which preceded the heating. Spot checks indicated that the gas collected in the known volume was essentially pure hydrogen. A liquid nitrogen trap was used between the specimen and the collector diffusion pump; the term "hydrogen content" as used in this paper does not include any

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Fig. 1. Effect of age and humidity on the weight of specimens 1B (circles) and 6A (triangles). Weight gain is relative to the weight at age 1.3 days and 15% humidity. The curve represents the effect of age alone. See Fig. 2.



Fig. 2. Effect of humidity on the weight of specimens 1B (circles) and 6A (triangles). The ordinate of each point is the vertical distance between the corresponding point in Fig. 1 and the curve in Fig. 1.

hydrogen evolved from the specimens in the form of water vapor. Hydrogen content was calculated graphically from the rate-of-evolution data. In some cases rate measurements were not made, and hydrogen content could be calculated directly from the pressure/volume data; where cross checks were possible, the two methods gave identical results for hydrogen content.

Oxygen analyses by vacuum fusion and carbon analyses by combustion were performed by the Analytical Chemistry Branch of Watertown Arsenal Laboratories. In some cases we extracted the oxides from annealed specimens and submitted these to the Analytical Chemistry Branch for chromium analysis by standard procedures. The reported chromium content was then multiplied by the factor 48/104 to give the oxygen content. For extraction, a 1g specimen was placed in a solution of 10 ml bromine and 100 ml methanol. When solution of the metal was complete the mixture was filtered and the residue washed thoroughly with a solution containing 7g of ammonium bromide per 100 ml of methanol.

#### Results

Figure 1 shows how the weight of specimens 1B and 6A changed with age, age being reckoned from the time of removal of the deposit from the plating bath. The first weighing of specimen 1B was at age 1.3 days, and that of 6A, 14 days. To bring the two sets of measurements into conformity, a hypothetical 1.3-day weight was chosen for specimen 6A such that the two sets of data coincided as closely as possible. Spot checks with specimens 1G, 1H, and 1I gave agreement with the data for specimen 1B. The relative humidity of the laboratory atmosphere at the time of weighing is also shown in Fig. 1; for specimen 1B up to age 6 days direct humidity readings were not available, and the values shown were calculated from indoor temperature and outdoor dew point. These calculated values are probably a little low. It is clear that both age and



Fig. 3. Effect of age on hydrogen content. See also the data for specimens 1D and 2 P in Table I.



Fig. 4. Effect of age on hydrogen evolution during annealing at 3°/min.
Table 1. Details of vacuum annealing experiments. In each case the specimen was pumped at room temperature for the time shown, and then annealed at 3°/min to the temperature shown. Annotations: a, days elapsed from removal of deposit from plating bath to beginning of pumping in the vacuum system; b, corrected for hydrogen recovered and to 15% humidity; c, by alcoholic bromine extraction; d, the specimen was not continuously in contact with normal air: see text; e, plus 30 min at 800°.

		1	Pumping		Wt loss <sup>b</sup> .	Hydrogen recovered.	Oxygen content.	Carbon content.
Specimen	Weight, g	Age <sup>a</sup> , days	hr	Anneal, ℃	ppm	ppm	w/o	ppm
1A	2.40	1.3	18	700	354	361	0.333	21
6B	0.89	15	17	1085	404	223		
2D	2.12	50	23	1000		210		
1H	0.80	56	19	700	235	192	0.396	28
1D	2.43	61d	2	800e	260	304	0.344	24
6E	2.06	86	18	1000			0.388c	
6H	2.40	104	22	650	118	181		
6R	1.98	107	3	915			0.410c	
6S	2.24	110	26	1019			0.379c	
6U	2.30	110	26	1019			0.401c	
6V	2.03	120	18	850			0.396c	
6X	2.56	120	18	850			0.383c	
$2\mathbf{E}$	3.05	182	20	800	196	184	0.393c	
2P	1.05	190d	20	800		313	0.316c	
11	0.91	244	22	600	-19	172		65
1M	0.91	259	21	650		175	0.399	
2L	2.22	<b>3</b> 01d	26	800	303	176	0.399	56
61	1.87	317	22	800e	324	164	0.404c	
1E	2.27	<b>3</b> 29d	24	800	364	293	0.394	33
2B	2.33	333d	20	800	206	177	0.419	39
2N	3.48	341d	19	800	309	180		
2K	2.57	364d	24	830	191	176		
2A	0.99	<b>3</b> 91d	24	800	213	176		
1F	1.95	396d	23	800	186	171		
1B	3.80	399	24	800	199	175		
6J	1.94	496	20	600		159		

Table II. Summary of dilatometric experiments

Specimen			Linear shrinkage		
	Length, cm	Age, days	To 1040° %	To 400° %	
1J	4.38	1.4	0.708	0.140	
1K	4.39	5	0.694	0.128	
3A	5.04	57	0.664	0.100	
6F	2.37	112	0.638	0.086	
6G	2.72	113	0.637	0.080	
3B	5.04	237	0.634	0.090	
3D	5.97	313	0.623	0.085	
3C	4.51	319	0.633	0.086	
6K	5.44	575	0.608	0.061	

humidity affect the weight, and the separate effects are shown by the curve in Fig. 1 and the line in Fig. 2.

Figure 3 shows how the hydrogen content changes with age, and Fig. 4 shows how age affects the details of the hydrogen-evolution process. Since aging produces a hydrogen loss but a weight gain, it follows that something is absorbed from the atmosphere during aging. If this material were lost during vacuum treatment, there should be a corresponding trend in the data for age vs. weight loss during vacuum treatment; the appropriate data from Table I are plotted in Fig. 5, and we see there is no such trend. When data for oxygen content vs. age are examined, however, as in Fig. 5, the correspondence between weight gain and increase in oxygen content is readily apparent. Thus, either oxygen or water vapor is absorbed during aging.

The easy access of oxygen and/or water to the interior of the deposits can be attributed to an inclusion system which forms a finely divided skeleton throughout the entire deposit. Conventional sectioning, polishing, and microscopy do not easily reveal this system, but by dissolving the metal in alcoholic bromine as described above, the skeleton is isolated in the form of a pseudomorph, of composition approximating  $Cr_2O_3$ , which under the microscope has a spongelike appearance with an average pore diameter of roughly 1 $\mu$ . Annealing the specimen slightly (say 3°/min to 300°, which is too slight to give rise to any doubts as to whether the skeleton has been changed appreciably in size or shape by annealing) is necessary to obtain a good



Fig. 5. Effect of age on oxygen content of annealed specimens (circles) and weight loss during annealing (triangles). Weight losses are corrected for hydrogen recovered and for humidity variations. The curve is the sum of weight gain and hydrogen loss, from Fig. 1 and 3. See also the data for specimens 1D and 2P in Table 1.

pseudomorph. Very old unannealed specimens also gave good pseudomorphs; slightly aged unannealed specimens gave broken pseudomorphs; and it appears that a very fresh unannealed specimen would yield no pseudomorph at all.

Figure 6 shows the effect of age on the shrinkage characteristics of the deposits. The curves have been slightly idealized to eliminate random variations not related to age. The increase in the 300° peak from age 1.4 days to 60 days could be spurious. The other trends shown in Fig. 6 are qualitatively reliable. Figure 7 compares the observed decrease in length during aging with the observed loss, during aging, of capacity to shrink during annealing. The data for length vs. age were obtained by mounting specimen 4A, of length 4.15 cm, in a dial micrometer which could be read with a precision of 5 x  $10^{-5}$  cm. It will be noted that there is a discontinuity at 5 or 6 days, preceded by five points of constant length. We believe that this was caused by sticking of the micrometer, and accordingly are reluctant to place too much reliance on Fig. 7. However, it does provide some indication that the oxygen or water absorbed during aging does not compensate dilatationally for the hydrogen lost during aging.

Some specimens were stored in special atmospheres and weight was followed as a function of time after returning the specimens to the normal atmosphere. Figure 8 shows one set of experiments in which specimens were placed in the special atmos-



Fig. 6. Effect of age on shrinkage during annealing at 3°/min. Slightly idealized: see text.



Fig. 7. Effect of age on the length and shrinkage capacity of deposits. Triangles show the loss in linear shrinkage during annealing at 3°/min to 400°, relative to specimen 1J of age 1.4 days. Circles show the loss in length of specimen 4A relative to 1.4 days. The two curves are identical except for vertical displacement.



Fig. 8. Effect of storage in special atmospheres on the weight gain relative to age 1.3 days. Specimen 1F (circles) was in pure saturated water vapor from age 4 to 39 days; specimen 2N (triangles) was in an evacuated glass capsule from 4 to 68 days; specimen 1E (squares) was in a mixture of carbon dioxide and air from 4 to 151 days. The dashed line is the curve in Fig. 1. All weighings were corrected for humidity variations.



Fig. 9. Effect of storage in special atmospheres on the weight gain relative to age 1.3 days. Up to age 46 days, all four specimens were part of a single piece, which was in an evacuated glass capsule from 4 to 42 days. After the original piece was broken up, specimen 2A (solid circles) was left exposed to normal air; specimen 2K (open circles) was in 0.7 atm pure nitrogen from 46 to 76 days; specimen 2B (squares) was in 0.7 atm pure carbon dioxide from 46 to 76 days; specimen 2L (triangles) was in 0.7 atm pure oxygen from 46 to 76 days. All weighings were corrected for humidity variations.

pheres at age 4 days and retrieved at some later age as indicated by the dotted lines. Figure 9 shows a second set of experiments in which the beginning of treatment in special atmospheres was at age 46 days. Because of the late start, the experiments in Fig. 9 were made with specimens which had been stored in an evacuated glass capsule from age 4 days to 42 days. With specimen 1E the carbon dioxide atmosphere was provided by storing the specimen in a bottle which was filled by gravity with carbon dioxide and then stoppered; presumably air was also present. In every other case a

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glass capsule of volume about 100 cc was used, and air was pumped away with a high vacuum system before admitting the special gas and sealing by fusion of a constriction. The duration of pumping before admitting the special atmosphere was  $1\frac{1}{2}$ hr for specimens 2B, 2K, and 2L; 17 hr for 2A; and 20 for 2N. Observed weights were corrected for deviation of relative humidity from a standard value by means of the line in Fig. 2. For each specimen the standard value was chosen as the humidity prevailing at the time of opening the capsule, so that no humidity correction would have to be applied to the weight of the freshly retrieved specimen. The use of different standard humidity values for different specimens does not vitiate direct comparison of the curves in Fig. 8 and 9, because each curve is based on a reference weight which was also adjusted to the same standard humidity. The values of the standard humidities were 2L, 25%; 1E, 42; 2B, 25; 2N, 24; 2K, 25; 2A, 30; 1F, 32. The hydrogen content of each specimen was measured immediately after the last weighing shown in Fig. 8 or 9 and is listed in Table I.

The hydrogen content of two specimens was measured after a period of storage in sealed evacuated glass capsules. Specimen 2P was stored from age 4.3 days to 190 days, and its hydrogen content at 190 days was 313 ppm. In addition there was 9 ppm free hydrogen in the capsule. Specimen 1D was stored from 4.2 days to 60.05 days, and at 61.06 days its hydrogen content was 304 ppm.

## Discussion

The results with specimens 1D and 2P strongly suggest that the hydrogen loss during aging takes place according to the reaction

$$4H(Cr) + O_2(gas) = 2H_2O(gas)$$
 [1]

where H(Cr) represents hydrogen dissolved in the metal, presumably stabilized at imperfections or impurity atoms, since the true solubility of hydrogen in chromium is very small (3). Equation [1] is also supported by the experiment in which specimen 2L, after storage in pure dry oxygen, lost weight immediately after being returned to the normal atmosphere, whereas with specimens 2A, 2B, 2K, and 2N there was an initial rapid weight gain, followed in a day or so by a rather abrupt change (not clearly visible in Fig. 8 and 9 because of the small scale) to a slower rate of weight gain. This behavior suggests that the humidity in the capsule containing 2L was higher than that in the laboratory.

That accounts for about half the initial hydrogen content. It is reasonable to assume that the other half is in hydrous form, as a constituent of hydrous oxide inclusions (4). One plausible interpretation of the weight gain during aging and of the shift of hydrogen evolution to higher annealing temperatures as shown in Fig. 4 is based on the hypothesis that some or all of the chromium in the hydrous oxide inclusions is in the divalent state. Then on annealing

$$2CrO + H_2O(oxide) = Cr_2O_3 + H_2(gas)$$
 [2]

$$2Cr + 3H_2O(oxide) = Cr_2O_3 + 3H_2(gas)$$
 [3]

and during aging

$$4CrO + O_2(gas) = 2Cr_2O_3$$
 [4]

where the symbols CrO and H<sub>2</sub>O(oxide) represent constituents of the hydrous oxide inclusions. Reaction [4], which is known to occur at room temperature (5), would account for the weight gain during aging, and perhaps also for the observation that the inclusions become more insoluble in alcoholic bromine as aging proceeds. From Fig. 5, reaction[4] would occur to the extent of 600 ppm oxygen. Thus reaction [2] would occur to the extent of 600 x 4/32 = 75 ppm hydrogen in fresh specimens, but not at all in old specimens. Correspondingly, reaction [3] would increase with aging by 75 ppm hydrogen. This would account for the shift of hydrogen evolution to higher annealing temperatures, as shown in Fig. 4, since reaction [2] is known (6) to occur rapidly in the vicinity of 100°, and reaction [3] probably occurs in the general vicinity of 300° (7). We have been attempting, so far without success, to prepare some hydrous chromous oxide by the method of Lux and Illman, in order to determine its behavior more precisely.

Other possible but less credible interpretations of the aging behavior have been discussed in ref. (2).

A puzzling feature of our results is the effect of carbon dioxide on the weight and hydrogen content of the deposits. The effect is both profound and sensitive to the details of the experimental conditions, perhaps to presence of oxygen or water vapor. These characteristics suggest that further study might prove very instructive. However, because of the difficulty of maintaining a supply of the fresh deposit, we do not at present have any plans for such a study.

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# Thallium-Activated ZnS Phosphors

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### ABSTRACT

Firing of ZnS with Tl<sub>2</sub>S + S in sealed tubes results in yellow photoluminescence peaked at  $590\mu$  as well as thermoluminescence and infrared-stimulated emission with the same color. In the presence of Cu or Ag, the photoluminescence is red and peaks at 835 m $\mu$ . This emission is excited at wavelengths where ZnS: Cu,Cl or ZnS: Ag,Cl, respectively, emit. The thermoluminescence and infrared-stimulated emission, at room temperature, of ZnS:Ag,Tl is yellow; in the case of ZnS: Cu, Tl, the stimulated emission contains yellow and red components.

Recent work in this laboratory has shown that Tl can be incorporated into ZnS. Because of lack of published data on Tl-activated ZnS (1)<sup>1</sup>, an attempt was made to correlate the results of the present investigation with data on ZnS:Cu or ZnS: Ag coactivated by Al, Ga, or In (2-7), as well as ZnS activated by In alone (8).

### **Phosphor** Preparation

Thallium salts are known to be quite volatile. and numerous samples of ZnS:Cu.Tl fired at atmospheric pressure indicated at best incomplete incorporation of the added Tl under such firing conditions. Because of the high limit of spectrographic detectability of Tl (100 ppm), it was also considered difficult to obtain accurate analytical data on such phosphors. A more practical approach, therefore, consisted of conducting all firings for 1 hr in sealed, evacuated silica tubes. Additions of Cu or Ag were made from aqueous solutions prior to a preliminary firing in H<sub>2</sub>S at atmospheric pressure which, in such cases, is always necessary to enable the proper degassing of the sample during the subsequent evacuation. Quantitative incorporation of the added Tl was not proven, but at least extensive incorporation was assumed on the basis that no separate phase of Tl-sulfide was discernible<sup>2</sup>

<sup>1</sup>Ballentyne's phosphor (1) was prepared with Tl, but was stated to contain no Tl after firing.

 $^2$  Unavoidable temperature gradients always cause a separate phase with high vapor pressure to segregate in clearly visible form on one side of the tube.

on the fired phosphors, except after additions as large as 10<sup>-s</sup> g atoms Tl/mole ZnS. X-ray diffraction analyses showed that both firing temperatures of 950° and 1100°C resulted in essentially cubic phosphors which, moreover, had the same emission spectra. Therefore, the presence of Tl evidently favors the formation of the cubic phase.

All of the phosphors described in this paper were fired in sealed tubes. At this time, it should however be pointed out briefly that, depending on composition and firing schedules, some ZnS:Cu,Tl phosphors fired at atmospheric pressure displayed similar properties. With increasing Cu addition and firing temperature (decreasing Tl retention), green luminescence was obtained, however, without evidence of special properties such as deep traps which could be ascribed to the presence of Tl. For this reason as well as their necessarily uncertain composition,3 they are not further described until such samples can be duplicated under more controlled conditions.

#### Results

Table I shows the compositions employed and the visually observed photoluminescence properties. Sample 1 was prepared by firing ZnS with TlCl (in the absence of S) in an effort to obtain Tl<sup>1+</sup> acceptor centers. This was unsuccessful because the phosphor showed only the characteristics of self-activated

<sup>3</sup> To avoid complete loss of Tl, firing in capped silica tubes was necessary in such cases. This, however, made it impossible to avoid the presence of some oxygen.

Table I. Visually observed luminescence of TI-activated ZnS Phosphors

Sam-	am- Phosphor-composition		n 5	77	•К		Room te	mperature		400°K	
No.	Ag	Cu	TI	Cl	Photo- lumin.	Infrared stimulation	Thermolum. below r. t.	Photo- lumin.	Infrared stimulation	Thermolum. above r. t.	Photo- lumin.
1	0	0	10-3	10-3	s. blue	blue	blue	s. blue	none	none	v.w.blgr.
2	0	0	$3 imes 10^{-5}$	0	w. orange	w. orange	yellow	yellow	s. yellow	yellow	yellow
3	0	0	10-4	0	s. orange	s. orange	s. yellow	s. yellow	s. yellow	s. yellow	s. yellow
4	0	10-4	$3 imes 10^{-5}$	0	w. lavender	yellow	w. yellow	w. orange	yellow	none	w. yellow
5	0	10-4	10-4	0	w. orange	v. w. orange	v. w. yellow*	orred	oryellow	none*	v. w. red
6	0	10-4	$3 \times 10^{-4}$	0	w. orange	v. w. orange	none	red	orange	none	v. w. red
7	0	10-4	10-3**	0	w. orange	v. w. orange	none	deep red	orred	none	v. w. red
8	10-	4 0	10-4	0	v. w. orange	s. orange	none*	deep red	s. yellow	yellow	orange

Glow curves show thermoluminescence but visible evidence is uncertain.
 Separate phase of a TI-sulfide noted after firing.
 s strong, w = weak, v = very.



Fig. 1. Room-temperature emission spectra of phosphors. Excitation: 365µ. Perkin-Elmer Model 13-U Spectrometer.

ZnS:Cl. In all other samples, Tl was added as Tl<sub>2</sub>S (absence of Cl) with a small excess of elementary S so as to favor the formation of Tl<sup>3+</sup> centers. Measurements on sample No. 3 (ZnS:Tl), No. 5 (ZnS:Cu,Tl), and No. 8 (ZnS:Ag,Tl) are shown in Fig. 1 to 4. The numbers in the figures refer to the sample numbers in Table I.

The room temperature emission spectra (Fig. 1) indicate that each phosphor emits a single band. In the case of ZnS:Tl, the emission is peaked at 590 mµ<sup>t</sup> and has a band width of 0.38 ev, *i.e.*, nearly the same as that of the ZnS:Cu,Cl luminescence. The emission bands of ZnS:Cu,Tl and ZnS:Ag,Tl peak at 835 mµ with half widths of 0.43 and 0.33 ev, respectively. The narrower distribution of the latter is made apparent by a deeper red visual appearance of the photoluminescence. The accuracy of the difference between the band widths of the Cu- and the Ag-activated phosphors is questionable because of the low sensitivity of the detector (PbS) which was required to measure the long wavelength emission.

The excitation spectra (Fig. 2) show some interesting features: ZnS:Tl is excited primarily in the fundamental band, and in addition, there is excitation in the neighborhood of 370 and 380 m $\mu$  which is the region where excitation of blue ZnS:Cl emission has been noted (9). Excitation of the red emission of ZnS:Cu,Tl and ZnS:Ag,Tl is predominantly

<sup>4</sup> By means of sensitive equipment (RCA 7102 photomultiplier), an extremely weak band peaked at  $915\mu$  was also observed. This, however, could not be detected with the apparatus used to measure the spectra shown in Fig. 1, and its existence is therefore questionable.



Fig. 2. Excitation spectra, corrected for equal number of quanta of exciting radiation. Thin powder layers, measured on side opposite to excitation. Below  $420\mu$ : Xe-lamp and RCA 1P21 photomultiplier. Above  $400\mu$ : W-lamp and RCA 7102 photomultiplier. B&L 500 mm Grating Monochromator.



Fig. 3. Diffuse reflectance spectra of TI-activated phosphors in comparison to ZnS:CI. Beckman Model DU Spectrophotometer. Measurements relative to MgO.

in the same bands where ZnS:Cu,Cl and ZnS:Ag,Tl are known to emit. A similar phenomenon has been noted in the excitation spectrum of ZnS:Cu,Li,Ti (10). The diffuse reflectance spectra, as shown in Fig. 3, indicate the presence of absorption in the neighborhood of 370-380 m $\mu$  and an additional absorption of the Cu-activated phosphor at longer wavelengths. Despite the poor resolution obtained in this type of measurement, there appears to be general agreement between the observed wavelengths for absorption and excitation. For comparative purposes, Fig. 3 also shows the diffuse reflectance spectrum of a typical blue emitting ZnS:Cl phosphor.

The yellow thermoluminescence of ZnS:Tl is very strong. Its glow curve (Fig. 4) shows two peaks above room temperature which are obtained more clearly by excitation at room temperature (filled points). In contrast, the thermoluminescence of ZnS:Cu,Tl is extremely feeble, and its color could not be observed with certainty. ZnS:Ag,Tl, however, showed a clearly visible yellow thermoluminescence at higher temperatures and in addition, one of the glow peaks ( $265^{\circ}$ K) is also obtained with the Cu-activated phosphor. Unfortunately, agreement of the positions of glow peaks for ZnS:Tl with



Fig. 4. Glow curves obtained after  $365\mu$  excitation and 10 min decay. Detector: RCA 1P22 photomultiplier. Heating rate: 10°/min.

those shown by ZnS:Cu,Tl and ZnS:Ag,Tl is uncertain. The visually observed emission colors, however, seem to be similar for all phosphors.

In this work, only visual observations were taken on infrared-simulated emission (Table I). The source of infrared was an incandescent lamp equipped with a Corning No. 2540 filter. The emission of ZnS: Tl is fairly strong and persistent during infrared irradiation and, at room temperature, of the same color as the ultraviolet-excited fluorescence. This phosphor also shows a persistent yellow phosphorescence. Introduction of  $10^{-4}$  Cu results in decreased yellow and increased red emission, depending on the amount of Tl in the phosphor.<sup>5</sup> The effect of Cu on the emission color is weaker for the stimulated emission than for room temperature photoluminescence. The same holds true for the effect of Tl concentration, as seen in Table I.

Copper also quenches the room temperature phosphorescence and reduces the infrared-stimulated emission to a brief flash. The latter effect seems to differ very slightly for the two emission bands, and consequently, both yellow and red stimulated emission can be discerned side by side. In order to indicate the relative strength of the respective bands, Table I shows only the over-all color impression. It can be seen that it is always less red than that of photoluminescence; if the phosphor is excited simultaneously by ultraviolet and infrared and then the infrared is turned off, a distinct change to a deeper red color can be noted in all ZnS:Cu,Tl samples.

The effect of  $10^{-4}$  Ag on the infrared stimulated emission seems to be less pronounced than that of Cu.<sup>6</sup> The emission is weaker than in ZnS:TI, but still persistent and appears to contain no red component. The more greenish-yellow color obtained with Ag may be due to a weak blue band whose origin has not been ascertained. It could easily arise from contamination by traces of Cl. ZnS:Ag,TI also showed no room temperature phosphorescence.

Careful heating of a mixture of CuS and Tl<sub>2</sub>S with excess S resulted in a black product whose x-ray diffraction analysis is shown in Table II. The tetragonal structure, a = 5.58Å, c = 11.16Å (c/a = 2.0) is similar to that listed for CuGaS<sub>2</sub> (11). The substance is therefore likely to consist of CuTlS<sub>2</sub>. Continued heating results in loss of S, followed by sublimation of Tl<sub>2</sub>S. Therefore, no attempts to prepare phosphors at atmospheric pressure, analogous to ZnS:CuGaS<sub>2</sub> (4), seemed worthwhile. Nevertheless, the existence of this compound suggested the possibility of charge compensation of Cu<sup>1+</sup> by Tl<sup>3+</sup> in ZnS.

### Discussion

Because of the position of Tl in the periodic table, it is tempting to seek an analogy between the present phosphors and the properties of phosphors coactivated by Al, Ga, and In as reported by others. The emission which may be associated with trivalent substituents in Cu-activated phosphors shifts to

Table II. X-ray diffraction data for CuTIS<sub>2</sub>

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hkl		$CuK_{\alpha}$ radiation $d(A)$	Intensity
		8.15	5
	112	3.22	100
		3.11	3
		3.04	5
	004, 200	2.79	15
	201, 113	2.72	52
	The second se	2.04	4
	220, 204	1.973	30
	312, 115	1.685	17
	224	1.614	5

longer wavelengths with increasing atomic weight of the substituent; therefore, one should expect a further shift in the case of Tl. Figure 1 shows that this is the case. The narrower spectral distribution of the Cu- and Ag-activated phosphor, as compared to that reported for ZnS:Cu,In (7), may be explained by the absence of pronounced subsidiary emission bands such as are clearly shown in measurements reported by Melamed (6).

A further analogy of ZnS: Cu,Tl in comparison to Al, Ga, and In coactivated phosphors may be desirable on the basis of systematically increasing trap depths as reported by Hoogenstraaten (12). Unfortunately in the present system, there is no definite evidence of thermoluminescence either in the long wavelength emission band characteristic for the Cu and Ag activated phosphors, or of green Cu  $(520\mu)$  or blue Ag  $(445\mu)$  emission. Therefore, the observed glow peaks may arise from processes which differ from those proposed for Al, Ga, and In coactivated phosphors. The same argument may be advanced with respect to the infrared-simulated emission of ZnS: Ag, Tl. It is felt that conclusions as to the nature of the trapping states in Tl-activated phosphors will require identification of the spectral distributions of thermoluminescence and stimulated emission, as well as measurements of the latter as a function of wavelength of infrared radiation. Further investigations will also be necessary on phosphors prepared with varying amounts of Ag and Cu.

The similarity of the blue luminescence of ZnS: Al and ZnS: Ga (2) with the blue emission band in ZnS: In (8) (470 m $\mu$ ) suggests that the wavelength for this transition (which is generally associated with a Zn vacancy) is not strongly affected by the atomic weight of the donor. One should therefore expect that "self-activated" emission caused by Tl<sup>\*</sup> should be similar, which was, however, not observed. The question as to whether the 590 m $\mu$  band of ZnS: Tl is caused by transitions proposed either for the 535 m $\mu$ band or the 620 m $\mu$  band in ZnS: In (8) is much more difficult. At this time, it is felt that the large polarizability of Tl, as well as its ability to exist in an additional (monovalent) state, adds to the complexity of this system.

#### Summary

The important results obtained in this investigation are: (A) The 590 m $\mu$  emission of ZnS: Tl which is also visually observed (although not identified) in thermoluminescence and infrared-stimulated

 $<sup>^5</sup>$  No samples with Cu additions other than 10-4 were prepared.

 $<sup>^6</sup>$  The comparison can be made only with ZnS:10-4 Cu, 10-4 Tl (sample No, 5), No ZnS:Ag phosphors with more than 10-4 Tl were prepared, and the possibility' of stimulated red emission in such samples must be left open.

emission of the Cu and Ag activated phosphors. (B) The 835 m $\mu$  emission which is shown in the photoluminescence of the Cu- or Ag-activated phosphors, while at least in the case of Ag, it does not seem to appear during thermoluminescence of infraredstimulated emission. (C) The fact that the 835 m $\mu$  luminescence of the Cu and Ag activated phosphors is at least nearly identical. (D) The fact the excitation spectra of the Cu- and Ag-activated phosphors are different and correspond to the emission bands of ZnS:Cu,Cl and ZnS:Ag,Cl, respectively. At present, no mechanism can be proposed to explain all of these observations.

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# The Effect of Li and Ti on ZnS:Cu and ZnS:Ag Phosphors

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#### ABSTRACT

ZnS: Cu,Li fired in H<sub>2</sub>S or H<sub>2</sub> shows blue and green photoluminescence peaked at 443 and 510 m $\mu$ , respectively. Addition of Ti quenches this emission and causes red and infrared emission peaked at 730 and 830 m $\mu$ , respectively. Infrared radiation stimulates the red emission and also quenches the blue and green bands. ZnS: Ag,Li,Ti emits in the orange with a band peaked at 640 m $\mu$  and an infrared band peaked at 810 m $\mu$ . In the absence of Ti, ZnS: Ag,Li shows properties essentially similar to those of ZnS: Cu,Li, except for a weak orange-yellow infraredstimulated emission.

Kröger (1) has shown that Li or Na can form activator centers in ZnS, provided that Cl is present. If the concentration of Cl is decreased sufficiently, the presence of Li then quenches the self-activated (blue) photoluminescence which can otherwise be observed. Recent work in this laboratory has shown that, in the presence of Cu and Li, blue and green photoluminescence is obtained even in the absence of halides. If the phosphor has been fired in H<sub>2</sub>S or  $H_2$  (preferably at 1100°C), it also shows a deep red photoluminescence which can be stimulated by infrared radiation either during or after excitation by 365 m $\mu$  u.v. (ultraviolet). At the same time, the blue and green emission is quenched. Spectrographic analyses of specimens with more pronounced red emission indicated the presence of Ti which was therefore investigated in more detail.

#### **Phosphor** Preparation

The samples were prepared in 10-g lots, fired in small open silica tubes in a current of purified  $H_2S$  at 1100°C for 1 hr. The raw materials were ZnS (RCA LM476) and solutions of  $Cu(C_2H_3O_2)_2 \cdot H_2O$  or AgNO<sub>8</sub>, LiHCO<sub>2</sub>·H<sub>2</sub>O, and Ti [(CH<sub>8</sub>)<sub>2</sub>CHO]<sub>4</sub>, hydrolyzed in (CO<sub>2</sub>H)<sub>2</sub> solution. The activator additions were kept at 3 x 10<sup>-5</sup> g-atoms Cu or Ag, and 10<sup>-3</sup>

g-atoms Li per mole ZnS.<sup>1</sup> Owing to volatility, the concentration of Li in the fired phosphors was probably much lower, but was not determined. Any free Li<sub>2</sub>S formed during the firing in H<sub>2</sub>S was removed by washing in dilute acetic acid.

#### Results

Figure 1 shows room-temperature 365 m $\mu$ -excited emission spectra of phosphors prepared with or

<sup>&</sup>lt;sup>1</sup> Preliminary experiments indicated that for red emission, the optimum Cu concentration is between 1 and  $3 \times 10^{-5}$ . The higher concentration was chosen in order to minimize the effect of any unwanted contaminations. The effect of Li addition was less marked; the amount chosen is nominal.



Fig. 1. 365 mµ-excited emission spectra of 1, ZnS:Cu,Li and Zns:Ag,Li; 2, ZnS:Cu,Li, 10<sup>-5</sup> Ti; 3, ZnS:Ag,Li, 10<sup>-5</sup> Ti. Perkins-Elmer Model 13-U Spectrometer.

without additions of 10<sup>-5</sup> Ti. It should be noted that, except for intensity,2 the spectral distributions of the blue and green emission bands of ZnS: Cu,Li and ZnS: Ag,Li were identical. Only in the presence of Ti did the Ag-activated phosphor show a different emission spectrum, the visual impression of this being orange. Moreover, the same blue and green emission bands remained unchanged in phosphors prepared with the addition of 3 x  $10^{-5}$  Al (as well as Li). Therefore, the possibility that they are due to coactivation by Al (spectrographically detectable in the ZnS raw material) cannot be ruled out. On the other hand, the blue-green emission in ZnS:Cu,Na and ZnS:Cu,K as well as in ZnS:Cu (presumably caused by Al contamination) was much weaker. Samples prepared without Cu or Ag were nonluminescent.

The identity of the emission spectra of ZnS: Cu,Li and ZnS: Ag,Li suggests that the latter emits only by virtue of traces of Cu whose presence can rarely be avoided. This does not explain the absence of a distinct blue band in ZnS: Ag,Li (*i.e.*, different from that of the Cu-activated phosphor), even when fired with additional Al. The absence of any luminescence of ZnS fired only with Li also indicates that no significant contamination by Cu was likely. On the other hand, ZnS fired with Li and  $1 \ge 10^{-6}$  Cu showed not only weak blue-green photoluminescence, but also a very weak orange (rather than red) IR-stimulated flash, similar to that observed on the 3  $\ge 10^{-6}$  Ag-activated phosphor.

The excitation spectra for the blue-green emission of ZnS:Cu,Li and ZnS:Ag,Li (Fig. 2 filled points) show the same similarity, except for the shift of the short wavelength band of ZnS: Ag,Li to 325 m $\mu$ , corresponding to an energy appreciably more than the band gap of ZnS. No such discrepancy can be noted in the diffuse reflectance spectra as shown in Fig. 3. In all other cases, the fundamental excitation band (peaked at 338  $m\mu$ ) is shown quite clearly. In the u.v., no additional band due to Ti (long wavelength emission, open points) can be observed; for the most part, the excitation bands for short and for long wavelength emission differ only in relative height. In the visible region, the excitation bands for the red and infrared emission of ZnS: Cu,Li,Ti (open circles) are conspicuous inasmuch as they appear to match the two emission bands (blue and green) of the same phosphor prepared without Ti. To facilitate this comparison, the emission spectrum of ZnS:Cu,Li (from Fig. 1) is reproduced in Fig. 2, dashed line. A similar effect was also noted with ZnS:Cu,Tl and ZnS:Ag,Tl phosphors (2). In the case of the orange and infrared emission of ZnS: Ag, Li,Ti (open triangles), the excitation peak at  $415\mu$ cannot be similarly correlated; the concept that it may correspond to a hypothetical distinct blue emission of ZnS: Ag, Li (which was not obtained experimentally) is too speculative to be of serious concern.

The pronounced influence of variations of the concentration of Ti on the blue-green and red

photoluminescence of ZnS:Cu,Li,Ti is illustrated in Fig. 4. Addition of  $1 \ge 10^{-6}$  Ti decreases the bluegreen photoluminescence by a factor of 16. The increase in red emission obtained between the additions of zero and  $1 \ge 10^{-6}$  is indeterminate because of the questionable validity of the point corresponding to "zero Ti", excited without infrared. The par-



Fig. 2. Excitation spectra of phosphors, corrected for equal number of quanta of exciting radiation. Below 420 m, $\mu$ : Xe lamp, measurements with RCA 1P21 photomultiplier. Above 400 m, $\mu$ : W lamp, measurements with RCA 7102 photomultiplier. Phosphor powder layers veiwed on side opposite to excitation. B&L 500 mm Grating Monochromator. •—• ZnS:Cu,Li (blue-green emission);  $\Delta$ — $\Delta$  ZnS:Ag,Li (blue-green emission); O—O ZnS:Cu,Li, 10<sup>-5</sup> Ti (red emission);  $\Delta$ — $\Delta$  ZnS:Ag,Li, 10<sup>-5</sup> Ti (orange emission); - - - emission spectrum of ZnS:Cu,Li from Fig. 1.



Fig. 3. Diffuse reflectance spectra of phosphors, relative to MgO. Beckman Model DU Spectrophotometer, •—● ZnS:Cu,Li; ▲—▲ ZnS:Ag,Li; ○—○ ZnS:Cu,Li, 10<sup>-5</sup> Ti; △—△ ZnS:Ag,Li, 10<sup>-5</sup> Ti.



Fig. 4. Relative intensity of 365 m $\mu$ -excited photoluminescence of ZnS:Cu,Li,Ti as a function of Ti addition. Infrared obtained by W-lamp with Corning No. 2540 Filter. Measurements with Spectra Brightness Spot meter set on "Blue" and on "Open" with Corning No. 2030 Filter.

<sup>&</sup>lt;sup>2</sup> The quantum yields under 365 m $\mu$  excitation of ZnS:Cu,Li, ZnS:Ag,Li, ZnS:Cu,Li,10-<sup>5</sup> Ti, and ZnS:Ag,Li,10-<sup>5</sup> Ti were measured to be 48, 29, 56, and 34%, respectively, of that obtained with ZnS:3 × 10-<sup>6</sup> Cu,Cl.

ticular sample<sup>3</sup> on which it was measured is the same whose emission spectrum (Fig. 1) shows only a very weak long wavelength band.4 Therefore, the measured value may incorporate a contribution from the long wavelength tail of the green band. The red flash which can be stimulated by infrared after u.v. excitation of this phosphor is, however, strong and unmistakable. Nevertheless, it is still an open question as to whether this is due to spectrographically undetectable traces of Ti, or an intrinsic property of ZnS:Cu,Li. In connection with Fig. 4, it may be mentioned that phosphors with higher Ti additions were also prepared. It was interesting to observe that with as little as  $1 \ge 10^{-4}$  Ti, the red emission was appreciably quenched; at higher concentrations, it became very weak. Inasmuch as the same was observed with respect to Cu addition, this seems to be a system requiring unusually low activator concentrations.

Figure 5 shows the 365 m $\mu$ -excited intensities of blue-green and red emission of ZnS:Cu,Li as a function of wavelength of infrared radiation simultaneously incident on the phosphor plaque. All points represent differences between the measured intensities with and without u.v. excitation. The latter represents stray light from the monochromator (used as source of infrared) whose intensity was usually equal to or greater than that of the red radiation (open circles) to be measured. These points, therefore, show considerable scatter. Below 830 m $\mu$ , the reflected primary radiation from the monochromator dominated, and no meaningful differences could be obtained. In the case of ZnS: Ag,Li, no long wavelength emission could be measured. For blue-green emission, it can be seen that the dependence of the intensity on infrared wavelength shows considerable differences for the Cu- and Agactivated phosphors.

An attempt was made to determine the influence of Ti by performing similar measurements on ZnS:Cu,Li,4 x 10<sup>-6</sup> Ti (blue-green emission weak but still measurable). The results (inverted triangles, dashed curves) show that the quenching of blue-green emission (filled points) is shifted from 1150 to 1300 m $\mu$ , and that the red emission (open points) is stimulated at all wavelengths below 1700

 $^{3}\,\mathrm{A}$  selected sample with minimum infrared-stimulated red emission.

 $^4$  The red bands became pronounced at 4  $\,\times\,$  10-6 Ti. With 7  $\,\times\,$  10-6 Ti, the peak heights of the green and red bands were equal.



Fig. 5. Relative intensity of  $365\mu$ -excited photoluminescence as a function of wavelength of infrared radiation. Measurements as in Fig. 4. •—• ZnS:Cu,Li, blue-green emission; •—• ZnS:Ca,Li, blue-green emission; •—• ZnS:Cu,Li, 4 x 10<sup>-6</sup> Ti, blue-green emission;  $\nabla$ — $\nabla$  ZnS:Cu,Li, 4 x 10<sup>-6</sup> Ti, red emission.

 $m\mu$ . Especially toward shorter infrared wavelengths, the interference from stray radiation was considerable, and no attempt was made to extend the curve into that region.

The glow curves or blue-green and red or orange emission are shown in Fig. 6 and 7, respectively. In the case of ZnS:Cu,Li and ZnS:Cu,Li,Ti, excitation was performed not only at  $90^{\circ}K^{\circ}$  (open circles), but also at room temperature, followed by continued excitation during cooling (filled circles). In the latter case, one usually observes an intensification of the





Fig. 6. Glow curves of blue-green emission of phosphors, measured through Corning No. 5433 Filter. Heating rate:  $10^{\circ}$ /min.  $\bigcirc$ — $\bigcirc$  ZnS:Cu,Li, excited at 90°K only;  $\bullet$ — $\bullet$  ZnS:Cu,Li, excited at room temperature and at 90°K;  $\Box$ — $\bigcirc$  ZnS:Cu,Li,  $10^{-5}$  Ti, excited at 90°K only;  $\bullet$ — $\bullet$  ZnS:Cu,Li,  $10^{-5}$  Ti, excited at 90°K only;  $\bullet$ — $\bullet$  ZnS:Cu,Li,  $10^{-5}$  Ti, excited at 90°K only;  $\bullet$ — $\bullet$  ZnS:Ag,Li, excited at 90°K only; x—x ZnS:Cu,Li, 3 x  $10^{-5}$  Al, excited at 90°K only.



Fig. 7. Glow curves of long wavelength emission of phosphors, measured through Corning No. 2404 Filter.  $\bigcirc -\bigcirc$  ZnS:Cu,Li, excited at 90°K only,  $\bullet -\bullet$  ZnS:Cu,Li, excited at room temperature and at 90°K;  $\bigcirc -\bigcirc$  ZnS:Cu,Li, 10<sup>-5</sup> Ti, excited at 90°K only;  $\blacksquare$  ZnS:Cu,Li, 10<sup>-5</sup> Ti, excited at room temperature and at 90°K;  $\bigtriangledown -\bigtriangledown Z$ nS:Su,Li, 10<sup>-5</sup> Ti, excited at 90°K only.

higher temperature glow peaks, as reported by Garlick and Mason for CaS:Bi (3). The present results show this effect especially for the  $275^{\circ}$ K peak for ZnS:Cu,Li (Fig. 6). This method of excitation of the same phosphor also prevents all red thermoluminescence below room temperature (Fig. 7), although the excitation was continued down to  $90^{\circ}$ K.

Except for intensity, the glow curve for blue-green emission of ZnS: Ag,Li does not significantly differ from that of ZnS: Cu, Li. The orange thermoluminescence of ZnS: Ag, Li, Ti (Fig. 7) is, however, distinct from the red thermoluminescence of the Cuactivated phosphors.

Particular attention should be drawn to the effect of Al on the glow curve of blue-green emission of ZnS:Cu,Li. It was mentioned earlier that  $3 \times 10^{-5}$  Al had no influence on the emission spectrum of this system. A critical comparison of the glow curve for ZnS:Cu,Li,Al shown in Fig. 6 with that of red emission of ZnS:Cu,Li (or ZnS:Cu,Li,Ti) in Fig. 7 shows that the two characteristic red glow peaks at 217° and 265°K seem to be reproduced, but now represent the short wavelength radiation.

#### Discussion

The complex nature of the system precludes definite conclusions as to the nature of the activator centers responsible for the phenomena observed. In order to avoid further complications at this time, no attempt has been made to differentiate between the blue and the green emission bands separately, although such investigations have proven to be fruitful in the case of single crystals of ZnS: Cu, Cl (4). Similarly, the infrared emission bands were not detected in the measurements described in Fig. 4 to 7. Therefore, one can only summarize those data which tend to suggest the occurrence of certain processes.

Regardless of which model for the blue and green emission of Cu in ZnS one wishes to accept, the presence of such emission requires the concept of some donor which is capable of compensating the single charge produced by Cu at a Zn site. In the present system, the only possibility seems to be interstitial Li. To support this, it may be pointed out that the sizes of the alkali metal ions are such that Li (strong emission observed), but not Na or K (little emission observed) can enter ZnS interstitially. The Cu-Li emission bands are displaced slightly to shorter wavelengths with respect to accepted values for hex. ZnS: Cu,Cl (5); the difference possibly arises from the influence of the different coactivator. Any simple analogy of this nature fails, however, because of the identical emission spectra observed in Cu-Li and Ag-Li activated phosphors.

Figure 5 shows that the infrared wavelength for maximum quenching of blue-green emission of ZnS: Cu,Li,Ti agrees with the value of 1300 m $\mu$  reported by Melamed for ZnS: Cu,Co (6). In the absence of Ti, there is, however, no agreement. Substitution of Cu by Ag causes a shift of one of the bands to longer wavelengths. It can probably be assumed that the mechanism of quenching involves electron capture, from the valence band, by ionized acceptor centers and the creation of a hole in the valence band (7). Inasmuch as the infrared band causing the quenching also stimulates the red emission, the latter evidently depends on the presence of such holes. Among different models which may be proposed, there seems to be none which satisfactorily explains all of the observed phenomena. The fact that the orange ZnS: Ag, Li, Ti emission band peaks at a shorter wavelength than the red ZnS:Cu,Li,Ti band suggests that the long wavelength transitions may occur from the conduction band to ionized Cu or Ag centers which, in association with Li or Ti, would have to occupy positions only 1.6 to 1.9 ev below the conduction band. If one wishes to avoid the concept of acceptor levels in those positions, transitions from highly associated donor levels may be visualized, such as proposed by Apple and Williams for the long wavelength emission in Ga- and In-activated phosphors (8).

It has been shown that in the absence of infrared radiation, efficient red emission depends on small but appreciable concentrations of Ti. The firing conditions (H<sub>2</sub>S or H<sub>2</sub>) suggest that Ti may be present in trivalent form and therefore acts as a donor, although not independently, i.e., in the absence of Li. Accordingly, it should have no influence on the excitation spectra, as was observed. The shape of the glow curves shown in Fig. 7 indicates that red thermoluminescence originates from sites whose position is quite independent of Ti concentration<sup>6</sup> and may therefore not be associated with Ti. On the other hand, the lack of red thermoluminescence, below room temperature, of ZnS: Cu,Li after room temperature excitation, suggests that the number of electrons available for trapping at these sites was limited, evidently by lack of Ti. The concept of Ti as an auxiliary donor is involved and certainly requires further experimental evidence. Nevertheless, the fact that under simultaneous u.v. and i.r. excitation, the red emission of ZnS: Cu,Li was only 4 times smaller than the maximum obtained with Ti (see Fig. 4) indicates that Ti is not directly involved in this process. Qualitatively, its action rather resembles that of infrared radiation, i.e., it facilitates the thermal filling of acceptor levels from the valence band. The mechanism by which this occurs has not been ascertained.

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- $^{\rm 6}$  The glow curves obtained on phosphors with 1, 2, 4, and 7  $\times$  10-6 Ti were identical except for relative intensities.

# Fabrication and Characteristics of Phosphorous-Diffused Silicon Solar Cells

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## ABSTRACT

Results of an experimental study of fabrication processes for making phosphorous-diffused silicon solar cells are presented. Solar cells having sheet resistance of 10 ohm/sq, high long-wavelength collection efficiency, and efficiencies above 10% were fabricated by diffusion at 975°C. Diffusions carried out at 875°C for ½ to 1 hr periods resulted in cells having high short- and longwavelength collection efficiency. Gridded contacts applied to such cells to minimize effects of their comparatively high sheet resistance raised the efficiencies of the cells to values above 10%. Phosphorous-diffused cells in general have superior radiation resistance as compared to boron-diffused cells because of the slower rate of degradation of lifetime of minority carriers in p-type silicon as compared to n-type silicon under bombardment by atomic particles. The high short-wavelength collection efficiency of the 875°C diffused cells results in increased radiation resistance of these cells. Cells having efficiencies above 10% were made from 13-ohm-cm material and found to have higher radiation resistance than cells made from 1-ohm-cm material. Low junction reverse currents and contact resistances of approximately 0.2 ohm have also been achieved.

Until recently commercial silicon solar cells have been made by diffusion of boron into n-type silicon having a resistivity of 0.5 to 1 ohm-cm. Industrial efforts to improve the efficiencies and spectral response of silicon solar cells were concentrated on modification of boron-diffusion processes. A possibility completely overlooked was that phosphorous diffusion could be more successfully adapted to the creation of better solar cells.

The purpose of this paper is to present the results of a 2-yr study of phosphorous-diffused solar cells. The information will be presented in two sections. The first part deals with the diffusion conditions and processing methods that were found to yield phosphorus cells having desirable characteristics. The second part discusses the results obtained and the interrelationship of fabrication processes and solarcell characteristics. The various characteristics considered are: (a) forward current-voltage behavior of the solar-cell diode, (b) contact resistance, (c) junction reverse current, (d) collection efficiency, (e) radiation resistance, and (f) temperature behavior.

#### Experimental

Material preparation.—Single-crystal silicon ingots were grown from transistor grade material, using the Czochralski technique, a necked down seed (1), a rotation rate of 14 rpm, and a pull rate of 4 in./hr. The melt was doped with a master boron-silicon alloy to produce p-type ingots with selected resistivities in the 0.2 to 40-ohm-cm range. Etch pit counts using the Dash etch (2) gave counts below 1000/cm<sup>2</sup> on wafers cut from several ingots. Typical counts were less than 100/cm<sup>2</sup>.

Wafers cut from ingots were lapped with No. 1000 silicon-carbide abrasive in a planetary lapping machine and then given a finish lap with No. 3000 aluminum-oxide abrasive. After the wafers were thoroughly degreased and cleaned ultrasonically in organic solvents and distilled water, they were given a 5-min etch in a solution consisting of 20:12:2 parts of acetic acid, nitric acid, and hydrofluoric acid, respectively. Etching time was not found to be critical; however, prolonged etching (greater than 10 min) resulted in poor adhesion of subsequently plated nickel contacts to the surface of the wafers.

Diffusion.—After the wafers were etched, they were rinsed in distilled water, dried, and laid flat on a quartz-slab diffusion boat. The boat was inserted into a high-temperature zone of a laboratorydesigned two-zone diffusion furnace, shown in Fig. 1. Dry oxygen, used as a carrier gas, was passed through the quartz diffusion tube at a flow rate of approximately 40 cc/sec. The constancy of wafer boat thermocouple readings indicated that the boat had reached temperature equilibrium. Following the attainment of equilibrium, a hollow quartz boat containing phosphorus pentoxide was moved forward in the source zone to a point that had been precalibrated for a temperature of 220°C. The phosphorous pent-



Fig. 1. Phosphorous-diffusion furnace

oxide vapors formed were transported to the diffusion zone by the carrier gas.

The establishment of a proper flow pattern of carrier gas and the degree of dryness of the carrier gas is critical. A silica-gel drying tube followed by two liquid-air traps removed water vapor from the carrier gas. The diffusion tube was sealed at its front end to prevent the entry of water vapor from the external environment. The diffusion process was terminated by withdrawal of the source boat and shutoff of power to the furnace. Carrier-gas flow was continued until the source vapors were removed from the system. The wafers were withdrawn from the furnace after they had cooled to a temperature of  $600^{\circ}$ C or less.

The process incorporates the following features that establish a flow pattern, yielding solar cells with very good junction characteristics: (a) the sequence of introduction of wafers, source vapors, and carriergas flow; (b) use of a moderate source temperature and a slow rate of carrier-gas flow; (c) a special fritted glass carrier-gas disperser, as shown in Fig. 1.

Application of contacts.—When the diffusion process was completed, the bottom surfaces of the wafers (those in contact with the quartz slab) were marked with acid-resistant paint. The surface layers formed on the wafers were removed by a 5-min soak in hydrofluoric acid, a 5-min treatment in boiling aqua regia, and a 1-min cleanup in hydrofluoric acid. The resultant surfaces were clean, without any traces of foreign films or discolorations, and presented a satinsmooth gray appearance.

A photoresist pattern was applied to mask the top surface. Nickel was plated in the form of a thin grid pattern with one wide stripe on the unmasked regions of the wafer by use of the electroless nickelplating method (3). The bottom surface of the wafer was lapped to remove the nickel plating. The photoresist mask was removed from the top surface and Divco No. 335 Liquid Flux<sup>1</sup> brushed over the nickelplated pattern on the top surface. The nickel-plated pattern was then covered with solder by dipping the wafer into a molten solder bath. The bottom of the wafer was lapped with No. 600 silicon-carbide abrasive and plated electrolytically with rhodium. Plating-current densities of  $3-5 \text{ ma/cm}^2$  have yielded adherent low-resistance contacts.

Edge and surface finish.—The final fabrication steps consisted of dry-lapping the periphery of the wafers, using No. 600 silicon-carbide paper on a belt sander, and applying crystal-clear Krylon<sup>2</sup> over the active top surface to form an antireflective coating. The completed solar-cell structure is shown in Fig. 2.

# Results

Diffusion.—A polished "control" wafer was diffused in each run to determine junction depths and sheet resistances. Junction depths were measured by angle lap and stain techniques (4). The estimated error of measurement is  $\pm 0.1\mu$ . Sheet resistances were calculated from 4-point probe measurements applying appropriate correction factors. Table I pre-

<sup>2</sup> Trademark, Krylon Inc., Norristown, Pa.





sents data typical of the results obtained using various diffusion temperatures and time periods for material of different resistivities.

No significant variation in junction depth with resistivity of material for equal temperatures and time periods of diffusion was detected. Sheet resistances for equal junction depths were found to depend primarily on carrier-gas flow pattern for investigated rates of flow between 10 cc and 40 cc/sec. Turbulent flow patterns introduced wide variation in sheet resistances of wafers diffused in the same run. Turbulence was decreased by use of a slower rate of carrier-gas flow, and better junctions were obtained. However, a flow rate of 40 cc/sec was necessary to achieve sheet resistances of less than 50 ohm/sq for 875°C ½-hr diffusions. The upper limit of 50 ohm/sq of sheet resistance was set by imposing a minimum efficiency requirement of 10% for cells made by the process. The 10 ohm/sq sheet resistance of 975°C diffused cells was sufficiently low to permit attainment of efficiencies above 10% without the use of gridded contacts. However, cells made by 875°C diffusion having sheet resistances above 50 ohm/sq were found to be limited to efficiencies below 10% even with the use of gridded contacts.

Calculations of surface concentrations were not made because of the anomalous characteristics of shallow phosphorous-diffused layers noted in this investigation and by other investigators (5).

Forward-diode characteristic.—The "n" value measurement is a nonconventional solar-cell measurement applied very successfully in this investigation to monitor diffusion processes. The n value as given in the modified ideal diode equation,  $I = I_o(e^{a_{V/RT}} - 1)$ , was determined from the slope of the log I vs. V plot of the solar-cell diode in the re-

Table I. Effects of diffusion temperature and time

ρ, ohm-cm	Temp, °C	Time, min	Junction depth, $\mu$	ohm/sq
0.2	975	15	1.2	9
1	975	15	1.1	10
1	975	5	0.9	9
1	875	30	0.6	50
1	875	60	0.9	36
13	975	5	0.9	16
13	875	30	0.6	45
13	875	60	0.9	35

<sup>&</sup>lt;sup>1</sup> Trademark, Division Lead Co., Summit, Ill.



Fig. 3. Typical cell forward characteristic with n value below 2

gion of 1-100 ma of forward current. A typical n value characteristic showing a constant value of n over two decades of current is shown in Fig. 3.

The n value was found to be extremely fabrication dependent and a sensitive parameter for optimizing fabrication processes and controlling them. By the use of the process described, n values below 2 were normally obtained. High n values or increases in n value of cells made in particular runs have been related to the presence of excess water vapor during diffusion or turbulent flow patterns of carrier gas. The n value is directly related to junction reverse current and influences the open-circuit voltage and solar-cell junction impedance (6). Values of n of commercial boron cells and of boron cells made in this investigation (7) are generally well above 2. Often n values cannot be specified for boron-diffused cells because of the nonlinear relationship of log I vs V of such cells. The fact that the n value is fabrication dependent was further substantiated by the measurement of three selected boron-diffused cells that had n values below 2 and efficiencies in the range of 13 to 14.5%.

Contact resistance.—The slope of the solar-cell diode characteristic in the range of forward currents of 300-400 ma determines what is commonly referred to as the limiting diode forward resistance (LDFR). The LDFR depends primarily on contact resistance. This measurement was used in the investigation to determine the effects of various plating conditions and surface preparations on contact resistance. Typical values of LDFR presently obtained are in the 0.2-ohm range and this compares with values in the 1-ohm range common to commercial cells.

Instrumentation.—Monitoring of n value, LDFR, and junction reverse current was carried out rapidly by displaying "dark" cell voltage-current curves on the calibrated oscilloscope face of the Tektronix-575 Transistor Curve Tracer. Display of the illuminated solar-cell characteristic curve on the same instrument permitted rapid visual measurement of opencircuit voltage, short-circuit current, and comparative sheet resistance. Precise measurements of voltages and currents with a potentiometer and precision decade resistance box showed that the values obtained from oscilloscope readings are sufficiently accurate for evaluation of cell characteristics.

Where measurements in sunlight are indicated, these were made using a double-barrel narrow aperture system especially designed by the Eppley Laboratories for solar-cell measurements. The solar cell was mounted in one barrel while the incident radiation was monitored by a temperature-compensated thermopile in the other barrel. The system was mounted on an equatorial mount for tracking the sun.

Junction reverse current.—Dark cell reverse currents were measured for 0.6-v reverse bias. Reverse currents of 10-30  $\mu$ a were commonly obtained. The only periphery treatment given the cells was dry belt sanding. The low junction reverse currents of these cells represent better than an order of magnitude improvement as compared to typical commercial boron-diffused cells and boron cells made in the investigation (7). The three selected boron cells previously mentioned had junction reverse currents of 10-20  $\mu$ a.

Collection efficiency.—The ability of the process to preserve high values of lifetime in the base region of solar cells is evident from comparison of the integrated long-wavelength collection of the cells, as shown in Table II.

Table II gives the values of short-circuit current/ cm<sup>a</sup>,  $I_{sc}$ /cm<sup>a</sup>, obtained by illuminating cells with light passed through a long-wavelength pass filter having a cutoff at  $0.65\mu$ . Under these conditions, hole-electron pairs were generated in the base well below the junction, and the integrated collection was an indication of lifetime of minority carriers in the base.

The equivalent collection values obtained for  $975^{\circ}$  and  $875^{\circ}$ C diffusions into material of the same resistivity indicated that the process preserved base lifetime equally well for both diffusion temperatures. The more than 10% higher collection obtained for the 13-ohm-cm cells represents a considerable difference in the lifetime in the base of these cells as compared to the lifetime in the base of the high-efficiency 1-ohm-cm cells. The reason for this is that collection

Table II. Comparison of integrated long-wavelength collection

1-ohm	-cm base re	sistivity	13-ohm-cm base resistivity			
Cell	<sup>Isc</sup> , ma/cm <sup>2</sup>	temp, °C	Cell	Isc, ma/cm <sup>2</sup>	Diff. temp, °C	
324-3D	7.4	975	331-1B	8.3	875	
324-3E	7.6	975	331-1D	8.2	875	
324-4B	7.3	975	331-2B	8.4	875	
324-4C	7.8	975	331-2C	8.9	875	
324-5B	7.5	975	331-2D	8.8	875	
324-5C	7.3	975	331-3B	8.7	975	
324-6B	7	875	331-3C	8.2	975	
324-7B	7.5	875				
324-7C	7.3	875				

All cell surfaces bare.



Fig. 4. Relative collection efficiency for 975° and 875°C diffusions (normalized to 10 at maximum).

increases slowly with increasing base lifetime for values of lifetime above 1 µsec.

Measurements of diffusion lengths of minority carriers generated in the base by electron bombardment revealed that lifetimes of 10-15 µsec were preserved in the 13-ohm-cm cells, whereas the lifetimes in the 1-ohm-cm cells were  $3-5 \ \mu sec$  (8).

Although high long-wavelength collection can be achieved with diffusion temperatures of 975° or 875°C, high short-wavelength collection has only been obtained by 875°C diffusion. This is shown by the plots of relative collection efficiency vs. wavelength in Fig. 4. The curves are shown for cells having equal junction depths, and the only difference in fabrication is that the cells with the high "blue" collection were made by an 875°C diffusion. The curve for the 975°C cell (Fig. 4) is similar to that obtained for boron cells having "good blue" collection. High "blue" collection can also be obtained for comparatively deep junction depths (1-hr diffusion at 875°C), as shown in Fig. 5. Measurements of collection efficiency vs. wavelength of the USASRDL cells were made at several industrial laboratories, and the results agree with those presented here.

Table III. Comparison of short-circuit currents

	13-ohm-c	m base		1-ohm-cm base					
Cell	I <sub>sc</sub> , ma/cm <sup>2</sup>	temp, °C	Time, min	Cell	Isc, ma/cm²	temp, °C	Time, min		
331-1B	33.5	875	30	324-4C	24.5	975	5		
331-1C	32	875	30	324-6B	28	875	30		
331-2B	30	875	30	324-7B	28	875	30		
331-2C	34.4	875	30	324-7C	28.4	875	30		
331-2D	32	875	30	13.5% Boron	31.2				
331-3B	28	975	5	14.5% Boron	31.4				
331-4B	26	975	5						
331-4C	27	975	5						

All measurements in sunlight. Phosphorous cells Krylon coated; boron cells boron-diffusion coated.



Fig. 5. Relative collection efficiency for a junction depth of 0.9µ (normalized to 10 at maximum).

The effects of high base lifetime and high "blue" collection on the short-circuit current of cells are shown in Table III.

Analysis of the data shows that an increase in short-circuit current per sq cm, Isr/cm<sup>2</sup>, of approximately 15% was obtained from the improved shortwavelength collection of 875°C diffused cells. An additional increase of 10% in  $I_{sc}/cm^2$  was obtained from the higher long-wavelength collection of the high base lifetime 13-ohm-cm cells. The net increase results in values of Isc/cm<sup>2</sup> of 13-ohm-cm 875°C cells above that obtained for a selected 14.5% borondiffused cell. The referenced boron cell was the highest efficiency cell ever measured at this Laboratory.

The phosphorous-diffused cells were coated with Krylon, as indicated in Fig. 2. Cells of this type were sent to several industrial laboratories for application of more effective antireflective coatings. The shortcircuit currents of the cells after coating with silicon monoxide were 8-10% higher than those obtained with Krylon coatings. The percentage increase in short-circuit current obtained by application of coatings, using the uncoated cell short-circuit current as a reference, is 15-20% for Krylon coatings and 30% for optimized silicon-monoxide coatings.

The efficiencies of the 13-ohm-cm cells were limited by sheet resistance and comparatively lower open-circuit voltages because of Fermi-level considerations. However, the very high short-circuit currents and low n values of these cells decreased their junction impedance, as shown in Fig. 6. The junction impedance is defined as  $r_i = dV/dI$  under constant illumination.

Eleven per cent efficiencies were obtained for Krylon-coated high-resistivity cells (Table IV).

Application of optimum antireflective coatings should raise the short-circuit current of the cells by 8-10% and increase the efficiencies. Cells similar in characteristics to those shown in Table IV were made using 10-ohm-cm and 40-ohm-cm material.



Fig. 6. Output characteristics of a 13 ohm-cm and a 1 ohm-cm cell.

Table V compares the characteristic "limits" of cells made in this investigation from material of several different resistivities.

It is difficult to obtain n values in the range of 2 and high open-circuit voltages in solar cells made from highly doped material. As shown in Table V, both open-circuit voltages and short-circuit currents are comparatively low for cells made from 0.2ohm-cm material. The listed characteristics of the 1-ohm-cm base cells are similar to those of borondiffused cells with the exception of the limiting diode forward resistance.

The high short-circuit currents obtained for cells made from high-resistivity material was a result of the high base lifetime and high short-wavelength collection of these cells.

Radiation resistance.—Analysis of collection efficiency vs. wavelength curves of solar cells before and after atomic bombardment revealed that the lifetime of minority carriers decreased more slowly in the p-type base material of phosphorous cells than in the n-type base material of boron cells (9-13). Direct measurement of base diffusion length degradation as a function of atomic bombardment was carried out for electron and proton bombardment over a wide range of bombarding particle energies (8). The collected data show that the phosphorous-diffused cell has superior radiation resistance compared to the boron-diffused cell.



Fig. 7. Postbombardment collection degradation (absolute output in arbitrary units for equal photon input); - - - original; — after bombardment.

Table IV. Characteristics of 13-ohm-cm 875°C cells

Cell	I <sub>sc</sub> /cm², ma/cm²	Voc	Temp, °C	Radiation, mw/cm <sup>2</sup>	Efficiency, %
331-A	25.8	0.538	30	85.5	11
331-B	27	0.538	30	86	11
331-C	25.9	0.536	30	86	10.8
Boron 14.5%	27.8	0.623	18	89.6	14.96
Boron 13.5%	27.6	0.620	18	89.6	13.96

All measurements in sunlight. Phosphorous-diffused cells gridded, Krylon-coated. Boron-diffused cells gridded, boron-diffusion coated.

Table V. Characteristics vs. resistivity of base material for typical solar cells

Resistivity, ohm-cm	Voc, v	I <sub>sc</sub> , ma/cm <sup>2</sup>	LDFR, ohm	Efficiency, %
0.2	< 0.56	<22	0.2	<10
1	< 0.60	<26	0.2	10-12
13	<0.55	<31	0.2	10-12

All cells measured in sunlight (intensity 88 mw/cm<sup>2</sup>).

The comparative radiation resistance of cells is also dependent on the short-wavelength collection efficiency. This dependency becomes stronger with increasing integrated bombardment flux. Measurements of absolute collection efficiency vs. wavelength showed that after bombardment which reduced the total "sunlight" short-circuit current of cells to 75% of their initial value, the collection at short wavelengths ( $0.6\mu$  or less) had decreased by less than 5%. Figure 7 illustrates this effect for very heavy bombardment. Since approximately one-third of the short-circuit current of the 875°C phosphorous-diffused cells is obtained from short-wavelength collection, these cells have improved radiation resistance.

Further improvement in radiation resistance was obtained by fabricating cells with high-resistivity base material using 875°C diffusions. Table VI compares the short-circuit current degradation of cells in relation to diffusion temperature and base resistivity.

Although only small quantities of high-efficiency high-resistivity cells were subjected to bombard-

Table VI. Relationship of  $I_{sc}/I_{so}$  to  $\rho$  and diffusion temperature

1-Mev electron bombardment*								
Cell	$\rho$ , ohm-cm	Diffusion temp, °C	$\frac{I_{sc}}{I_{so}}, \%$					
326-2	1	875	73					
331-1	13	875	81					
331-2	13	875	81					
331-4	13	875	81					
	1.2-Mev proton k	ombardment**						
324-3	1	975	45					
324-5	1	975	66					
331-5	13	875	90					

Cell original efficiencies >10% measurements in sunlight or equivalent.  $I_{wo}$ , prebombardment value of  $I_{sc}$ . Based on measurements by Dr. W. Rosensweig and colleagues

of BTL. \*\* Based on USASRDL measurements (13). ment, it is significant that good consistency in results was obtained.

Temperature behavior.—The changes in opencircuit voltage, short-circuit current, and efficiency of phosphorous solar cells with increasing temperature in the  $25^{\circ}$ - $125^{\circ}$ C temperature range were found to be similar to those of boron-diffused cells (14).

#### Conclusions

The investigation resulted in a phosphorous-diffusion process that yields solar cells with the following desirable characteristics: 1, efficiencies above 10%; 2, n values of 2 or less; 3, junction reverse currents of 10-30  $\mu$ a for reverse bias of 0.6v; 4, contact resistances in the range of 0.2 ohm; 5, high short-wavelength collection (1/3 of  $I_{sc}$  from short-wavelength collection); 6, very-high long-wavelength collection efficiency for high-resistivity base cells; 7, superior radiation resistance.

The 875°C diffusion process has already been adapted for production of solar cells for use in communications satellites (15). A recent outer space experiment has verified the superior radiation resistance of the phosphorous-diffused solar cell (16).

The most promising approach to further improvement of phosphorous-diffused cells is believed to be the study of effects of electrically inactive impurities in silicon on characteristics of solar cells. Another area requiring research is the interactions of impurities and imperfections in the region of the junction.

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# Purification of Tellurium by Distillation

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#### ABSTRACT

A rapid method is described by which tellurium and materials of similar vapor pressures may be separated from less volatile impurities such as antimony and various oxides. The technique consists of multiple distillation under a continuously pumped vacuum. A mechanical arrangement has been devised which employs a reusable crucible, thereby increasing the speed of the operation. Evaluation indicates that one operation will produce tellurium with an electrically active impurity concentration of  $4 \ge 10^{14}/\text{cc}$  from material with considerable surface oxides.

The increasing interest in thermoelectric energy converters during the past few years has resulted in a large research effort in the area of intermetallic semiconducting tellurides, notably bismuth telluride and lead telluride. In addition, mercury telluride,

cadmium telluride, and molybdenum telluride also are receiving increased attention. As research in each of these materials progresses, it is necessary to produce crystals of the highest possible perfection, both chemically and crystallographically speaking, if de-



Fig. 1. Tellurium distillation apparatus

tailed experiments on their transport properties and band structure are to yield meaningful results. In an effort to produce such high-quality single crystals by both the Bridgman and Czochralski techniques, it was determined experimentally that the "highpurity" tellurium as commercially supplied required further purification. Accordingly, the scheme of multiple distillation under a continuously pumped vacuum was employed with considerable success.

A system was designed to employ a reusable sample tube. This feature reduced the time required to purify a given sample inasmuch as glass blowing operations associated with individual sample tube preparation have been eliminated. At present, using a 25 mm tube the system has an output capability of approximately 35g of purified tellurium per hour.

## System Description

A schematic diagram of the tellurium distillation apparatus is shown in Fig. 1. It consists of a sample tube, surrounded by a moveable heater and connected to a vacuum system by means of a groundglass ball joint. The sample tube, made entirely of Vycor, consists of three sections formed by semicircular indentations of the tube wall. The tube is sealed at one end and provided with a Vycor ground ball-joint at the other. This ball-joint mates with a Pyrex ball-joint on the vacuum system, thereby eliminating the need for a graded seal. The heater power is controlled by a Variac, and the temperature is monitored by a thermocouple mounted on the inside wall of the heater.

The tellurium to be distilled is placed at the closed end of a clean, dry sample tube. The tube then is connected to the vacuum system and pumped down to a pressure of approximately  $1\mu$ . The movable heater is placed so that only the end section of the sample tube will be above the melting point of tellurium. The heater temperature is then brought up to approximately 500°C, whereby the molten tellurium condenses in the center section of the tube. The heater is then moved so that the center section is now included and the temperature raised to approximately 600°C. The tellurium then recondenses in the third section. It is important that a temperature pro-

<sup>1</sup>American Smelting and Refining Co., South Plainfield, N. J.; semiconductor grade, 99.999% pure tellurium. file similar to that shown in Fig. 1 be maintained along the sample tube. Otherwise, if the temperature of the right-hand section is allowed to drop below that of the center section, back-distillation will take place, with a resulting loss of some of the tellurium. Finally, the condensed tellurium in the third section is melted down by moving the heater to form an ingot, and the tube is cooled rapidly in air by retracting the movable heater. After the tube is cooled, the purified tellurium may be removed without breakage by rotating the tube and sliding the ingot past the last indentation and out through the ball joint. In this way, the tube may be reused.

#### **Experimental Evaluation**

In order to obtain some quantitative measure of the effectiveness of this method of purification, an evaluation program was proposed and executed. Considerable information is available (3, 4) on the effects of impurities on electrical conductivity in tellurium. Since these data established that most acceptors are nearly fully ionized down to liquid nitrogen temperature and for impurity concentrations less than  $10^{so}/cc$  the mobility may be assumed constant at a given temperature, it was decided to employ electrical conductivity measurements as a measure of the purity of tellurium. In addition to measurements of improvement on commercially supplied "high-purity" tellurium, the effect on antimony impurity also was investigated.

Sample preparation.—In order to reduce the effect of anisotropy  $(\sigma_{||}/\sigma_{\perp} = 2)$  (4) in the conductivity measurements, samples were taken from large grain material and the current axis was chosen along the parallel direction. Samples measured approximately 0.2 x 0.2 x 1 cm. Current contacts were soldered with indium solder, and voltage probes were attached by welding fine gold wires. Samples were etched in dilute aqua regia momentarily prior to measurements.

Estimation of carrier concentration.—The dashed line in Fig. 2 represents an experimentally determined curve of hole concentration as a function of electrical conductivity at  $167^{\circ}$ K ( $10^{s}/T = 6.0$ ). This relationship will be used to estimate the carrier concentrations quoted in the following sections. We believe that these estimations will be accurate within



Fig. 2. Impurity and carrier concentrations in tellurium as a function of conductivity at 167°K.



Fig. 3. Effect of distillation on commercial high-purity tellurium

perhaps a factor of two and hence sufficient for this evaluation program.

Commercial high-purity tellurium.-It has been found that by distillation commercial high-purity tellurium can be further purified. This material as supplied consists of large lumps as well as small pieces and fine powder. Sample 8 was cut from a large piece of tellurium as received. Sample 3 was cut from an ingot produced by melting under vacuum small pieces and powder as received. Even though the tellurium is stored under vacuum, the small pieces and dust absorb a considerable amount of oxygen due to their large surface to volume ratio. From Fig. 2 and 3 we find that in the low-temperature extrinsic range sample 3 exhibits greater than  $10^{18}$  holes/cc compared to 8 x  $10^{14}$  holes/cc for sample 8. Sample 10 was produced by one distillation from a batch of small pieces and dust, special care being taken to keep the oxidized material out of the section where the final product is cooled. As usual, a sizeable quantity of white residue remained in the initial section of the distillation tube. The compositon of this residue is unknown, but certainly contains oxides of tellurium. The hole concentration at 167°K in sample 10 is on the order  $4 \ge 10^{14}/cc$ . The conductivity curve for sample 10 represents the limit which has been achieved consistently for one distillation of commercial high-purity material. The carrier concentration in sample 10 agrees with the best materials prepared by Kronmuller et al. (4) and with tellurium which has been zone refined with 300 passes by Aigrain (1). This limiting value of carrier concentration may represent the best that can be obtained by distillation or zone refining or may be due to the large number of crystal imperfections introduced by even the most careful handling of the material.

Antimony doped tellurium.—Since the conductivity of tellurium is very sensitive to antimony doping and since at 600°C the vapor pressure of antimony is 10° less than that of tellurium, it was decided to attempt separation of antimony by distil-



Fig. 4. Effect of distillation on antimony concentration in tellurium.

lation. A sample doped with 5 x  $10^{19}$ /cc antimony atoms was distilled successfully and samples prepared. The results of this experiment are presented in Fig. 4. Using Fig. 2 it may be seen that one distillation reduced the antimony concentration to 6 x  $10^{17}$ /cc and two distillations reduced it to 7 x  $10^{18}$ /cc. A third distillation yielded essentially the same result as two distillations, indicating that an equilibrium situation was reached with two operations.

# Conclusions

It has been shown that the quality of commercial high-purity tellurium can be improved substantially by a simple vacuum distillation technique. The success of this method has been measured directly by carrier concentration improvement as summarized in Table I, and indirectly by success in growing high quality single crystal material by both the Bridgman and Czochralski techniques. In the case of antimony, a limiting impurity level of  $7 \ge 10^{16}$  was obtained after two distillations.

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Table I. Summary of purification of tellurium by distillation

Impurity	Initial hole con- centration No. /cc $T = 167^{\circ}K$	Number of distil- lations	Final hole con- centration No. /cc $T = 167^{\circ}K$
Large lumps (oxides)	8 × 10 <sup>14</sup>	1	$4  imes 10^{14}$
Small pieces and pow- der (oxides)	10 <sup>18</sup>	1	$4 imes 10^{14}$
Antimony	$5 imes 10^{19*}$	3	$7 imes 10^{16*}$

Antimony concentration.

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# Sources of Contamination in GaAs Crystal Growth

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## ABSTRACT

Current evidence indicates that the purity of GaAs is now limited by contamination during crystal growth, rather than by the purity of the starting materials. A careful study has been carried out to identify sources of such contamination in the preparation of GaAs. Vacuum baking of gallium at 650°C for several hours in a quartz boat to remove oxides was found to increase the copper content, but not the silicon or other spectrographically detectable impurities. Back diffusion of impurities from a contaminated high vacuum pump was observed to affect properties of GaAs even when pressures of 10<sup>-6</sup> torr were maintained. Sealing under vacuum of large (20 mm) diameter quartz ampoules introduces significant quantities of silicon and copper onto the inner ampoule walls, which subsequently contaminate arsenic vapor when heated to above 1000°C. During growth, it was found that there is no appreciable diffusion of atmospheric gases through quartz at 1200°C. However, nearly 1018 molecules of gas are released due to outgassing of the walls. The most serious contamination, especially with silicon, occurs from the reaction between the GaAs melt and the quartz boat, and the reaction increases rapidly with increasing melt temperature.

The application of GaAs for transistors and transistor-like devices requires a material of extremely high purity in single crystal form. Past efforts to increase the purity of GaAs have centered on the purification of the component elements, gallium and arsenic, because of the existence of impurities that could not readily be removed from GaAs by zone refining. The impurity content of commercially available gallium and arsenic has now been reduced to the point where it is comparable to or below the amount of impurities introduced into GaAs by contamination during its preparation. The following evidence supports this conclusion.

First, emission and mass spectrographic analyses have detected impurities, such as silicon and copper, in GaAs in concentrations greater than that present in the starting materials. Second, series of GaAs crystals produced from the same lots of gallium and arsenic have had widely varying electrical properties. However, variations in the lots of gallium and arsenic have produced only minor changes in the electrical properties of the resulting GaAs. Third, special purification treatments carried out for gallium and arsenic have improved the properties of other compounds such as InAs, but have had little or no effect on the properties of GaAs.

For these reasons, this investigation was carried out to determine the sources of such contamination and thus provide guidance in devising improved methods of preparation. The investigation is specifically concerned with the horizontal Bridgman technique of crystal growth; however, the results are applicable to other methods of crystal growth. The details of the preparation of a GaAs growth ampoule for this growth technique are described in the following section. In subsequent sections each step in this procedure is carefully examined for possible sources of contamination. Throughout this paper, it is implicit that careful precautions were taken to remove the obvious contamination sources such as dust and similar foreign matter, to use gloves where required, etc.

### Preparation of GaAs

The arsenic was received in chunks each weighing approximately a gram, sealed in a Pyrex ampoule in 50 or 100 g lots. After being opened, the Pyrex ampoule was stored under vacuum in a larger Pyrex ampoule, sealed by a vacuum stopcock. The gallium is received in a polyethylene bag as a large lump. To remove pieces, the gallium was cooled to liquid nitrogen temperature, placed in "Glassine" paper bags, and cracked by squeezing in a vise. It was subsequently stored in these bags within a closed glass jar inside an air tight cabinet.

The ampoule, shown in Fig. 1, consists of a quartz tube of 20 mm bore with a ball joint at each end and a breakseal dividing it into two chambers. All quartz ware, including the tube, growth boat, and slug for

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rupturing the breakseal, was cleaned by first washing it in a detergent such as "Alconox", then treating it with aqua regia, then etching with a 1:1 mixture of HF and HNO3, and finally cleaning in a mixture of triple distilled HNO<sub>3</sub> and HCl. Each step was followed by extensive rinsing in triple distilled water, and after the final rinse, the water was removed using transistor-grade acetone which was drained, and the quartz allowed to dry in air. The quartz slug and the arsenic were loaded in air into one chamber of the tube, and the tube was then connected through a liquid nitrogen trap to a diffusion pump and evacuated. The arsenic was heated in a vacuum of below 10<sup>-6</sup> torr for 1 hr at 300°C to remove surface oxides and then that section of the ampoule was sealed under vacuum after first collapsing the tube with a broad flame produced by a brass hydrogen-oxygen torch.

Next, the growth boat containing solid gallium was placed in the other chamber of the tube, which was then evacuated before the gallium was melted. A vacuum heat treatment of 3 hr at  $650^{\circ}$ C was given to remove oxides of gallium as Ga<sub>2</sub>O, after which the gallium was refrozen and the ampoule sealed off using the same technique as for the arsenic section. The final ampoule is shown in Fig. 1.

After the breakseal was ruptured by causing the quartz slug to strike it, the GaAs was synthesized and grown into a crystal in a typical two zone horizontal Bridgman furnace (1). In synthesizing the GaAs, the entire system was brought up to the arsenic reservoir temperature of about 600 °C, and then the temperature of the reaction zone containing the molten gallum was gradually raised to about 1260 °C. The crystal was then grown by moving the entire furnace over the stationary quartz tube at a rate of about 1 cm hr<sup>-1</sup> for a total period of 16 hr.

# Effects of Cleaning and Handling Procedures

It was first determined whether the ordinary rinsing with distilled water is sufficient to remove the acids used for cleaning. This was found by measuring the resistivity of the water after each rinse. A 1:1 mixture of HCl-HNO<sub>3</sub> was placed in a quartz ampoule for 1 hr. This mixture was then discarded and replaced with deionized water, which remained in the ampoule for various times (usually 10 sec). After a number of rinses, the rinse water was also boiled in the ampoule. Typical results are shown in Table I. It can be seen that even ten rinsings with cold deionized water is not sufficient to remove all traces of impurities subsequent to acid cleaning. Instead, it is at least necessary to boil the water for a half hour in the vial.

Experiments were also carried out to determine if the cleaning procedure itself was adequate. Many

Table I. Effect of rinsing treatment on removal of acids from ampoules

linse No.	Conditions	Water resistivity, megohm-cm
0	Original water	2
4	e e	0.035
5		0.2
6	All rinses through No. 10	0.3
7	in ampoule for 10 sec.	1.0
8	entro transmissione de la companya d	1.5
9		1.8
10		2
11	Boiled for ½ hr	0.8
12	10 sec	2
13	Boiled for 1-1/2 hr	1.8
14	10 sec	2
15	10 sec	2

variations were tested, such as treating different ampoules with HF only, HF followed by agua regia, or aqua regia alone, using nondistilled acids, eliminating the acetone rinse, etc. It was noted that a scouring agent such as "Ajax" should be avoided since it is not dissolved by aqua regia. Variations were also attempted in the handling of the elements such as weighing out and transferring gallium as a liquid rather than a solid (2), the use of filter paper instead of "Glassine" paper, and plastic instead of stainless steel forceps. Despite all of these variations. no difference could be seen in the properties of the resulting GaAs. The conclusion can be drawn that the cleaning procedure used for quartz and the handling techniques for the elements are not significant variables compared to contamination sources described in the sections to follow.

# Effects of Vacuum Baking and Sealing

During the vacuum annealing of the gallium and arsenic to remove oxides and the subsequent sealing of the evacuated ampoules, there are several ways in which contamination might occur. The three which have been investigated are back diffusion of impurities from the vacuum pump, reaction between gallium and the quartz boat during bakeout, and evolution of material from the quartz while it is being sealed.

Contamination from vacuum pumps .- Both oil and mercury diffusion pumps have been used in the preparation of GaAs ampoules, and no significant difference was noted in the purity of the resulting GaAs. On certain occasions, the vacuum pumps have been cleaned or new vacuum pumps have been used. In general, this has caused no improvement in the properties of the GaAs, except on one occasion (2). In this case, a series of crystals were produced with electron mobilities on the average below 4000 cm<sup>2</sup> v<sup>-1</sup> sec<sup>-1</sup>. Many variations were attempted, but the mobilities did not improve until the mercury diffusion pump was dismantled and cleaned. The resulting change in the mobility is shown in Fig. 2. The points with the attached bars indicate crystals of GaAs produced from the same lots of gallium and arsenic. Not all crystals grown are included in the graph, because some were doped or else grown under special conditions. The importance of a clean vacuum



Fig. 2. Electron mobility of GaAs crystals before and after cleaning of the mercury diffusion pump.

system is manifest from these results. However, this result is somewhat surprising since the system was producing vacuums of the order of  $10^{-6}$  torr both before and after the cleaning. At this pressure, the number of residual gas molecules in the ampoule is about  $10^{15}$  while the change in properties corresponds to  $10^{17}$  atoms or more. It would appear that material was continuously diffusing back from the pump through the trap and condensing on the walls.

In further tests of the effects of vacuum systems, the vacuum grease in the ball and socket joints used to attach the cold trap and growth ampoule to the vacuum system was replaced by black vacuum wax. This wax does not have a tendency to flow out of the joint into the system and reportedly has a vapor pressure of only  $10^{-s}$  torr at room temperature. However, this substitution did not improve the purity of GaAs prepared with this vacuum system.

Vacuum baking of gallium.—The next possibility is that gallium might react with the quartz boat during the vacuum anneal and become contaminated. especially with silicon. Gallium is known to react with quartz readily at higher temperatures (3), so there was reason to suspect that this reaction might also be occurring a 650°C to a significant extent. To test this possibility, gallium samples were subjected to the same annealing conditions used in preparing an ampoule, except that the annealing time was increased to 12 hr from the usual 3 hr to exaggerate any effects. Changes in the impurity content of the gallium were determined by emission spectrographic analysis before and after the anneal. In each case, several samples were analyzed, and the reported impurity concentration is the geometric mean of the results. This averaging process was necessary, since the spectrographic analysis was semiquantitative and accurate to within only a factor of three. To differentiate between bulk contamination of the gallium and impurities which collect on, or segregate to the surface of the gallium, two types of samples were taken for analysis. The first consisted of pieces from the interior of a 5g ingot of gallium, obtained by fracturing the ingot. The other type was a piece of gallium small enough to be used directly in the spectrograph, thus including the entire original surface. The samples were treated simultaneously in a suitably compartmented boat. Table II shows the results

Table II. Impurities introduced during the vacuum baking of gallium in guartz

Gallium treatment	Type of sample	No. of samples	Spectro Si	ographic ontent ir Mg	imp ppn Fe	urity Cu
As received		5	<0.1	0.3	2	<1
12 hr at 650°C, pressure of 3 $ imes$ 10 <sup>-6</sup> torr	interior exterior	2 3	${<}0.1 < 0.1$	0.2 0.3	$1 \\ 2$	2 3
12 hr at 650°C, pressure of 5 × 10 <sup>-5</sup> torr (air leak)	interior exterior	2 3	1 5	<0.1 0.5	2 3	<1 1

of such a heat treatment on the gallium using both a tight vacuum system and one with a small air leak. It can be seen that no detectable silicon contamination occurs due to the baking process at 650 °C provided there is no oxygen present. However, one of the oxides of gallium apparently attacks quartz at this temperature. It can also be seen that there is no evidence for iron and magnesium contamination, but that the copper content is increased. The copper could be leached from the quartz boat, since quartz is known to contain copper that easily diffuses out (4). Since copper has a small distribution coefficient in GaAs, this source of contamination has little effect on the electrical properties of the grown crystals.

Sealing of the ampoule.—During the sealing of the ampoule the quartz is heated above its softening point. The quartz vaporizes with some decomposition at these temperatures and redeposits in part on cooler portions of the quartz as manifested by the appearance of a rough white film. The decomposition products include oxygen (5) which could enter the ampoule, as could the gases from the oxy-hydrogen flame. Thus, the sealing procedure might first introduce gaseous impurities into the ampoule; second, directly contaminate gallium or arsenic within the ampoule; and third, contaminate the inner ampoule walls and thereby contaminate the arsenic vapor during growth.

The first possibility was investigated by attaching a thermocouple gauge to a quartz ampoule, which was subjected to the same cleaning and vacuum baking process used for growth ampoules. After sealing of the ampoule, the pressure in the ampoule was below the  $10^{-3}$  torr detection limit of the gauge, indicating that a total of less than about  $5 \times 10^{15}$  gas molecules are trapped in the ampoule due to the sealing process. This represents a comparatively negligible amount of contamination in the GaAs crystal, which is usually about 4 cm<sup>8</sup> in volume.

The possibility of direct deposition of decomposition products onto the gallium was investigated by preparing an ampoule containing a compartmented boat with both large and small gallium samples similar to the experiment described in the previous section. After the usual vacuum baking and freezing, the quartz ampoule was sealed at a point beyond the boat and vacuum pump. Thus, if there were a flow of material toward the vacuum pump, it would enhance the effects of deposition. Subsequent to the sealing, the samples were spectrographically analyzed. Results are shown in Table III, which also includes reTable III. Impurities introduced during the sealing of an ampoule

	No. and type of	Spectr	ographic	impu	rity
Material and treatment	sample	Si	Mg	Fe	Cu
Gallium (as received)	5	< 0.1	0.5	3	<1
Gallium (after vacuum	2	< 0.1	1	nd	1
bake and sealing)	interior				
	3	< 0.1	1	1	1
	exterior				
Arsenic (as received)	3	0.1	< 0.1	nd	nd
Arsenic (after vacuum bake and sealing)	3	<0.1	nd	nd	nd

sults for a similar experiment with arsenic. The analysis of the interior samples of gallium indicates that no accidental introduction of impurities occurred during the vacuum baking within the limits of error. It can be concluded, therefore, that direct deposition of impurities onto the elements is not a significant source of contamination.

The third experiment on the sealing of quartz tubing dealt with the possibility of the deposition of impurities on the ampoule walls from the sealing operation with subsequent contamination of the arsenic vapor during crystal growth. The procedure was again designed to duplicate the conditions prevailing in the growth of GaAs. A 20 mm bore quartz ampoule, cleaned in the usual manner, was degassed in vacuum for 2 or 3 hr at 700°C, cooled, and about 0.3g of arsenic was then introduced without breaking the vacuum. This amount of arsenic was calculated to be just sufficient for complete vaporization. After vacuum baking to remove arsenic oxides, the ampoule was sealed under vacuum and placed in a twozone furnace for periods of about 16 hr with the sealed end held at 1220°C and the opposite end at 600°C. After this treatment, care was taken to cool the ampoule slowly and at the cooler end first. In this manner the arsenic condensed in the form of lumps, rather than as large area thin sheets. The condensed arsenic was recovered by breaking the ampoule. Changes in the impurity content of the arsenic were determined by spectrographic analyses before and after this exposure to quartz. In all cases, the arsenic starting material was found to contain only two impurities: copper at or below the detection limit of 1 ppm, and silicon at or below 0.2 ppm. For each run, four samples of arsenic were analyzed. The reported impurity concentration represents the geometric mean of the four results.

The typical contamination of arsenic that is observed due to the sealing is shown in the first two rows of Table IV for two separate runs. A large in-

Table IV. Effect of sealing quartz on contamination of arsenic after heating at 1220°C for 16 hr

No. of seals

crease in both the silicon and copper content of the arsenic can be seen. To try to enhance this effect, several runs were made in which multiple seals were performed on the ampoule, each seal being made closer to the arsenic. The results of one such run using 6 seals is shown in the third row. The absence of a proportional increase in the contamination is probably caused by much of the vaporized material depositing very close to the seal, so that most of the contamination comes from only the last seal.

In the above experiments the possibility existed that the arsenic simply attacked the quartz walls, and the contamination was not related to the sealing process. To test this possibility, ampoules were constructed with the 20-mm bore quartz ampoule terminating with 6-mm bore tubing. Much less heating is required to seal 6-mm bore quartz tubing than 20-mm bore tubing so less quartz is vaporized. As shown in Table IV in the last two rows, this reduces the arsenic contamination to below the limits of detection.

Next, the effect of temperature on the above reaction was investigated. To exaggerate any effects so that they could be easily observable, four to five seals were made on the 20 mm bore tube for each run. The sealed end of the ampoule was held in different runs at 700°, 1000°, and 1220°C while the opposite end was held at 600°C. The improve reliability, separate runs were made two or three times at each temperature. The results in Table V represent geometric averages of 8 or 12 analyses. The usual contamination discussed previously is shown in the first row. It can be seen that reducing the temperature to only 1000°C is not sufficient to remove the contamination completely; and to do so, a temperature as low as 700°C must be employed.

Although contamination due to sealing of quartz has been demonstrated, no unambiguous effect of sealing has been noted on the electrical properties, indicating that other sources of contamination are more important.

# **Contamination during Crystal Growth**

Gaseous impurities from quartz.—In general, it is known that fused quartz can release considerable quantities of gases when heated, and is quite permeable to both helium (6) and hydrogen (7) at elevated temperatures. The latter fact suggests that atmospheric gases might also diffuse through the quartz ampoule at the melting temperature of GaAs. Therefore, the effect of both diffusion through and desorption from quartz has been investigated at temperatures used during GaAs crystal growth.

The literature on the diffusion of gases other than  $H_2$  and He through fused quartz is conflicting, and does not include studies above 1000°C. T'sai and

Table V. Contamination of accoria at various tomosouthers due

Quartz bore,		Spectrograph analysis, ppr Si	n n Cu	to sealing of 20-mm bore quartz tubing				es que
	20	3	4	No. of runs	No. of seals	Temp, °C	Spectro analys Si	ographic is, ppm Cu
	20	4	9	•	F	1990		
	20	10	1	3	5	1220	4	3
	6	0.05	<1	3	4	1000	1	1
	6	0.2	1	2	4	700	0.1	1

Hogness (7) report no observable diffusion of air through quartz at 1000 °C. Nevertheless, based on Barrer's (8) data, Dushman (9) calculates a permeability rate for  $N_2$  at 1100 °C high enough to allow over 10<sup>19</sup>  $N_2$  molecules to enter an ampoule during a routine crystal growth. However, Barrer's work failed to take account of the outgassing of quartz. In order to distinguish between diffusion and degassing as the source of this gas, experiments were conducted with an apparatus similar to that of T'sai and Hogness (7).

The present apparatus consisted of two fused quartz tubes, one inside the other and so connected that the outer one could be either evacuated or open to the atmosphere. The inner tube was connected to a thermocouple gauge and to a diffusion pump by means of a stopcock. After the inner tube was evacuated with the diffusion pump, the stopcock was closed and the rate at which the pressure increased in the inner tube was measured. Every 12 hr the stopcock was again opened, and the process repeated. In this way the rate at which gas collected in the inner tube was obtained when it was alternately surrounded by air and by vacuum for these 12-hr periods. A temperature of 1200°C was used throughout, because it is the maximum temperature to which an evacuated fused quartz tube can be heated in air for several hours without collapsing.

The typical results of one of these experiments are shown in Fig. 3. The units of the ordinate are chosen to correspond to the maximum area of fused quartz that is heated above the melting point of GaAs in a routine crystal growth. It can be seen that the rate at which gas is collected is independent of whether there is air or vacuum around the tube. Thus, the amount diffusing through the walls is below the detection limit of the experiment, which is estimated to be 2 x 10<sup>15</sup> molecules hr<sup>-1</sup>. Furthermore, the fused quartz used in these tests was about 1/2 as thick as that used in a standard growth ampoule. It is also noteworthy from Fig. 3 that the rate of evolution decreases exponentially with time, which is not to be expected for the general case of the permeation of gases through a wall from a relatively large source



Fig. 3. Time dependence of the rate of gas evolution from fused quartz at 1200°C.

Table VI. Outgassing of quartz for 16 hr at indicated temperatures after various treatments

Drobalting	t tracting out	Outga	assing
Time, hr	Temp, °C	Temp, °C	molecules
3	650	1200	$7 imes 10^{13}$
1	350	650	$2 imes 10^{12}$
40	1100	1200	$3 imes 10^{12}$
40	1200	1200	$2 imes 10^{17}$
80	1200	1200	$8  imes 10^{16}$
100 hr at 1	1200°C, ex-	1200	$2 imes 10^{12}$
posed to a	air at 25°C,		
then 3 hr	at 650°C		

such as the atmosphere. Nevertheless, this type of behavior was always observed. Thus, the diffusion of gases through the quartz walls during crystal growth is not considered an important source of contamination of GaAs.

To determine the number of molecules entering the ampoule during the usual 16-hr growth period due to the desorption, apparatus similar to that previously described was used but with no outer tube. Results are shown in Table VI. In the first line is shown the number of gas molecules desorbed from the section of the ampoule containing the gallium. The second line gives the molecules desorbed from the arsenic end of the ampoule. Therefore, a total of nearly 10<sup>16</sup> molecules of gases enter the growth ampoule, which could dope a 20g GaAs crystal to a level of roughly 3 x 10<sup>17</sup> cm<sup>-3</sup>.

The effect of predegassing at 1100° and 1200°C is shown by the data in the third and fourth lines in Table VI. It can be seen that predegassing is not very effective since the rate of degassing is quite slow, which is also indicated by the data in Fig. 3. As would be expected, predegassing at the higher temperature is always more effective. The fraction of the total degassing that is due to adsorbed gases as compared to absorbed gases is indicated in the final two lines of Table VI. Prebaking the ampoule at 1200°C for 80 or 100 hr reduces the evolution of absorbed gases to below 10<sup>17</sup> molecules. Subsequently, a short exposure to the air will introduce  $2 \ge 10^{17}$  adsorbed molecules, which is a sizable fraction of the total number of molecules desorbed from quartz that has not been prebaked. Therefore, quartz ware that has been prebaked and subsequently exposed to air will still introduce significant contamination during GaAs growth.

A preliminary mass spectrometric analysis of the gases evolved from quartz *in vacuo* has been obtained by Honig (10). His results were reported as percentage of the total gas evolved at 600° and at 1150°C. The analysis at 1150°C was obtained after the quartz had been prebaked in vacuum at 1200°C for about 1 hr. The amount of helium evolved was not investigated. Results are given in Table VII. In accord with these results is the separate observation that most of the gas evolved at 600°C can be condensed at liquid nitrogen temperature, while very little of the gas evolved at 1200°C is thus condensible. Even if one assumes that hydrogen is not harmful to GaAs, there is still a total of 3 x 10" molecules

Table VII. Composition of gases evolved from fused quartz in Vacuo at 600° and 1150°C

Component	Percentage at 600°C	Percentage at 1150°C
H,O	68.7	17.5
CÕ	8.2	7.5
$CO_2$	5.5	3.0
H,	5.0	71
$\tilde{\mathbf{HF}}$	4.5	·
NO	2.2	
N.	2.0	0.8
$O_2$	1.6	0.2
HC1	1.4	
$BF_3$	0.8	
SiF.	0.1	

Table VIII. Impurities introduced into GaAs during crystal growth

			Spectro	graphicall	y det. im	o., ppm
	Samp	le	Si	Mg	Fe	Ĉu
Gallium	(as	received)	< 0.1	0.5	3	1
Arsenic	(as	received)	< 0.1	0.1	_	1
GaAs	0	Front	3	1	_	1
		Middle	1	0.3	_	<1
		Tail	10	1		10

of water vapor and  $7 \ge 10^{16}$  molecules of carbon monoxide introduced into the growth ampoule due to the desorption from both its sections. In addition, it has been found that the presence of arsenic in the reaction tube will increase by an order of magnitude the number of molecules of the major species of gaseous molecules found in the growth ampoule (11). To determine the effect of these impurities on the electrical properties, growth procedures must be devised to eliminate this source of contamination so as to provide control samples.

Contamination from the boat.—It has been previously found (1) that silicon is the main donor in GaAs, and tests have shown that the major source of silicon contamination is due to a reaction of molten GaAs with the quartz boat. The type of contamination that occurs is shown in Table VIII. The crystal was grown with a maximum temperature in the range  $1265^{\circ}-1275^{\circ}C$ . It is seen that both copper and silicon are introduced; however, the copper segregates to the tail end of the crystal due to its small distribution coefficient. There is also some evidence for a little magnesium contamination.

The contamination shown in Table VIII is not due to the sealing process, since it depends strongly on relatively small variations of the growth temperature. The effect of the maximum temperature to which the melt is heated is shown in Table IX. It can be seen that higher growth temperatures simultaneously increase the electron (or silicon) concentration and decrease the electron mobility. The scatter in the data in Table IX is due in part to the use of nonuniform preparative techniques for all of the crystals. It should be remembered that in these tests 16-hr growth periods were used, so that the melt remained at or near the elevated temperatures for periods of several hours. An extremely rapid change in the stability of quartz at these temperatures is also manifest by the amount of devitrification of the

Table IX. Properties of n-type GaAs crystals grown at various temperatures

Maximum	300°	к	78°K		
growth		μ (cm <sup>2</sup> v <sup>-1</sup>		$\mu$ (cm <sup>2</sup> v <sup>-1</sup>	
temp, °C	n (cm-3)	sec-1)	n (cm-3)	sec-1)	
	$3.4 imes10^{17}$	2210	$2.8 imes10^{17}$	2290	
	$2.5 \times 10^{17}$	3300	$2.4 imes10^{17}$	2880	
1265 to 1275	$1.4 \times 10^{17}$	3500	$1.1 \times 10^{17}$	3960	
	$1.6 \times 10^{17}$	3650	$1.5 \times 10^{17}$	3950	
	$3.7 imes10^{17}$	3790	$2.5 imes10^{\scriptscriptstyle 17}$	3680	
	$1.4 imes10^{17}$	4100	$1.3 imes10^{\scriptscriptstyle 17}$	4250	
1255 to 1265	$2.6 imes10^{17}$	3700	$2.4 imes10^{17}$	3700	
	$6.5 imes10^{16}$	4000	$5.0 imes10^{16}$	5470	
	$9.3 imes10^{16}$	4550	$7.5 imes10^{16}$	5300	
	$4.1 \times 10^{16}$	4850	$3.4 imes10^{16}$	7250	
1250 to 1255	$2.8 \times 10^{16}$	4320	$2.1 imes10^{16}$	7460*	
	$5.4 \times 10^{16}$	5300	$4.3 \times 10^{16}$	7850*	
	$5.9 imes10^{16}$	4550	$4.8 imes10^{16}$	5200	

\* Grown at higher speeds.

quartz ampoule. After a 16-hr run at  $1270^{\circ}$ C, the devitrification is so bad that the quartz becomes opaque; while at  $1250^{\circ}$ C devitrification causes only slight clouding. It can be concluded that reaction of the GaAs melt with the quartz boat constitutes the major source of contamination.

# Conclusions

A study has been carried out of the contamination introduced during the preparation and growth of GaAs by the horizontal Bridgman technique in a quartz ampoule and quartz boat. The major source of contamination, especially with silicon, is due to reaction of the GaAs melt with the boat. Contamination with silicon and copper has also been observed during sealing of the quartz ampoules, with copper during vacuum baking of gallium, and with water vapor and carbon monoxide during growth due to outgassing of quartz. Contamination has also been observed to occur due to back diffusion of impurities from a vacuum system.

Atmospheric gases were not observed to diffuse through quartz at the growth temperature, and the cleaning procedures used for the quartz had no significant effect on the properties of GaAs. No direct reaction of gallium with the boat was observed during vacuum baking at  $650^{\circ}$ C.

To reduce the contamination of GaAs crystals, it is most important to control the reaction of the melt with the boat. As a first step in this direction, the melt temperature must be maintained as close as possible to the melting point and the crystal grown in a short time. In addition, other boat materials such as BN, AlN, BeO, etc., might prove to be more suitable than quartz if they can be made ultrapure and impervious. To minimize the outgassing of the quartz ampoule, the ampoule should be maintained well below 1000°C by employing heating methods such as r.f. induction. The high vacuum pumps used in processing the ampoules should be cleaned at regular intervals. Finally, alternative growth procedures might be investigated, in which lower temperatures are employed, such a growth from solution, or from the vapor phase.

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# Polarization Curves of Redox Systems Involving Consecutive Electron-Transfers: Some Theoretical Aspects

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## ABSTRACT

An equation, first worked out by Vetter, describing the complete polarization curves for redox systems involving two consecutive electron transfer steps, has been examined in detail by computer solutions. It is shown that quite wide variations in the values of the individual transfer coefficients have little effect on the shape of the theoretical curves. However, as the ratio of the individual exchange currents approaches 100:1, two definite linear-logarithmic regions appear in one branch of the curve. It is further shown that in many cases the diffusion current masks the true Tafel portion, leaving the "pseudo-Tafel" part as the only observable linear-logarithmic region.

In one of a series of papers (1, 2-9) describing the use of reaction order methods in determining mechanisms of electrode reactions in redox systems, Vetter derived an equation which describes the theoretical polarization curves for a redox system which proceeds by two consecutive electron transfer steps. The conditions and assumptions for the applicability of his equation are the usual constancy of activity coefficients, compression of the double layer to constant and nearly negligible zeta potential, suppression of the transference number of the reacting species, etc. Most of these conditions, it should be noted, are accomplished by addition of a large excess of inert electrolyte to the system. There is, however, one additional assumption in this particular case, *i.e.*, that the actual electrode reactions involve the transfer of only one electron between individual solution species. For an over-all electrode reaction  $A + 2\epsilon \rightleftharpoons C$ , the reaction scheme thus can be formulated:

$$A + e \rightleftharpoons B \qquad [1]$$

 $B + e \rightleftharpoons C$  [2]

Each of these reactions is characterized by its own transfer coefficient,  $\alpha_1$  or  $\alpha_2$ , and by its own exchange current,  $i_{0,1}$  or  $i_{0,2}$ .

This assumption excludes reactions which involve simultaneous electron transfer and molecular combination, such as

$$A + H' + e \rightleftharpoons HA \qquad [3]$$

It does not exclude purely chemical equilibrium reactions involving any of the substances in Eq. [1] and [2], provided only that they are rapid equilibria. The over-all reaction can thus include other species which do not enter into the actual electron transfer processes. A notable example is the quinone/hydroquinone system, in which the over-all reaction involves hydrogen ion and a two electron transfer, while the electrode reactions, according to Vetter (10), involve single electron transfers in which hydrogen ion does not participate.

For the conditions as stated, then, the equation which describes the complete polarization curves for a system which proceeds by the two consecutive transfer steps 1 and 2 above is given by Vetter as

$$\frac{i}{2} = \frac{\exp(\alpha_1 + \alpha_2) \frac{\mathbf{F}\eta}{RT} - \exp\left[-2 + (\alpha_1 + \alpha_2)\right] \frac{\mathbf{F}\eta}{RT}}{\frac{1}{i_{\alpha,2}} \exp\alpha_1 \frac{\mathbf{F}\eta}{RT} + \frac{1}{i_{\alpha,1}} \exp\left[-(1-\alpha_2)\right] \frac{\mathbf{F}\eta}{RT}}$$
[4]

In this equation *i* is the net external current and  $\eta$  the overvoltage. Both *i* and  $\eta$  are positive for anodic, negative for cathodic, polarization. It should be noted that the factor 2 (in *i*/2) does not appear in the original article (1), but was introduced as a correction in a subsequent note (11).

Vetter examined this equation in the four simplified forms to which it reduces when one assumes  $\eta$  "large and positive,"  $\eta$  "large and negative," when  $i_{o,1} = \infty$ , and when  $i_{o,2} = \infty$ . From this examination he has drawn the following three conclusions, which may be used as criteria for the existence of two consecutive electron transfer steps in the reaction mechanism:

1. Since  $\alpha_1$  will not generally be equal to  $\alpha_2$ , the slopes of the anodic and cathodic linear-logarithmic regions which occur at high overvoltages will not add up to 1, as they must for a single transfer step  $[\alpha + (1-\alpha) = 1]$ .

2. Extrapolation of the linear-logarithmic regions to  $\eta = 0$  will give two values of exchange current. Because of the factor 2 mentioned above, the values at the intercept are actually  $2i_{o,1}$  from extrapolation of the cathodic branch and  $2i_{o,2}$  from extrapolation of the anodic branch.

3. For either exchange current equal to infinity, the linear-logarithmic regions extrapolate to the exchange current characteristic of the slower step, but exhibit slopes which add up to 2 instead of 1.

In a research program designed to extend Vetters' reaction order methods to organic systems somewhat more complicated than the quinone-hydroquinone case, some of the experimental results (which will be presented in subsequent papers) led to the conclusion that an exchange current ratio in the range 1-1000 was a more practical case than a ratio of infinity. As a matter of fact, it seems reasonable that the large majority of electrode systems of this type will involve exchange current ratios up to perhaps only 100, from which it follows that a detailed examination of Eq. [4] in these regions is desirable. With the use of modern computers, such an examination is actually rather straightforward, and can even be extended to the general case of n electron steps with little additional effort.

# Solutions of Eq. [4] at Intermediate Exchange Current Ratios

Visual examination of Eq. [4] reveals that, regardless of the magnitudes of the two exchange currents, there exists a value of  $\eta$  sufficiently large and positive to justify neglecting the second term in both numerator and denominator. The same holds true for the first terms for  $\eta$  large and negative. However, it is also apparent that the criterion for  $\eta$  sufficiently large in either direction to justify dropping of terms is dependent on the values of the exchange currents. The same reasoning process holds true for dropping either term in the denominator on the basis of a "sufficiently large" value of either exchange current.

The questions which can be answered, then, by complete solutions of the equation are:

1. For various magnitudes and ratios of the two exchange currents, what values of overvoltage are required to put one in the linear-logarithmic region, i.e., Vetter's limiting cases?

2. What is the character of the polarization curves in the intermediate overvoltage regions (40-300 mv) when the exchange current ratio is large, but not infinite?

A computer program was established to obtain values of *i* as a function of  $\eta$  as  $\eta$  ran the series 1, 2, 4, 7, 10, 20, 40, . . . *etc.*, mv. Solutions were cut off at 2v. Exchange current densities of various values and various ratios were used through the range  $10^{-7}$ to  $10^{-4}$  amp/cm<sup>2</sup>. Transfer coefficients of 0.2, 0.4, 0.5, 0.7, and 0.8 were used in various combinations. Plots were made of log *i* vs.  $\eta$  for the complete polarization curves and of *i* vs.  $\eta$  in low overvoltage ranges (0-50 mv). Although literally dozens of such curves have been obtained (the limiting factor is the time required to plot the data), only the more significant are presented here.

Figure 1 shows the complete polarization curves for  $\alpha_1 = \alpha_2 = 0.5$ , with  $i_{0,2}$  fixed at  $10^{-4}$  amp/cm<sup>2</sup> and  $i_{o,1}$  varying. Note that an average value for a diffusion limited current density in well stirred  $10^{-2}N$ solutions (conditions used in the experimental work for this program) is about  $10^{-2}$  amp/cm<sup>2</sup>, which is indicated by the horizontal dashed line in the figure. The most interesting part of the curve is the progression on the anodic side as the cathodic exchange current decreases. At a ratio of  $i_{0,1}/i_{0,2}$  of 100, a welldefined linear-logarithmic region covering nearly two orders of magnitude appears and becomes even more distinct and extended as the ratio increases. This branch of the curve thus contains two linearlogarithmic regions, the true Tafel region at values of overvoltage above about 250 mv, and a "pseudo-Tafel" region at the lower values. For  $\alpha_1 = \alpha_2 = 0.5$ the slope of this pseudo-Tafel region varies between about 1.0 at the lowest ratio of exchange currents (50-100) at which it is observable, and 1.5 at the



Fig. 1. Theoretical current-voltage characteristics of redox system with two consecutive electron transfers, varying  $i_{0,1}$ .

limiting case of one exchange current equal to infinity.

The difficulties to which the existence of this "pseudo-Tafel" region can lead are illustrated by Fig. 2 and 3. Figure 2 is a redrawn portion of Fig. 1 with the approaches to the limiting current densities sketched in as would be observed in an actual experiment. It is apparent that the true values of anodic exchange current and anodic transfer coefficient are completely obscured. Figure 3 is an actual experimental curve obtained with platinum electrodes in a 10-3M toluguinone-10-2M toluhydroguinone system. The measured cathodic  $\alpha$  from these data is -0.49, an entirely reasonable value, but the measured slope of the well-defined linear-logarithmic region in the anodic curve corresponds to an apparent anodic  $\alpha$  of 1.2. The similarity of these curves to the theoretical curves of Fig. 2 is not of itself sufficient proof of the existence of consecutive electron transfers and a "pseudo-Tafel" region. Curves which show two welldefined linear-logarithmic regions below the limiting current, plus agreement between the exchange current ratios and transfer coefficients would constitute unequivocal proof.

Curves obtained by using values of  $\alpha_1$  and  $\alpha_2$  other than 0.5 are quite similar to those of Fig. 1, except for the slopes in the true Tafel region. It is interesting to note that if from actual data one true Tafel slope and one exchange current are known, as will usually be the case, a fair prediction of the other exchange current and the other transfer coefficient can be obtained by comparison with the various theoretical curves. The accuracy of such a prediction is markedly dependent on the accuracy of the polarization data in the pseudo-Tafel region.

As in most electrode kinetic studies, additional information about the nature of the electrode reactions can be obtained from data very near the reversible potential. Differentiation of Eq. [4] with respect to  $\eta$  and determination of  $(d\eta/di)_{i=0}$  yields



Fig. 2. Theoretical curves at exchange current ratio of 100 (from Fig. 1) with limiting diffusion current of 10<sup>-2</sup> amp/cm<sup>2</sup> superimposed.

$$\frac{4\mathbf{F}}{RT}\left(\frac{d\eta}{di}\right)_{i\to 0} = \left(\frac{1}{i_{0,1}} + \frac{1}{i_{0,2}}\right) \qquad [5]$$

Vetter denoted this quantity by  $1/i_*$  and used it to check the values of individual exchange currents obtained by extrapolation in his quinone/hydroquinone paper.

Plots of the computer calculations in the low overvoltage regions (+20 to -20 mv) show that the curves pass through the origin at the slopes predicted by Eq. [5], and that variations in  $\alpha$  values tend to spread the curves apart somewhat in this region, but probably not enough to make firm determinations of  $\alpha$ . Figure 4 is a plot for  $i_{o,1} = i_{o,2} = 10^{-4} \text{ amp/cm}^2$ , and for five different combinations of  $\alpha_1$  and  $\alpha_2$ . Figure 5 is a similar plot for  $i_{o,1} = 10^{-4}$ ,  $i_{o,2} = 10^{-5} \text{ amp/cm}^2$ . It is notable that even at this small ratio of exchange currents, the plots possess a definite curvature at the



Fig. 3. Experimental polarization curves for  $10^{-s}M$  toluquinone,  $10^{-s}M$  toluhydroquinone.



Fig. 4. Theoretical low current density polarization curves, two consecutive electron transfers, equal exchange currents.

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Fig. 5. Theoretical low current density polarization curves, two consecutive electron transfers, exchange current ratio equals ten.

origin, while at  $i_{\circ,1} = i_{\circ,2}$  they pass through the origin in a straight line. This curvature persists at the higher ratios of exchange currents, but does not become significantly more pronounced. For values of  $i_{\circ,2} > i_{\circ,1}$ , the curvature is an exact mirror image of Fig. 5.

Examination of Eq. [5] reveals that the value of  $i_{o}^{*}$  obtained from the slope at the origin can be obtained by many combinations of perfectly reasonable values of  $i_{0,1}$  and  $i_{0,2}$ . If values of the individual exchange currents as obtained by extrapolation of Tafel regions combine in the manner of Eq. [5] to give close agreement with the measured  $i_0$ \*, then certainly the extrapolated values merit a greater confidence. However, in those cases where one exchange current is about 100 times larger than the other (the condition, incidentally, which leads to the pseudo-Tafel region of Fig. 1 and 2), the larger exchange current no longer has any influence on i.\*. For cases of this type, the combination of curvature in the lowovervoltage region and a greater than usual slope in the linear-logarithmic region, or, even more convincing, two linear-logarithmic regions in one branch of the curve, will lead one to expect a large ratio of exchange currents. It would then be hoped that further experiments could be designed to ferret out the elusive electrokinetic parameters.

# General Solution for *n* Consecutive Steps, with Some Solutions for the Three Electron Case

The solution for the general case of n consecutive electron transfer, represented as

$$S_{1} + e \rightleftharpoons_{k_{2}} K_{2} = - - - - \text{ with } \alpha_{1} \text{ and } i_{\alpha,1}$$

$$S_{1} + e \rightleftharpoons_{k_{2i-1}} S_{i+1} = - - - \text{ with } \alpha_{i} \text{ and } i_{\alpha,i} \quad [6]$$

$$K_{2i} = k_{2i}$$

is obtained by solving simultaneously a group of equations of the form

$$\frac{i}{n} = k_{2i} C_{s_{i+1}} \exp \frac{-\alpha_i \mathbf{F} \epsilon}{RT} - k_{2i-1} C_{s_i} \exp -\frac{(1-\alpha_i) \mathbf{F} \epsilon}{RT \quad [7]}$$

With the exchange current expression

$$i_{v,i} = k_{zi} \overline{C}_{s_{i+1}} \exp rac{lpha_i \mathbf{F} \boldsymbol{\epsilon}_o}{RT} = k_{z^{i-1}} \overline{C}_{s_i} \exp -rac{(1-lpha_i) \mathbf{F} \boldsymbol{\epsilon}_o}{RT}$$
[8]

Equation [7] reduces to

$$\frac{i}{n} = i_{o,i} \left[ \frac{C_{s_{i+1}}}{\overline{C}_{s_{i+1}}} \exp \frac{\alpha_i \mathbf{F} \eta}{RT} - \frac{C_{s_i}}{\overline{C}_{s_i}} \exp - \frac{(1-\alpha_i) \mathbf{F} \eta}{RT} \right]$$
[9]

The barred concentrations are the equilibrium concentrations (at the reversible potential) of the intermediate substances; the unbarred concentrations are those at the electrode surface during current flow. In the absence of concentration polarization, the ratios  $C_{s_1}/\overline{C_{s_{n+1}}}$  are unity. Therefore n-1 variables exist besides *i* and  $\eta$  in the *n* equations. These n-1 variables can be eliminated by simple determinantal solution. To simplify expression of the determinant, let

$$\mathbf{F}_1 \equiv \mathbf{n} \exp \frac{-\alpha_s \mathbf{F} \eta}{RT}$$
[10]

$$\mathbf{G}_{2} \equiv -n \exp{-\frac{(1-\alpha_{i})\mathbf{F}\eta}{\mathbf{RT}}} \qquad [10']$$

$$X_i = C_{s_i} / \overline{C_{s_i}}$$
 [11]

Equation [9] then forms a system of n linear equations with i and  $X_i$  as unknowns. The general solution for i can be written as

i = N/D

where



Fig. 6. Theoretical polarization curves—three consecutive electron transfer steps,  $i_{\rm o,2}$  varying.

Evaluating the indicated determinant and substituting back for  $F_i$  and  $G_i$  from Eq. [10] and [10'] gives the resulting general expression:

$$\frac{i}{n} = \frac{\exp\left(\sum_{j=1}^{n} \alpha_{j}\right) \frac{\mathbf{F}\eta}{RT} - \exp\left[-\left(n - \sum_{j=1}^{n} \alpha_{j}\right) \frac{\mathbf{F}\eta}{RT}\right]}{\sum_{k=1}^{n} \frac{1}{i_{o,k}} \exp\left[-\left\{(n-k) - \sum_{j=1}^{n'} \alpha_{j}\right\} \frac{\mathbf{F}\eta}{RT}\right]}$$
[12]

This equation can be put into many different forms, some of which are more convenient for examination of limiting cases and/or computation, by simply multiplying both numerator and denominator by appropriate exponential terms. One of these forms, which was used for the computer solutions of the three electron case is

$$\frac{i}{ni_{o,1}} = \left[1 - \exp\left(\frac{n\mathbf{F}\eta}{RT}\right)\right]$$

$$\frac{\sum_{j=1}^{n} \gamma_{o,j} \exp\left\{-\left[(n-j) + \alpha_{j}\right] \frac{\mathbf{F}\eta}{RT}\right\}}{i_{o,1}} \quad (13)$$

where  $\gamma_{o,j} = \frac{-1}{i_{o,j}}$  with  $\gamma_{o,1} \equiv 1$ . This represents a normalization with respect to  $i_{o,1}$ , and eliminates

many operations by introducing exchange current ratios directly.

Equation [13] was solved for n = 3,  $\alpha_1 = \alpha_2 = \alpha_3 = 0.5$ , and both  $\gamma_{0.2}$  and  $\gamma_{0.3}$  varying from 1 to 1000. The number of possible combinations of  $\alpha$  values and exchange current ratios for n = 3 is so large as to make it impractical to examine the situation in detail, although again the limiting factor is the mere plotting of the data. However, examination of only a few of the more interesting cases reveals that much the same situation prevails here as with the two electron case, *i.e.*, the appearance of pseudo-Tafel regions at intermediate ratios of exchange currents, the slopes of which approach limiting values which sum to three when a single exchange current controls. This is illustrated by Fig. 6 in which the terminal exchange currents are fixed and equal while the center exchange current ranges from 10<sup>3</sup> to 10<sup>-3</sup> of the terminal values. Essentially no effect is noted on the curves while the center reaction is faster or even of equal speed, but as it becomes slower the pseudo-Tafel regions appear and approach a slope of 1.5 on each branch. Further illustration is given by Fig. 7 in which  $i_{0,2}$  and  $i_{0,3}$  are increased until  $i_{0,1}$  controls and by Fig. 8 in which i., is made progressively smaller until it alone controls. Note that in each of these last two figures one branch of the curve exhibits a true Tafel slope of  $\pm 0.5$ , while the pseudo-Tafel slope approaches  $\pm 2.5$ , so that in all three figures the limiting slopes sum to 3, although in different manners. Note also that in each limiting case, extrapolation of both the true and pseudo-Tafel regions yields the value of the smallest exchange current. Still it is entirely plausible that both linear-logarithmic regions may be observable in some experimental systems, thereby vielding sufficient information to solve the reaction parameters completely.

There are, of course, other interesting combinations of transfer coefficients and exchange currents for the three electron case, as well as for the higher n values, but those given are sufficient for the present paper. For those who desire to examine other cases, it need be noted only that the equations are



Fig. 7. Theoretical polarization curves—three consecutive electron transfer steps,  $i_{\rm 0,3}$  and  $i_{\rm 0,3}$  varying.



Fig. 8. Theoretical polarization curves—three consecutive electron transfer steps,  $i_{o,s}$  varying.

solved readily in a matter of seconds on almost any modern computer, once a satisfactory program is established.

# Conclusion

The use of complete solutions of equations describing the particular process of consecutive electron transfers can improve materially the interpretation of experimental data over the previously used methods of approximation and limiting cases. Certainly this is true in the majority of practical systems, where intermediate values of the kinetic parameters will be prevalent, and limiting cases not often encountered. The biggest drawback to the use of such complete solutions for interpretation lies in the fact that the experimental data need to be considerably more accurate to obtain full value from comparison with the theoretical curves. As a matter of fact, it is easy to see how one can be led to a false conclusion by data which are only a few per cent in error. Nevertheless, one can also be led (and probably more often) to a false conclusion by very accurate data if it is *not* realized that perfectly sound theoretical curves describing the data exist. As the procedures for obtaining data in electrode kinetics improve in accuracy, then, it is desirable to extend the use of computers and complete solutions of the kinetic equations into those areas where only approximations and limiting cases have been used previously.

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# Cathodic Oxygen-Evolution Reaction of the Peroxo Cobalt Complex [(NH<sub>a</sub>)<sub>a</sub>CoO<sub>a</sub>Co (NH<sub>a</sub>)<sub>a</sub>]\*

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# ABSTRACT

At a bright platinum cathode in H<sub>2</sub>SO<sub>4</sub> solutions, the complex ion  $[(NH_a)_s$  CoO<sub>2</sub>Co  $(NH_a)_s]^{s_+}$  is reduced quantitatively to  $2Co^{2+}$  in a one-electron reaction, with evolution of one molecule of oxygen gas. The same products also are produced by chemical reduction with silver powder. A probable mechanism for the cathodic reduction is outlined and its applicability to chemical reduction described. A cell containing an acid solution of this cobalt complex and platinum electrodes evolves 1.25 O<sub>2</sub>/F, and may be used as an oxygen generator or as a sensitive gas coulometer.

In the course of cathodic current efficiency measurements for the oxygen-dissolution reaction, some measurements were made using sulfuric acid solutions containing the pentavalent decammino- $\mu$ peroxo dicobalt ion I.

E

There has been considerable interest in this ion in the past due to the supposed tetravalency of one of the two cobalt atoms. Recent work has shown, however, that the single unpaired electron present in I is delocalized over the grouping  $CoO_2Co$  and that the two cobalt atoms are equivalent (1).

Solutions made by dissolving the corresponding sulfate, compound II, in molar sulfuric acid are relatively stable at ordinary temperatures. We have found that oxygen did not dissolve at a platinum cathode in these solutions, but instead oxygen was evolved. Preliminary experiments indicated that one mole of oxygen was liberated per Faraday. Since cathodic oxygen-evolution reactions are virtually unknown, we have investigated this reaction in some detail.

#### **Experimental Procedures**

Materials.—The preparation of  $[(NH_{s})_{5}$  CoO<sub>2</sub>Co  $(NH_{s})_{5}]$  (SO<sub>4</sub>)<sub>2</sub>-(HSO<sub>4</sub>)·3H<sub>2</sub>O was carried out by the method of Gleu and Rehm (2). The compound was recrystallized from 1M H<sub>2</sub>SO<sub>4</sub> and air-dried at room temperature. Cobalt analysis gave a value of 17.8% (theoretical 17.77%).

Acid solutions containing II were moderately stable, but detectable changes in the visible and ultraviolet spectra occurred after long standing at room temperature (> 24 hr). Hence the solutions were prepared, without heating, immediately before use. Solid compound II was stored in a refrigerator and appeared to be stable indefinitely.

Measurements of current efficiency for oxygen evolution.—Figure 1 presents a diagram of the Pyrex glass electrolytic cell, which was designed for measurements of gas-evolution or gas-dissolution efficiency. For cathodic efficiencies the vertical plate a was made anode and the horizontal screen c was cathode. Both electrodes were of bright platinum. The former was suspended by a thin platinum wire; the latter, a screen of total geometrical area 10 cm<sup>2</sup>, was held in place by means of a gold-plated clip and rod b, the latter being sealed through the cap of the cell. The cap was joined to the body of the cell with a standard taper rubber o-ring joint.

The catholyte was separated from the anolyte by a coarse fritted glass disk d, and was stirred magnetically by means of a Teflon-covered stirrer. Stopcocks e and f, attached to the cell with o-ring joints g, permitted the gas phase above the catholyte to be flushed and pressurized with oxygen or other gas.

A glass tube of uniform cross section was used for a 13 cm length of the anode compartment at and above the reference line, ref. Changes in the height h of anolyte level above catholyte level were restricted



Fig. 1. Diagram of cell for measurement of gas-evolution or gas-dissolution efficiency.

to this region during a current efficiency measurement. The total volume of the cell up to the reference line was determined by filling the cell with water and weighing. In each experiment the volume of electrolyte was fixed at 50.0 ml, so that the gas volume in the cathode compartment was known for any value of h.

The cell was calibrated with 1M H<sub>2</sub>SO<sub>4</sub> in an atmosphere of pure oxygen, with a current of 3.60 ma (0.36 ma/cm<sup>2</sup>). A 1-hr period of cathodic pre-electrolysis was used to remove reducible impurities, after which the oxygen pressure was adjusted so that the solution level h was near the top of the uniform bore tube. The level was allowed to stabilize; then the screen electrode was made cathode again and the change of level  $\Delta h$ , for passage of a measured number of coulombs, was determined with a traveling microscope.

The number of moles  $\Delta n$  of gas dissolved or evolved is related to  $\Delta h$  through the relationship (see Appendix)

$$\Delta n = \frac{\Delta h}{RT} \left[ A \left( P_{\star} - P_{\star} \right) + V_{t} d/13.5 \right] \qquad [1]$$

Here A is the internal cross-sectional area of the anolyte tube.  $P_i$  is the initial pressure and  $V_t$  the final volume of the gas in the cathode compartment.  $P_s$  is the vapor pressure of the solution and d its density; for dilute solutions the corresponding values for the solvent may be used. When the atmospheric pressure changes during the determination, a correction to  $\Delta h$  is applied by use of Eq. [2], Appendix. Calibration of the cell involved determining A from an experimental measurement of  $\Delta h$  and the corresponding value of  $\Delta n$ , the latter derived from the number of Faradays passed. The value of A thus obtained for cathodic oxygen dissolution agreed with that similarly obtained from anodic oxygen evolution measurements within 1%.

For measurements on solutions of compound II, the cathode compartment was flushed and filled with pure argon. Otherwise the procedure used followed that of the calibration experiments, using the same current (3.60 ma) and the same pre-electrolysis period (1 hr) for each measurement.

Reduction of the  $\mu$ -peroxo compound.—The number of moles of compound II reduced at the cathode per Faraday, as well as the reduction potential, were determined in a cell similar to that of Fig. 1 but with two modifications. (A) The cap of the cathode compartment contained an opening which permitted insertion of a saturated calomel electrode of the fiber-junction type. (B) The fritted disk was of very fine porosity; and the electrolyte level as well as the gas pressure (flowing argon above the catholyte, air above the anolyte) were the same on both sides. Thus diffusion of II between catholyte and anolyte was negligible.

The concentration of II in the catholyte was determined periodically by interrupting the current and removing a sample of the solution for analysis with a Cary recording spectrophotometer. The characteristic absorption peak at 6690Å (molar extinction coefficient = 880 for solutions in 1M H<sub>2</sub>SO<sub>4</sub>) was used for concentration measurements; none of the reduction products absorb significantly at this wavelength. Each sample was analyzed without dilution using an absorption cell of path length 0.20, 1.00, or 10.0 cm, as required The sample was returned as fully as possible to the electrolytic cell after measurement.

Cathode potential measurements, made with reference to the saturated calomel electrode, were converted to the hydrogen scale.

Determination of reduced cobalt-containing species .- Solutions which were analyzed for the guantity of II cathodically reduced also were subjected to cation-exchange chromatography to separate the cobalt-containing species. The ion-exchange column used (Bio-Rad AG 50W-X8 in the hydrogen form) and its effectiveness for acid solutions of some cobalt complexes have been described by the authors in a previous paper (3). The amount of eluted  $Co^{2+}$  was determined in acetate-buffered solutions by precipitation with 8-hydroxyquinoline (2). Since it was necessary to precipitate in the presence of a large amount of inert salts, which caused errors due to coprecipitation, simultaneous runs were carried out with standard CoSO4 solutions containing similar salt concentrations. The latter results were used to apply corrections for coprecipitation.

### **Results and Discussion**

Cathodic oxygen evolution.—A saturated solution of compound II in 1.00M  $H_2SO_4$  was studied at 25.0°C (±0.01) in the cell of Fig. 1. An excess of II was added to the cell as a finely ground powder, and vigorous agitation was used. Hence the concentration of II remained close to the saturation value, 0.0035M, during cathodic reduction. Mass spectrometer analysis of the gas above the catholyte after electrolysis showed that only oxygen was evolved.

A typical curve showing the change in h (corrected for changes in atmospheric pressure) during reduction of II at constant current is presented in Fig. 2.



Fig. 2. Current efficiency determination for cathodic oxygen evolution from saturated solution of compound II in molar H<sub>2</sub>SO<sub>4</sub>, 25.00°C, 3.60 ma.

#### Table I. Experimental results for cathodic reduction of a saturated solution of Co<sub>2</sub>O<sub>2</sub> (NH<sub>8</sub>)<sub>10</sub>(SO<sub>4</sub>)<sub>2</sub>HSO<sub>4</sub> · 3H<sub>2</sub>O in IM H<sub>2</sub>SO<sub>4</sub>

	mole/F	araday
C02O2 (NH3)10 (SO4)2HSO4 reacted	1.01,	1.00
O₂ evolved	0.99,	0.97
Co <sup>2+</sup> produced	2.00,	1.99

The indicating level h exhibited an initial time lag, caused in part by the presence of the fritted disk in the cell. Cathodic oxygen evolution per Faraday calculated from the slope of the curve, however, was the same as that derived from the total  $\Delta h$  and total coulombs passed, within experimental error. It should be noted that oxygen also was evolved at the anode, but the rate of evolution and bubble size were sufficiently small that there was no difficulty in reading the meniscus level h with the traveling microscope.

The cathodic oxygen evolution from compound II was found to be one mole per Faraday, Table I.

Moles of compound II reduced per Faraday.—In the first type of experiment the current efficiency for reduction of II, as well as the cathode potential, were followed as a function of concentration, beginning with an unsaturated solution. The concentration of unreacted II was determined spectrophotometrically. The data, shown in Fig. 3, demonstrated that one mole of the compound was reduced per Faraday over the concentration range studied.

At concentrations below 0.3 mM the cathode potential was decreasing rapidly. Small amounts of a second cathodic reaction, such as oxygen reduction, could be expected in this region, but were not detectable within the accuracy of the data.

A more precise determination of the reduction efficiency was carried out in a second type of experiment in which the cathode compartment contained a saturated solution of II in 1M H<sub>2</sub>SO<sub>4</sub>, together with an



Fig. 3. Change in concentration and cathode potential during dectrolysis of an unsaturated solution of compound 11 in IM MSO, 3.60 ma, 22°C.

excess of the powdered compound. After passage of 2.7 x  $10^{-1}$ F, the contents of the cathode compartment (dissolved and undissolved) were removed. Sufficient 1M H<sub>2</sub>SO, was added to effect complete solution and the resulting solution was analyzed spectrophotometrically to determine the quantity of II reduced. The results of duplicate experiments, included in Table I, show one electron per molecule of II reacted. There was evidently no simultaneous reduction of molecular oxygen (which would require 4 electrons per molecule) at the reduction potential, which was 0.82v in these experiments.

To test the possibility that a cathode surface of greater catalytic activity might give rise to a competing reaction, the latter type of experiment was repeated with a freshly platinized platinum screen in place of the bright platinum cathode. Results under these conditions were less reproducible but a lowered efficiency for reduction of II always resulted (moles II reacted per Faraday  $\leq 0.9$ ). Possibly the highly active platinized surface catalyzed the 5-electron reduction of II to Co<sup>\*+</sup> and water.

Cobalt-containing products.—Ion-exchange separation of cathodically reduced solutions of II in 1M  $H_2SO$ , yielded only one cobalt-containing product,  $Co^{2+}$  ion. Quantitative determination of  $Co^{3+}$  showed that two  $Co^{3+}$  ions were produced per electron (Table I). Under the conditions used, 8-hydroxyquinoline precipitates only  $Co^{3+}$  and does not interact with Co(III) species (2).

Reaction mechanism.—The above results establish unequivocally the over-all cathodic reaction

 $[(\mathrm{NH}_{3})_{5} \mathrm{CoO}_{2} \mathrm{Co} (\mathrm{NH}_{3})_{5}]^{5^{*}} + 10\mathrm{H}^{+} + e$  $\rightarrow \mathrm{O}_{2} + 2\mathrm{Co}^{2^{*}} + 10\mathrm{NH}_{4}^{+} [3]$ 

as well as the absence of side reactions.

The following reduction mechanism is proposed. The pentavalent ion is assumed to adsorb on the cathode with the peroxo group attached to the metal surface. Transfer of a single electron yields the adsorbed tetravalent ion III

$$M - - - \left[ \begin{array}{c} Co - (NH_{s})_{s} \\ O_{z} \\ Co - (NH_{s})_{s} \end{array} \right]^{s_{*}} + e \rightarrow M - - - \left[ \begin{array}{c} Co - (NH_{s})_{s} \\ O_{z} \\ Co - (NH_{s})_{s} \end{array} \right]^{s_{*}}$$
[4]

By means of the internal oxidation-reduction reaction [5], III decomposes to yield adsorbed molecular oxygen and an ammine complex of Co (II)

$$M - - - \begin{bmatrix} Co - (NH_a)_a \\ O_a \\ Co - (NH_a)_a \end{bmatrix}^{4*}$$
  
$$\rightarrow M - - O_a + 2 [Co (NH_a)_a]^{2*} [5]$$

The latter is known to be unstable in acid solutions

 $[Co (NH_3)_s]^{2*} + 5H^* \rightarrow Co^{2*} + 5 NH_t^* \qquad [6]$ Thus this simple mechanism is in complete accord with the observed over-all reaction [3]. Reaction [5] requires some justification in view of results reported previously (3) for decomposition of the ion  $[(NH_s)_5 CoO_2Co (NH_s)_5]^{4+}$  in H<sub>2</sub>SO<sub>4</sub> solutions. This ion was found to decompose rapidly to yield at least eight cobalt-containing species. The data described in the previous paper (3) indicated that the first step in this decomposition involved attachment of a hydrogen ion to the peroxo group. From this it may be assumed that the attachment of the tetravalent ion III to the cathode surface prevents bonding of hydrogen ion and forces ion III to follow the simpler decomposition path of [5].

In a recent paper Vlcek (4), using a vibrating platinum cathode, showed that the reduction of  $[(NH_s)_sCoO_sCo(NH_s)_s]^{s+}$  to  $[(NH_s)_sCoO_sCo(NH_s)_s]^{s+}$  occurs reversibly in ammoniacal solutions. In ammonia, unlike acid, the tetravalent ion is relatively stable and can exist in the bulk of the solution in equilibrium with dissolved  $O_2$  and Co (II) ammines. Thus the mechanism for cathodic reduction of I in ammonia differs from that in acid in that  $[(NH_s)_sCoO_sCo(NH_s)_s]^{s+}$  can desorb from the cathode and accumulate in the ammoniacal solution.

The only other published investigation on reduction of I concerned chemical reduction with  $As_2O_s$  in  $H_sSO_4$  solutions, in the presence of  $OsO_4$  as catalyst (2). A simple over-all reduction reaction was obtained. Oxygen was evolved, and  $Co^{3*}$  was the only cobalt-containing product. Incidental to the present work we studied a second, and more convenient, chemical reduction method. This involved merely shaking a mixture of powdered compound II and excess powdered silver metal with 1M  $H_2sO_4$ . The reaction proceeds quantitatively and relatively rapidly at room temperature in accordance with the over-all change

$$[(NH_{3})_{5} CoO_{2}Co (NH_{3})_{5}]^{5+} + Ag + 10H^{+}$$
  
$$\rightarrow O_{2} + 2Co^{3+} + 10NH_{4}^{+} + Ag^{+} [7]$$

Analytical results for  $Co^{3+}$ ,  $O_2$ , and  $Ag^+$  were all in good agreement with the theoretical values from [7].

That  $Co^{**}$  is the only reduced cobalt species produced in acid by either chemical-reduction method is readily explained by generalizing the mechanism represented by [4] to [6]. For chemical reduction, the reductant [As(III) or Ag] becomes attached to the peroxo group of the pentavalent complex I. Following electron transfer the oxidized form of the reductant, which is still bonded to the peroxo group, prevents the hydrogen ion addition step which is needed to produce the more complex cobalt-containing products observed in our earlier work (3).

Possible applications.—The fact that oxygen is evolved at both cathode and anode in an acid solution containing II provides a novel and potentially useful method for electrolytically introducing known amounts of oxygen, uncontaminated by other gases, into closed systems. Electrolysis of solutions containing II also should find application in gas coulometers such as those described by Lingane (5). The sensitivity of the coulometer is increased by the use of II since 1.25 moles of gas ( $O_z$ ) are evolved per Faraday, as compared with a total of 0.75 mole/**F** of hydrogen plus oxygen from the solutions commonly employed.

#### Conclusions

1. At a bright platinum cathode in  $H_2SO_4$  solutions, the pentavalent complex  $[(NH_8)_6 CoO_2Co (NH_8)_6]^{6+}$ is reduced quantitatively to  $Co^{2+}$  in a one-electron reaction, with simultaneous release of the peroxo oxygen as oxygen gas.

2. Simple chemical reduction with silver powder was found to yield the same products quantitatively.

3. A probable reduction mechanism is outlined, based on the assumption that the reducing ion or metal surface atom becomes attached to the pentavalent complex at the peroxo group.

4. Electrolysis of an acid solution of the pentavalent complex between bright platinum electrodes provides a convenient electrolytic generator of pure oxygen. This system may also be used as a sensitive oxygen coulometer, yielding  $1.25 O_2$  per Faraday.

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# APPENDIX

Relationship between  $\Delta n$  and  $\Delta h$  for the current-efficiency cell

Evolution of  $\Delta n$  moles of gas increases the gas volume above the catholyte by  $A(\Delta h)$ . It increases the pressure of the gas by  $(\Delta h) d/13.5$  and its water content by  $\Delta n_w = A(\Delta h) P_*/RT$ . From  $\Delta n + \Delta n_w = (P_t V_t - P_t V_t)/RT$ , one obtains

$$\Delta n = \frac{\Delta h}{RT} \left[ A \left( P_i - P_s \right) + V_f d / 13.5 \right]$$
 [1]

Dissolution of  $\Delta n$  moles of gas decreases the volume, pressure and water content of the gas by the same quantities as above. Since  $\Delta h$  is now negative, Eq. [1] still applies without any change of sign. A negative value of  $\Delta n$  refers to gas dissolution, a positive one to gas evolution.

If atmospheric pressure changes during the measurement, a correction  $\delta h$  must be applied to the observed value of  $\Delta h$  in Eq. [1]. An increase in atmospheric pressure,  $p_e$ , corresponds to an increase in gas volume of  $A(\delta h)$  and a net increase in gas pressure of  $[p_e + (\delta h) d/13.5]$ . By applying the approximation  $\Delta P/P_t = -\Delta V/V_t$ , one obtains, with sufficient accuracy

$$\delta h = -p_a [A P_t / V_t + d/13.5]^{-1}$$
 [2]

Thus  $|\delta h|$  must be added to  $\Delta h_{\rm obs}$  where atmospheric pressure has increased, and vice versa.

**Technical** Notes



# Conditions for the Formation of a or $\beta$ Lead Dioxide During the Anodic Oxidation of Lead

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The work of Kiseleva and Kabanov (1,2) concerning the behavior of the  $\alpha$  and  $\beta$  modifications of lead dioxide in sulfuric acid has led them to propose that the formation of the  $\beta$  form is a consequence of H<sub>2</sub>SO<sub>4</sub> chemisorption on the PbO<sub>2</sub> formed during anodic oxidation of lead. This explanation is open to challenge since it implies that sulfate or bisulfate anions perform, at least in part, a vital function in determining the lead dioxide modification formed. Recent work performed in this laboratory as well as other well-known facts support the contention that it is hydrogen ion concentration which influences the nature of the PbO<sub>2</sub> deposit.

Methods for the preparation of  $\alpha$ - and  $\beta$ -PbO<sub>2</sub> in the laboratory are well known. In this laboratory,  $\beta$ -PbO<sub>2</sub> has been readily prepared by electrodeposition from acidic solutions of lead nitrate, lead sulfamate, lead fluoborate, and lead perchlorate as well as by the anodic oxidation of lead in strong sulfuric acid. On the other hand,  $\alpha$ -PbO<sub>2</sub> has been electrodeposited from neutral solutions composed primarily of lead nitrate and lead acetate, and by the anodic oxidation of lead in alkaline solution at high current densities. Published descriptions of electrodeposition methods have been given by Rüetschi, Angstadt, and Cahan (3) and by Thomas (4). These conditions for electrodeposition suggest strongly that it is the pH which is the major factor controlling the modification of lead dioxide formed.

To test further the relative importance of  $H^+$ ,  $SO_4^-$ , and  $HSO_4^-$  ions, a lead electrode was anodized and cycled in solutions of 2M Na<sub>2</sub>SO<sub>4</sub>, 2M KHSO<sub>4</sub>, and 2M H<sub>2</sub>SO<sub>4</sub> at room temperature and the lead dioxide modification produced was identified by means of x-ray diffraction powder patterns. The electrode was Doe-Run lead 99.998% pure which was first etched, washed, dried, and after immersion in electrolyte, made cathodic for a short time to reduce residual oxide.

The anodic current density was 1.5 ma/cm<sup>2</sup> of geometric area while cathodic current density was 0.75 ma/cm<sup>2</sup>. Periods of charge were of the order of 10 times the capacity of the lead dioxide formed

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Electrolyte	pH	Electrode treatment	PbO <sub>2</sub> Modification
2M Na₂SO₄	7.6-8.0	Anodic only	100% a
		Anodic + 5 charge-discharge cycles	100% a
2M KHSO₄	0.7	Anodic only	100% a
		Anodic + 5 charge-discharge cycles	$30\% \alpha - 70\% \beta$ to $60\% \alpha - 40\% \beta$
$2M H_2SO_4$	<0	Anodic only	~50% α ~50% β
		Anodic + 3 charge-discharge cycles	<10% α >90%β

and discharges were carried to reversal of potential sign referred to a  $Hg/Hg_{*}SO_{4}$  reference electrode. The results are presented in Table I.

It is significant that only  $\alpha$ -PbO<sub>2</sub> was formed in neutral Na<sub>2</sub>SO<sub>4</sub> solution. Initial anodic oxidation of lead resulted in the formation of  $\beta$ -PbO<sub>2</sub> only in 2M H<sub>2</sub>SO<sub>4</sub>. In KHSO<sub>4</sub> solution,  $\beta$ -PbO<sub>2</sub> was produced only after charge-discharge cycling. It may be concluded, therefore, that the modification of lead dioxide formed on anodic oxidation of lead and even subsequent cycling depends primarily on the *p*H of the electrolyte. The only function of the sulfate species present other than electrical neutrality and conductivity of the electrolyte is the limit its concentration places on the solubility of lead II ions present in the solution.

Kiseleva and Kabanov have proposed that the formation of  $\beta$ -PbO<sub>2</sub> is retarded by the addition of Co<sup>++</sup> in the cell because the Co<sup>++</sup> displaces H<sub>2</sub>SO<sub>4</sub> which is chemisorbed on the oxide. The formation of the  $\alpha$  modification in turn is supposed to provide better protection against the anodic oxidation of the underlying lead. Our work as reported here together with the other facts previously described indicate that it must be the protons which are displaced by cobalt ions and not H<sub>2</sub>SO<sub>4</sub> as such.

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# The Effect of Electropolishing on the Codeposition of Hydrogen with Nickel

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A number of investigations have been made of the advantages of electropolishing as a pretreatment of the electrode in electrodepositions. These have been surveyed by Faust (1). As a part of an investigation of the effect of organic additives on the hydrogen content of nickel deposits (2), a short study was made of the variation in the amount of hydrogen codeposited with nickel as a function of the pretreatment of the electrode.

### **Experimental** Procedure

Nickel wires were used as the basis metal for nickel plating. They were 14 gauge and 1.5 cm in length. They were prepared for plating by two procedures. In one procedure the wire was polished mechanically by hand with number 2/0 emery cloth. In the other procedure the wire was polished mechanically in the same way and then electropolished at a current density of 60 ma/cm<sup>3</sup> in a bath containing 50 ml water, 370 ml 85% phosphoric and 80 ml 98% sulfuric acid. Nickel was plated from a standard Watts bath for a period of 12 min at a current density of 6.96 ma/cm<sup>2</sup>.

The hydrogen content of the deposits and the current efficiencies were measured in the manner previously reported (2). The codeposited hydrogen was oxidized electrolytically, and the number of coulombs necessary for the oxidation was a measure of the amount of hydrogen. Current efficiency was evolved during the deposition. **Results** and Conclusions

measured by measuring the volume of hydrogen

Table I summarizes the results of the measurements of the amount of codeposited hydrogen. The table shows clearly that electropolishing the electrode before plating cuts the amount of hydrogen codeposited down to the point where it was not measurable by this technique.

There are two possible explanations for these results: (a) the difference in strain in the surface could change the current efficiency of the deposition process; (b) the difference in surface strain and roughness could change the ability of the hydrogen to adsorb to the surface.

Table II shows that there is essentially no difference between the current efficiency on the mechanically polished and electropolished electrodes.

Apparently the difference lies in the ability of the mechanically polished electrode to adsorb hydrogen. This is further shown by Table III, in which is tabulated the hydrogen retained by the nickel electrodes when only hydrogen is electrically generated on the electrodes.

Table II. Effect of pretreatment of the electrode on the current efficiency for the evolution of hydrogen

		Current efficiency for the evolut	ion of hydrogen on:
n amount of	Electrode	Mechanically polished electrode, %	Electro- polished electrode, %
xidize codeposited	4	1.69	2.00
	5	1.83	1.64
Remarks	6	2.42	2.80

Table III	. Number	of	milli	coulombs	ne	cessary	to	oxidize
hydrogen	adsorbed	on	and	absorbed	in	nickel	ele	ctrodes

Electrode	Mechanically polished	Electropolished			
1	$4.05\pm0.23$	0.04			
2	4.38	0.02			
3	$3.62\pm0.03$	Not measurable			
4	$2.65 \pm 0.02$	Not measurable			

#### Table I. Effect of pretreatment of electrode on amount codeposited hydrogen

Number of millicoulombs necessary to oxidize

Electropolished electrode

measurable

measurable

Not measurable

Not

Not

Not measurable

Mechanically polished electrode

 $6.25 \pm 0.086$ 

 $3.12 \pm 0.51$ 

Electrode

1

2

2

3 3.26 hydrogen

Plated 12 min, elec-

Plated 12 min, elec-

Plated 60 min, elec-

Plated 12 min, elec-

tropolished 5 min

tropolished 2 min

tropolished 2 min

tropolished 2 min
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# Some Observations on Overpotential Variations During the Galvanostatic Electrodeposition of Copper

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The variation in the activation overpotential with time, which has been observed by several workers during studies of the mechanism of electrode processes (1a-1h), is a factor which may result in irreproducibility of the value of the overpotential. During a study of the electrodeposition of copper from acid copper sulfate solutions it was observed that the conventional method of determining the activation overpotential  $(\eta_A)$ , *i.e.*, allowing a predetermined time to elapse before recording the overpotential, did not always give reproducible results owing to the changing topography of the cathode surface during electrodeposition. As a result of these observations a reproducible substrate technique has been developed in which a platinum sheet is used as the cathode for each determination of  $\eta_A$  at each value of constant current. Removal of the copper deposit is effected by anodic dissolution before the next determination of  $\eta_A$  at another current. Full details of this apparatus and technique have been described in a previous publication (2).

Observations of the  $\eta_A - t$  curves using this technique for a series of acid copper sulfate solutions (including some with addition agents) has led to the conclusion that these curves can be classified into three types. In the initial time interval,  $t_1$ , which may be a fraction of a second, the rapid rise in  $\eta_A$  is due principally to the establishment of the electrical double layer;  $t_1$  is affected only slightly by variations in the substrate properties. If the surface topography of the substrate is unaffected by the electrode process, e.g., a reduction of ions to a lower valency state or hydrogen evolution, the activation overpotential should remain constant with time. However, in the present study it was observed that during the next time interval  $t_2$  (which could persist for several minutes),  $\eta_A$  could either increase or decrease immediately after the double layer was completely charged. The sign, magnitude, and duration of this change appeared to depend on the nature of the substrate (crystal orientation and size, crystal defects and thickness of deposit) and on the nature of the electrolyte (presence of co-depositable metallic impurities, active impurities such as chloride ions, concentration polarization, etc.). If the duration of  $t_2$  is appreciable, then clearly the experimental time involved in obtaining  $\eta_A - i$  plots will be unduly long and, in addition, other errors may be introduced by prolonged electrolysis.

A study has been made of the factors responsible for  $\eta_A$  changes during time  $t_2$ , and it has been established that the greater the amount of mechanical deformation applied to the platinum substrate (*e.g.*, by rolling or polishing) then the greater is the magnitude of  $\Delta \eta_A$  and  $t_2$ . Figure 1 shows some  $\eta_A - t$  curves which have been obtained using a platinum substrate, which had been subjected to different degrees of cold-rolling; before electrolysis the cathodes were lightly etched in boiling aqua regia for 10 sec.

It can be seen that the initial values of  $\eta_A$  differ according to the extent of cold-working of the platinum although the steady-state value is independent of any textural difference in the substrate which could have arisen during either cold-working or recrystallization. This indicates that the technique provides a sensitive method of detecting any effects caused by the structure of the substrate. It is relevant to observe that it has been previously postulated (3) that lattice building in electrocrystallization is accomplished by surface diffusion of transferred adions to edges, steps, or kinks; in the present study the number of these defects will be proportional to the degree of cold-work (4).



Fig. 1. Effect of metallurgical condition of the platinum substrate on the variation of  $\eta_A$  with time: electrolyte 0.5M CuSO<sub>4</sub> + 0.5M H<sub>2</sub>SO<sub>4</sub>, at 25°C and 0.25 amp/dm<sup>2</sup>: A,\* V.P.N. 48, heat treatment continued to allow grain growth; B, V.P.N. 48; C, V.P.N. 72; D, V.P.N. 90. X, is the steady-state  $\eta_A$ .

\* V.P.N. = Vickers Pyramid Hardness Number.



Fig. 2. A. (top) Platinum substrate surface, after light etching and prior to its being electroplated. Mag. 20X. B. (bottom) Localized growth of copper at the grain boundaries. Platinum substrate as described above, electroplated with copper and removed from plating solution when the steady  $\eta_A$  was reached.

Observations of the growth of thin layers of the deposits (Fig. 2A, 2B) show that deposition occurs preferentially at grain boundaries and in a direction which is perpendicular to the substrate. This would indicate that the more imperfect the substrate the greater will be localized deposition at imperfect sites (in this case crystal boundaries) and the greater the charge required to cover completely the platinum substrate. This is supported by the results shown in Fig. 1. In addition it has been observed that with any given substrate the  $\eta_A - t$  curve can be reproduced after any time t (within the time  $t_2$ ) without hysteresis during anodic and cathodic cycling. Further, it has been established that, irrespective of the current density, a constant charge is required to produce the same steady-state value of  $\eta_A$ .

The classical procedure (5) of allowing  $\eta_A$  to become constant at a given value of current is not always satisfactory owing to surface roughening of the deposit and other factors such as changes in concentration of active species in the electrolyte; such factors are insignificant in the reproducible substrate method owing to the very small charge used for each determination of  $\eta_A$ .

The present work has necessitated a study of the effect, and elimination, of adverse impurities in the electrolyte as it is well known that even trace amounts of impurities may have a very marked effect on  $\eta_A$  and the crystal form of the deposit (8). In particular, the effects of traces of chloride ions have been studied as, with normal reagents, this im-



Fig. 3. Effect of chloride ions, added to a chloride-free electro-lyte, on the variation of  $\eta_{4}$  with time: electrolyte 0.5M CuSO<sub>4</sub> + 0.5M H<sub>2</sub>SO<sub>4</sub>, at 25°C and 2.0 amp/dm<sup>2</sup>: A, 0.00 ppm Cl<sup>-</sup>; B, 0.08; C, 0.15; D, 0.60-5.00; E, 12.00; F, 40.00.

purity is usually present in significant quantities and is difficult to remove by, for example, repeated recrystallization of  $CuSO_1 \cdot 5H_2O$  (where 1-10 ppm Cl can still persist). Electrolytes, low in Cl<sup>-</sup>, were prepared in solution by one of the following reactions, and in both cases the reagents can be prepared virtually free of chloride

$$Ag_2SO_4 + Cu \rightarrow CuSO_4$$
 aq.  
CuO + H<sub>2</sub>SO<sub>4</sub> → CuSO<sub>4</sub> aq.

A further possibility of removing chlorides is by anodic oxidation at a platinum anode (6).

The effects of  $Cl^-$  on  $\eta_A$  are shown in Fig. 3, and it is evident that the amounts of chloride which are normally present, even in carefully prepared electrolytes, can markedly affect  $\eta_A$ .

The effect of Cl<sup>-</sup>, on depolarization generally, has been attributed to their action in facilitating the transfer of electrons at the cathode surface (7). The reduction in  $t_{2}$  with increasing chloride ion concentration may be explained on the basis that these ions encourage the electrodeposition of copper at otherwise unfavorable planar sites thereby resulting in a more rapid coverage of the platinum substrate.

It is considered from this preliminary study that the reproducible substrate technique may be of general application in studying the effect of the metallurgical condition of the substrate [providing that this is unaffected during electrolysis (2)] on electrocrystallization.

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# Chemical Etching of Germanium in HF-HNO<sub>2</sub>-H<sub>2</sub>O Solutions

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The kinetics of etching of germanium in HF-HNO<sub>3</sub>-H<sub>2</sub>O solutions have been reported by several authors and proposals of etching mechanisms have been made (1-4). Camp (5) has shown that both activation and diffusion control of the etching rate of germanium exist in solutions of HF-H<sub>2</sub>O<sub>2</sub>-H<sub>2</sub>O and similar systems. The work reported here is concerned with the etching of germanium in HF-HNO<sub>3</sub>-H<sub>2</sub>O solutions under isothermal conditions and gives the chemical etch rates of germanium over a wide range of solution composition and temperatures of the etching medium. The results indicate that diffusion control of the etching rate appears when the nitric acid concentration in the etchant is high. An abrupt shift to activation control appears at lower nitric acid concentration and holds over a wide concentration range.

#### Experimental

The etch rates of germanium in the HF-HNO<sub>3</sub>-H<sub>2</sub>O solutions were determined by measuring the loss in weight of germanium pieces which had been etched for given periods of time in solutions maintained at constant temperatures during the etching process. Pieces of germanium measuring 0.64x0.64x0.25 cm were cut from single crystal material with the 0.64x0.64 faces lying in the crystal plane. These pieces were weighed and then supported in the etchant with all faces except one 0.64x0.64 cm face masked with polystyrene cement. The polystyrene cement effectively masked all surfaces during the etching reaction with only very slight lifting occurring around the edges of this mask leading to an insignificant etching error. The etchant was maintained at a constant temperature during the reaction by placing the polyethylene reaction beaker containing about 30 cc of solution inside a glass cooling cell through which water circulated from a controlled temperature bath. Vigorous agitation of the etchant was maintained during the reaction by a magnetic stirrer in order that the surface temperature of the etching germanium would remain at a constant value. It had been previously determined, by cementing a thermocouple to the etching surface, that the surface temperature rose 30°-40°C above the bath temperature when stirring was omitted. After etching for 3 min the germanium was removed from the etchant, washed with water, and the mask removed by peeling off the cement. Following this, the germanium piece was washed in toluene to remove traces of the cement, dried under a heat lamp, and weighed. The amount of germanium removed from the pieces during etching varied from 1 to 30 mg, depending on the composition and temperature of the etch.

The etchants were prepared from reagent grade nitric acid (70%) and hydrofluoric acid (49%) and water was added to all mixtures to adjust its concentration to 33M, the concentration of water in the reagent hydrofluoric acid. Thus, the etching rates were made in solutions having a constant water concentration with varying concentration ratios of nitric acid and hydrofluoric acid.

#### Results

Table I lists the data obtained in etching 1 ohm-cm n-type {111} germanium crystals. The etch rates are given for four temperatures and each point is an average of four values.

A plot of the log etch rates vs. 1/T appears in Fig. 1 for some of the data in Table I. The activation energies calculated from the slopes of these curves are around 6 kcal for the mole ratios of HNO<sub>3</sub>/HF greater than 4.9. Below this ratio the energies range from 19 to 12 kcal. Figure 2 shows a plot of these activation energies vs. mole ratio HNO<sub>3</sub>/HF for the ratio range between 0.06 to 1.3.

Table I. Etching rates of germanium in HF-HNO<sub>3</sub> solutions at various temperatures

Mole ratio	Etch rate, $\mu$ /min				Activation energy*
HNO <sub>3</sub> /HF	15°C	25°C	35°C	40°C	$\Delta E$ kcal
0.06	0.76	1.5	3.1	4.2	12.3
0.14	0.94	2.8	4.9	7.4	12.7
0.23	1.2	4.0	5.7	9.7	14.5
0.36	1.6	3.6	6.8	14	15.3
0.55	1.2	4.2	9.3	15	16.2
0.82	1.2	5.6	12	27	19.6
1.30	2.2	5.6	12	26	18.5
2.20	2.2	5.6	16	31	17.9
4.90	7.0	13	16	18	6.2
10.4	4.3	5.8	7.0	9.3	5.6

\* Calculated from slope of the plot of log etch rate vs. 1/T.



Fig. 1. Temperature dependence of the dissolution rate of germanium in HF-HNO\_{3}-H\_{2}O solutions.



Fig. 2. Activation energy vs. mole ratio

#### Discussion

It is apparent from the activation energy curves shown in Fig. 1 that at higher concentrations of nitric acid the rate of etching is controlled by a transport process while at lower concentrations the controlling step is an activation process. This is to be expected since at high nitric acid concentrations the etch rate of germanium would be dependent on the ability of the hydrofluoric acid to diffuse to the oxide surface (probably the relatively insoluble GeO.) where it would react with the oxide forming the soluble fluoride complex ion. As the concentration of hydrofluoric acid is increased there is a change to activation control and also an increase in the etching rate. At nitric acid concentrations below those reported there is probably again diffusion control, with the rate limited by transport of the oxidizing agent to the solid surface.

The region between these two extremes is complicated by the presence of a thin film found on the solid surface. This thin gold-colored film, which is visible on the etched surface when the molar ratio of HNO<sub>3</sub>/HF is 0.36 or less (25°C), could possibly be caused by the formation of an amorphous germanium monoxide previously reported by Ellis (6) or by the formation of a polycrystalline germanium layer similar to that reported for silicon by Archer (7). The presence of this film accounts for the fairly low etch rate observed at the lower concentrations (Table I). It is interesting to note in the plot of activation energy vs. mole ratio (Fig. 2) that the activation energy increases linearly up to a mole ratio at about 0.8. This could possibly be an indication of the range of the film formation process.

If the film is amorphous germanium monoxide then it is conceivable that in this concentration range the dissolution of the germanium is a twostep reaction where the oxidation of germanium to the monoxide occurs at the surface with the subsequent solution and oxidation of this material to the tetravalent state followed by the function of the fluoride complex. The etch rate in this range would be dependent on the rate of solution of the monoxide. However, if the film is polycrystalline germanium then a mechanism similar to that proposed for silicon by Turner (8) may be involved where the divalent form of germanium would appear first, followed by disproportionation to polycrystalline germanium and germanium dioxide. The correct mechanism for the etching reaction could be determined possibly if an analysis of the reaction products including the film was made. Initial spectrographic analysis of a known weight of film removed from the germanium substrate by solution in 6N potassium hydroxide indicates that it is not pure germanium. This fact appears to support the germanium monoxide mechanism.

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# Mechanism of Stress Corrosion Cracking in Stainless Steels

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Recently Forty (1) proposed a restricted-slip theory of stress corrosion cracking which may be used to predict the susceptibility or immunity of metals to this type of cracking. The theory presupposes cyclic chemical-mechanical propagation, as first clearly described by Keating (2). In this method of propagation a short period of relatively slow chemical attack, or electrochemical attack in the case of aqueous corrodents, leads to localized stress concentration and embrittlement. A microscopic crack results; then further chemical attack occurs at the tip of the crack, and the cycle repeats. Direct observations of periodic crack extension were made by Edeleanu (3) on the surface of an  $\alpha$ -brass single crystal corroding in ammonia, and by Kirk, Beck, and Fontana (4) on commercial stainless steel surfaces in dilute NaCl solutions at 204°C. Hines (5), however, pointed out the need for other direct evidence, because it is possible for cracks growing smoothly in the bulk of the alloy to break through the surface periodically.

The chemical embrittlement process may be expected to vary with the type of corrodent and alloy involved. In studies on copper alloys, using the technique of electron transmission through thin films, Bassett and Edeleanu (6) and also Swann and Nutting (7) showed evidence for preferential chemical attack at or near stacking faults. They suggested that solute segregation at stacking faults may control the chemical embrittlement step, but as yet little is known of the embrittlement mechanism.

The restricted-slip theory refers to the mechanical-fracture step of the propagation cycle. According to this theory, when a crack is formed within the embrittled surface layer it will propagate into the underlying ductile metal only if dislocation movement is highly restricted. Propagation ceases when the crack enters a soft region, such as a preexisting slip band. Hence alloys which readily cross slip should be immune to this type of cracking.

Evidence that the restricted-slip theory may apply to copper alloys has been given by Swann (8). In the copper-zinc system, 3-37% Zn, it was shown that the stacking fault energy decreases with increasing zinc concentration, and a gradual change in dislocation distribution occurs. Pure copper has a high stacking fault energy, and the dislocation groups exhibit a cellular structure, which indicates that the dislocations can readily cross slip. As zinc

is added the stacking fault energy decreases and cross slip becomes more difficult. The cell structure disappears and dislocations become confined to slip planes, indicating restricted slip. Alloys having 15-37% Zn, which are known to be highly susceptible to stress corrosion cracking, were found to have low stacking fault energy and exhibited highly restricted slip, in agreement with the theory.

Similarly with aluminum additions to copper, Swann showed that increasing aluminum content in the range 3.5-8% continuously lowered the stacking fault energy and restricted slip. Although no stress corrosion data were given for the particular alloys studied, others have reported Cu-4% Al to be apparently immune to stress corrosion cracking (9, 10) while alloys in the range 5 to 10% Al have cracked (10).

We have now tested the applicability of the restricted-slip theory to stainless steels. Both the stress corrosion behavior and the dislocation pattern have been determined in a pair of purified vacuummelted 16 Cr-20 Ni steels. One of these was immune to stress corrosion cracking and the other susceptible. The immune alloy, E, has been shown in a previous paper (11) to remain uncracked in boiling 42% MgCl<sub>2</sub> under severe corrosion conditions. The susceptible alloy, K, has essentially the same composition except for the addition of 1.5% molybdenum, Table I. According to the theory, the molybdenum addition should have caused highly restricted

Table I. Alloy	composition	and stress	corrosion	behavior
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Alloy designation:		E	к	м
Composition (%):	Cr	Cr 16.2	16.1	16.5
	Ni	19.9	19.9	19.9
	Mo		1.51	5.06
	C	0.013	0.013	0.013
	N	0.010	0.011	0.018
	Mn			1.44
	Si	<u> </u>	-	0.45
	A1		<u></u> 0	0.059
	0	0.0015	0.027	0.018
	S	0.011	0.007	0.009
	P	0.003	0.003	0.002
Average time				
to fracture* (h	r): >	250 (no cracks)	6 )	14

\* Wires of 0.7 mm diameter, under constant tensile stress of 2800 kg cm^-2 (40,000 psi), in  $42\%~MgCl_2,\,146\,^\circ C.$ 

April 1962

dislocation movement. This was studied by electron transmission through thin films.

The thin films were prepared from annealed wire specimens (0.7 mm diameter) by first cold rolling the wires to 0.1 mm thick strips. The strips were annealed in vacuum (10<sup>-5</sup> mm Hg) at 1065°C for 15 min and quenched by rapidly moving them to a cold section of the vacuum system. They were then deformed 15-20% by cold rolling; this amount of plastic deformation was approximately the same as that which occurred during initial loading of the wire specimens in stress corrosion cracking tests. An area 2 x 20 mm, the perimeter masked with lacquer, was electropolished under the following conditions until thin edges were produced: solution:  $H_3PO_4$  (conc.)-60%,  $H_2SO_4$  (conc.)-40% by vol; temperature: 60°C; anode current density: 2.5 amp cm<sup>-2</sup>.

The thin areas thus produced, the order of  $1000\overline{A}$  thick, were examined by transmission electron microscopy, and typical micrographs are shown in Fig. 1. In these micrographs dislocations appear as dark lines. Although the dislocation density is high, the general distribution is evident. In the purest alloy E (top micrograph) the dislocations form a



Fig. 1. Transmission electron micrographs of deformed 16 Cr-20 Ni stainless steels. Top, alloy E, no added element; center, alloy K, 1.5 Mo addition; bottom, alloy M, 5.06 Mo-1.44 Mn-0.45 Si-0.06 Al additions. "cell structure" consisting of light regions, which are relatively dislocation-free, and boundaries which contain high dislocation density. This distribution is characteristic of deformed face-centered cubic metals which allow easy cross-slip and which have high stacking fault energy (12). Alloy K (center micrograph) exhibits a dislocation distribution in which there is a definite tendency for the dislocations to be concentrated along parallel (slip) planes. This is characteristic of deformed face-centered cubic metals in which slip is restricted and the stacking fault energy is low (12). As shown in Table I the former alloy is not susceptible to stress corrosion cracking, while the latter with molybdenum added cracks readily. Thus the molybdenum addition has caused restricted slip in the metal and also made it susceptible to cracking, in agreement with Forty's theory.

The only other data obtained with molybdenum addition to the 16-20 steel was for an air-melted alloy, M, containing 5% Mo plus smaller additions of Mn, Si, and Al (Table I). This alloy was susceptible to stress corrosion cracking, and the typical dislocation pattern found in the 20% cold-worked metal, Fig. 1 (bottom), again shows that restricted slip is associated with crack susceptibility.

The observations reported here all indicate that Forty's restricted-slip theory is applicable to these stainless steels. It is desirable to extend this work to include other single impurity additions to the purified 16-20 alloy, in order to isolate the effects of those which induce cracking and those which do not. In addition, direct measurements of stacking fault energy in stainless steels are needed for comparison with Swann's correlation of cracking in copper alloys having low stacking fault energy. These studies are now in progress.

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# Sealed Solid Method for Zone Melting Decomposable Compounds

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A number of procedures are used to crystallize materials containing or consisting of components volatile over the melt. Those in current use have limitations for achieving purification or for recovering material of uniform composition. Thus, the sealed tube Bridgman or directional freezing method results in general in ingots of varying composition along their length. Zone-melting in a boat or by floating zone requires that all of the sealed tube and hence the solid be heated by multiple furnaces at all times to control the partial pressures of the volatile components or impurities. With the solid always hot, movement of constituents in the solid either by diffusion in the solid or by a process of vapor transport and diffusion is possible. This can result in vitiating purification by zone melting or can result in inhomogeneous material if zone levelling is conducted. These problems can be overcome in a zone melting process in which there is no free volume for the movement of volatile constituents and in which the solid does not need to be maintained at an elevated temperature.

A schematic drawing of a sealed solid method of zone melting is shown in Fig. 1(b) in which the floating zone method is compared in (a). It has been found that many materials with volatile constituents can be weighed into a suitable tube, allowed to react, and cast without cracking the tube. Also, a narrow molten zone can be made to traverse the tube without causing cracking. If, as in Fig. 1(b), a molten zone is transported upward through the



Fig. 1. Comparison of normal (a) and simple (b) zone melting of decomposable materials.

sealed cast ingot, the solid above and below the melt acts as the seal for vapor. Thus vapor transport does not occur. The last zone width to freeze is the only region that need lose volatile material. This amount may be kept small by keeping the volume above the casting small and/or by heating, and also by using a narrow zone. A narrow zone can be readily maintained because, without having to heat the solid, a sharp temperature gradient between melt and solid is realized. Since the solid cools rapidly toward room temperature after the passage of a molten zone, solid diffusion is kept to a minimum.

In the application of this method to the preparation of bismuth telluride alloys, for example, since material of uniform composition is desired, the process is conducted for zone levelling. The equipment used is simple. The melted zone is created by a narrow resistance furnace. The mechanism used to move the tube through the furnace can be simple as long as a constant rate can be maintained with the tube kept concentric with the furnace. A relatively rapid rate for the zone movement is used in order that the effective segregation coefficients of the constituents approach unity as nearly as possible. The limiting rate is that permitting good oriented crystal growth. Even in these materials with low thermal conductivity, rates of the order 6-8 cm/hr can be used since the thermal gradients can be kept large. Cracking of the tubes is not encountered when care is exercised to remove oxides from the materials. Ingots of 28 cm length have been made in quartz tubes using a single zone pass and a zone width of 1-2 cm. Typical electrical resistivity profiles for ingots of p- and n- type alloys were flat, with a deviation of less than 10% over 90% of the length. These profiles were used as one criterion of the homogeneity of the ingot. By comparison, ingots of the same alloys made by the Bridgman process showed variations in resistivity of a factor of almost two from one end to the other. The other thermoelectric parameters of the zoned ingots are similarly uniform, resulting in a variation for the figure of merit of less than  $\pm 5\%$ of the average value obtained for a number of ingots.

A number of different materials, including I-VI, III-V, and V-VI compounds, have been successfully made by this process. Each compound may require a slightly different preparative technique in order to satisfy the requirement that the ingot be free to move in the tube before zoning. However, as long as the material does not react with or stick to the crucible material, the method should work.

#### Acknowledgment

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Manuscript received Dec. 21, 1961.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1962 JOURNAL.

# Electron Diffraction Study of the Ferrimagnetic Structure of Fe<sub>0</sub>O

## S. Yamaguchi

Institute of Physical and Chemical Research, Tokyo, Japan

It has been found possible to determine the orientation of magnetic induction in a magnetite crystal as described below.

A layer of a single crystal of magnetite (thickness about  $5\mu$ , area 2 x 1 mm<sup>2</sup>) was prepared by mechanical polishing. This layer contained some pinholes with diameters of about  $10\mu$ . The specimen was magnetized in a thin and homogeneous field which was prepared at the sharp edges (thickness about  $3\mu$ ) of two razor blades, whose remanence was about 2000 gauss. These two edges, separated by a narrow gap (ca. 1 mm), acted as magnetic poles (Fig. 1). A beam of electrons (diameter about  $50\mu$ ) of well-defined wavelength was passed through, grazing one of the pinholes found in the specimen in order to give rise to a diffraction pattern. Here the incident electron beam runs nearly perpendicular to the face of the layer or to the lines of force (Fig. 1).

The diffraction pattern from the cold specimen, i.e., at  $40^{\circ}$ C, was first registered, and then that from the heated specimen at  $300^{\circ}$ C was superimposed. In this process, the positions of the specimen and of the photographic emulsion, and the well-defined wavelength of the incident electrons were kept fixed. The double diagram thus obtained is shown in Fig. 2. The incident electrons in Fig. 2 are parallel to the [ $\bar{1}10$ ] zone axis of the Fe<sub>s</sub>O<sub>4</sub> crystal. The temperature of the specimen was controlled by regulation of the electronic irradiation (1).

Figure 3 is a single diagram obtained from the specimen kept at the higher temperature, *i.e.*, at 300°C. It is noted in Fig. 2 that every diffraction spot is split, with a constant separation and in a definite direction, whereas such splitting is not found in Fig. 3. This phenomenon of splitting re-



Fig. 1. Arrangement for the diffraction of electrons subjected to the magnetic lines of force in the Fe<sub>8</sub>O<sub>4</sub> crystal. A photographic plate is situated perpendicular to the incident beam.



Fig. 2. Diffraction patterns of the cold specimen (40°C) and of the hot specimen (300°C) obtained by the double exposure process. The diffraction spots corresponding to these two temperatures are split as the result of the Lorentz effect. The direction of the splitting  $\vec{Z}$  is perpendicular to the [111] axis, *i.e.*, to the induction  $\vec{B}$ . The incident beam is parallel to the [110] zone axis. Wavelength of the electrons: 0.0281Å; camera length: 495 mm. The positive enlarged 3.7 times.



Fig. 3. A single diagram obtained from the specimen kept at 300°C.



Fig. 4. Relations between the incident beam (E), the net planes of the Fe<sub>3</sub>O<sub>4</sub> crystal and the induction (B). E and the (110), (111), and (001) planes are perpendicular to the paper face. B and the  $(\overline{110})$  plane are parallel to the paper face.

sults from the difference between the action of the Lorentz force of the specimen when hot and when cold, on the electron trajectories. The direction of the observed splitting  $\vec{Z}$  is perpendicular to the crystallographic orientation of the magnetic induction found in the specimen, according to the Lorentz law. The direction of the induction  $\vec{B}$  thus determined agrees with the [111] axis of the crystal of

mined agrees with the [111] axis of the crystal of  $Fe_sO_4$  (Fig. 2). It is concluded in this way that the ferrimagnetic electron spin planes are parallel to the (111) planes of the  $Fe_sO_4$  crystal. This conclusion is in accordance with that reached by neutron diffraction (2). The relations between the incident beam (E), the orientation of the net planes, and the magnetic induction (B) are illustrated in Fig. 4.

Quantitative analysis of Fig. 2 results from a consideration of the Lorentz force F acting on an electron beam:

$$F=\frac{e}{c}\left[v\ B\right]$$

where e is the electron charge, c the velocity of light, v the velocity of the electrons, B the magnetic induction, and [ ] the vector product. From this expression we obtain a relation between the thermomagnetic splitting  $\Delta Z$  of the diffraction spots in Fig. 2 and the induction change  $\Delta I (\Delta B = 4\pi \Delta I)$  caused by the thermal perturbation under the experimental arrangement:

$$\Delta Z = \frac{eLl}{mv} \cdot 4\pi \,\Delta I \qquad (L \gg \overline{l})$$
$$= \frac{eL\lambda \overline{l}}{h} \cdot 4\pi \,\Delta I \qquad [1]$$

where *m* is the electron mass, *v* the velocity of the electrons, *e* the electron charge  $(1.6 \times 10^{-20} \text{ emu})$ , *L* the camera length (495 mm),  $\lambda$  the wavelength of the electrons (0.0281Å), *h* the Planck constant ( $6.6 \times 10^{-27}$  erg-sec), and  $\overline{l}$  the magnetic path of the electrons. We measure  $\Delta Z = 0.348$  mm on Fig. 2. Therefore, we obtain according to Eq. [1],  $\Delta I \approx 160$  gauss, if we assume  $\overline{l}$  equal to the thickness of the specimen layer,  $5\mu$  (Fig 1). This  $\Delta I$  value is plausible as the induction change of magnetite caused by the temperature change from 40° to 300°C.

Conclusion.—The present thermal perturbation procedure of electron diffraction is more to be recommended for the magnetic structure analysis of ferrites than neutron diffraction, especially when access to a nuclear reactor is not possible.

Manuscript received Sept. 26, 1961; revised manuscript received Dec. 15, 1961.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1962 JOURNAL.

#### REFERENCES

- 1. S. Yamaguchi, This Journal, 107, 1011 (1960).
- G. E. Bacon, "Neutron Diffraction," p. 241, Oxford at the Clarendon Press (1955).

# FUTURE MEETINGS OF The Electrochemical Society

#### С С

## Los Angeles, Calif., May 6, 7, 8, 9, and 10, 1962

Headquarters at the Statler-Hilton Hotel Session will be scheduled on Electric Insulation (including sessions on Ceramics and Integrated Circuits, Thin Film Dielectrics and Electrolytic Capacitors, Reliability, and Paper), Electronics (including Luminescence, Semiconductors, and Optical Masers), Electrothermics and Metallurgy (including a Symposium on Thermodynamics and Kinetics of Gas-Condensed Phase Reactions at High Temperatures), Industrial Electrolytics, Theoretical Electrochemistry (See pp. 53C-91C of March issue for complete program)

#### \* \* \*

## Boston, Mass., September 16, 17, 18, 19, and 20, 1962

Headquarters at the Statler-Hilton Hotel Sessions will be scheduled on

Batteries (General Sessions on primary and secondary batteries, and fuel cells), Battery—Theoretical Electrochemistry Joint Symposium on Porous Electrodes, Corrosion, Corrosion—Electronics Joint Symposium on Phenomena at Interfaces, Electrodeposition (including a Symposium on Alloy Electrodeposition), Electrodeposition—Electronics Joint Symposium on Electrochemical Processes for Semiconductor Devices, Electronics—Semiconductors (including a Symposium on Semiconductor Phenomena), Electrothermics and Metallurgy (including a Symposium on Hot Pressing), Electrothermics and Metallurgy—Corrosion Joint Symposium on High-Temperature Corrosion

\* \* \*

Pittsburgh, Pa., April 14, 15, 16, 17, and 18, 1963

Headquarters at the Penn Sheraton Hotel

\* \* \*

## New York, N. Y., September 29, 30, and October 1, 2, and 3, 1963

Headquarters at the New Yorker Hotel

## \* \* \*

Toronto, Ont., Canada, May 3, 4, 5, 6, and 7, 1964 Headquarters at the Royal York Hotel

Papers are now being solicited for the meeting to be held in Boston, Mass., September 16, 17, 18, 19, and 20, 1962. Triplicate copies of each abstract (not exceeding 75 words in length) are due at Society Headquarters, 30 East 42 St., New York 17, N. Y., not later than May 15, 1962 in order to be included in the program. Please indicate on abstract for which Division's symposium the paper is to be scheduled, and underline the name of the author who will present the paper. No paper will be placed on the program unless one of the authors, or a qualified person designated by the authors, has agreed to present it in person. An author who wishes his paper considered for publication in the JOURNAL should send triplicate copies of the manuscript to the Managing Editor of the JOURNAL, 30 East 42 St., New York 17, N. Y.

Presentation of a paper at a technical meeting of the Society does not guarantee publication in the JOURNAL. However, all papers so presented become the property of The Electrochemical Society, and may not be published elsewhere, either in whole or in part, unless permission for release is requested of and granted by the Editor. Papers already published elsewhere, or submitted for publication elsewhere, are not acceptable for oral presentation except on invitation by a Divisional program Chairman.

# Current Affairs



# LaQue, Yeager, and Campbell to Take Office in Los Angeles



F. L. LaQue

As a result of the recent annual election, in which the voting is by mail ballot, Frank L. LaQue has been elected the new President (1962-1963) of The Electrochemical Society, Ernest B. Yeager has been elected Vice-President (1962-1965), and Ivor E. Campbell has been reelected Secretary (1962-1965). They will take office at 8:00 A.M. Thursday, May 10, 1962, in Los Angeles, Calif., at the Annual Spring Meeting of the Society.



E. B. Yeager

Mr. LaQue, vice-president, Executive Dept., The International Nickel Co., Inc., New York City, replaces Henry B. Linford, professor of chemical engineering, Columbia University, New York City. Dr. Linford, as Past President, will continue as a member of the Board of Directors.

Ernest B. Yeager, professor of chemistry at Western Reserve University, Cleveland, Ohio, begins his three-year term as Vice-President.



I. E. Campbell

He will serve with the two previously elected Vice-Presidents, Walter J. Hamer and Lyle I. Gilbertson.

Ivor E. Campbell, director of research and development of the National Steel Corp., Weirton, W. Va., begins his second three-year term as Secretary.

Ernest G. Enck, consultant in longrange planning and general management, Gwynedd Valley, Pa., enters the second year of his three-year term (1961-1964) as Treasurer.

## Plans Completed for Los Angeles Meeting, May 6-10

Preparations for the Spring Meeting of The Electrochemical Society, to be held May 6 through May 10 at the Statler-Hilton Hotel in Los Angeles, are now complete. The program, including the schedule and abstracts of papers to be presented, was published in the March JOURNAL, pp. 53C-91C.

Credit for the program belongs to the Local Committee headed by the following chairmen: J. C. Schumacher, General Chairman (American Potash & Chemical Corp.); W. M. Hetherington, Arrangements Chairman (Hughes Aircraft Semi-



J. C. Schumacher

Conductor Div.); D. R. Stern, Financial Chairman (American Potash & Chemical Corp.); George Larchian, Registration Chairman, ECS Section Chairman (Hughes Aircraft Semi-Conductor Div.): Birke Luckenbill, Plant Tours Chairman (Morris P. Kirk & Son, Inc.); Roger Hoffman, After-Meeting Trip Chairman (American Potash & Chemical Corp.); Thomas Blair, Entertainment Chairman (Western Lead Products); Lahmer Lynds, Secretary, ECS Section Vice-Chairman (Atomics International); Mrs. J. C. (Theresa) Schumacher, Ladies' Chairman.

April 1962





Roger Hoffmann



D. R. Stern



Thomas Blair



George Larchian



Lahmer Lynds



Birke Luckenbill



Mrs. J. C. Schumacher

Here are a few reminders and some details hitherto unannounced in the day-by-day schedule:

Sunday, May 6.—Remember to obtain your tickets to the Annual Business Meeting, scheduled for 12:15 P.M. in the Golden State Ballroom, when you register on Monday. You won't want to miss the address by Dr. Willard Libby.

Sunday evening, May 6.—A slideillustrated preview of the places to go and the things to see will be a part of the informal get-together scheduled for 7:30-9:30 P.M., in the Garden Room. Coffee and conversation are the inducements

Monday, May 7.—Monday morning will be your last chance to pick up tickets for the Annual Business Meeting. Tickets for other events on the program will be available up until the time of the event. Remember, however, that the plant tours will be limited to 45 people each on a first-come, first-served basis.

Monday evening, May 7.—A touch of the Hofbrau atmosphere will prevail at the Monday Evening Mixer, scheduled from 8:30 to 11:30 P.M., with the appearance of a Tyrolian instrumental group. Ladies are reminded they are welcome.

Tuesday, May 8.—The College Day Program, scheduled for 2 P.M., will feature a distinguished panel of speakers. J. C. Schumacher, General Chairman of the Convention, will extend the Society's welcome to the visiting students and faculty members and introduce Henry B. Linford, the Society's President.

Dr. Linford, professor of chemical engineering at Columbia University, will provide a brief outline on the nature of electrochemistry, its position relative to the other branches of science, and future prospects in the field.

The program, which will be moderated by Dr. Ray M. Hurd, director, Chemical Research, Texas Research Associates, will include talks by Dr. Charles W. Tobias, professor, Dept. of Chemical Engineering, University of California at Berkeley; Dr. Milton J. Allen, director, Chemical Research Dept., Electro-Optical Systems, Inc.; and Dr. Morton Jones, a member of the research staff of Texas Instruments, Inc.

The talks will include a brief survey of the research activities of the electrochemical group at Berkeley, by Dr. Tobias; "The Application of Electrochemical Techniques to Synthetic Organic Chemistry," by Dr. Allen; "The Electrochemical Aspects of Semiconductor Technology," by Dr. Jones.

A round-table discussion will follow and the group then will adjourn for a Coffee Hour in the Cleveland Room.

**Tuesday evening, May 8.**—Added note to the Banquet program. A 30-man choral group, The North Americans, will provide a musical interlude in the evening's entertainment.

Wednesday, May 9.—Those planning to take the trip to Disneyland are advised to dress comfortably, paying particular attention to footwear. Despite the quantity and variety of transportation available in this vast land of make-believe, a great deal of walking is required.

#### Notice to Members and Subscribers

#### (Re Changes of Address)

To insure receipt of each issue of the JOURNAL, please be sure to give us your old address, as well as your new one, when you move. Our records are filed by states and cities, not by individual names. The Post Office does not forward magazines.

We should have this information by the 16th of the month to avoid delays in receipt of the next issue.

# Special Symposia Planned for Boston Meeting of Electrochemical Society, September 1962

#### Symposium on Porous Electrodes

The Battery Division in conjunction with the Theoretical Electrochemistry Division will sponsor a Symposium on Porous Electrodes at the Boston Meeting of the Society in September 1962. The objective of the symposium is to consider how pore structure influences electrode performance. The first part of the symposium will be concerned with: 1techniques for characterizing pore structure, 2-mass transport phenomena in porous solids, and 3-the general electrochemical properties of porous electrodes. The second part of the symposium will involve specific electrode systems in which the porous nature of the electrode is of major importance, i.e., fuel cell electrodes, oxide cathodes, sintered metal electrodes, etc.

Suitable papers are solicited for this symposium. Triplicate copies of abstracts (not exceeding 75 words in length) must be received at Society Headquarters, 30 East 42 St., New York 17, N. Y., by May 15, 1962.\* It should be indicated on the abstract that the paper is to be considered for the Symposium on Porous Electrodes; the name of the author who will present the paper should be underlined.

Inquiries and suggestions regarding the symposium should be addressed to the Symposium Chairman, Ernest Yeager, Dept. of Chemistry, Western Reserve University, Cleveland 6, Ohio.

#### **General Sessions**

In addition to the Joint Symposium, the Battery Division will hold General Sessions on batteries covering the field of primary and secondary types, and fuel cells. Abstracts of papers for the General Sessions should be submitted by May 15 as indicated above and marked for presentation at the Fall (Boston) Meeting.

• No paper will be placed on the program unless one of the authors, or a qualified person designated by the authors, has agreed to present it in person.

#### Symposium on Alloy Electrodeposition

The Electrodeposition Division announces a Symposium on Alloy Electrodeposition as a featured part of its program at the 122nd Meeting of the Society to be held in Boston, Mass., September 16-20, 1962.

The symposium will include invited papers by distinguished electrochemists, with the object of setting the stage for contributed papers on current research and practice. The invited papers will cover the following areas: 1—Introduction (history, terminology, development, and present commercial practice of alloy plating); 2—Kinetics of Electrode Processes, with special reference to alloy plating; 3—Protective Mechanisms of Alloy Electrodeposits (lowand high-temperature coatings).

The contributed papers which arise in response to this announcement should cover current research and practice in the field. They might include work on new electrodeposited alloys based on cobalt, tin,



A cordial invitation is extended to all members of the Society to drop in and see the new Headquarters whenever they are in New York. molybdenum, gold, *etc.*, on magnetic alloys, or on unusual electrochemical and metallurgical aspects of certain alloy plating systems, to mention a few possibilities.

If you have a paper to present, you should give notice, as soon as possible, of your intention to submit a paper, and of the title of your paper. Triplicate copies of each abstract (not exceeding 75 words in length) are due at Society Headquarters, 30 East 42 St., New York 17, N. Y. not later than May 15, 1962 in order to be included in the program.\* Please indicate on the abstract that the paper is to be scheduled for the Alloy Electrodeposition Symposium, and underline the name of the author who will present the paper.

If you have a contribution to make, please direct your reply to Leslie D. McGraw, Electrochemical Engineering Div., Battelle Memorial Institute, 505 King Ave., Columbus 1, Ohio.

We hope you will attend the Boston Meeting of the Society and join with us in this symposium.

**Electrodeposition Division** 

#### Symposium on High-Temperature Corrosion

A Joint Symposium on High-Temperature Corrosion will be held by the Electrothermics and Metallurgy Division and the Corrosion Division at The Electrochemical Society's Boston Meeting, September 16-20, 1962. The object of the symposium is to present information on the corrosion of metals and nonmetals at elevated temperatures in media other than aqueous solutions and oxygen or air. The media will include gases or vapors of elements and compounds, liquid metals, fused salts, fuels and fuel products, metallic vapors, etc.

Suitable papers are solicited for this symposium. Review papers will be welcome. Triplicate copies of abstracts (not exceeding 75 words in length) must be received at Society Headquarters, 30 East 42 St., New York 17, N. Y., by May 15, 1962.\* It should be indicated on the abstract that the paper is to be considered for the High-Temperature Corrosion Symposium. The name of the author who will present the paper should be underlined.

Titles of the papers and authors' names should be sent as soon as possible—*April 15, 1962 at the latest*—to Clifford A. Hampel, 8501 Harding Ave., Skokie, Ill. Inquiries and suggestions regarding the symposium also should be addressed to Mr. Hampel.

#### Symposium on Hot Pressing

A special Symposium on Hot Pressing will be held by the Electrothermics and Metallurgy Division of the Society at its Boston Meeting, September 16-20, 1962. Emphasis will be placed on the consolidation of metallic and nonmetallic powders by hot pressing, the phenomena involved, and the application of new energy sources to hot pressing.

Suitable papers are solicited for this symposium. Review papers will be welcome. Triplicate copies of abstracts (not exceeding 75 words in length) must be received at Society Headquarters, 30 East 42 St., New York 17, N. Y., by May 15, 1962.\* It should be indicated on the abstract that the paper is to be considered for the Hot Pressing Symposium. The name of the author who will present the paper should be underlined.

Titles of papers and authors' names should be sent as soon as possible—*April 15, 1962 at the latest*—to Clifford A. Hampel, 8501 Harding Ave., Skokie, Ill. Inquiries and suggestions regarding the symposium also should be addressed to Mr. Hampel.

## Symposium on Stress Corrosion of Metals, ECS Fall 1963 Meeting

The Corrosion Division is planning a Symposium on Stress Corrosion of Metals for the 1963 Fall Meeting of The Electrochemical Society to be held in New York City, September 29 to October 3, 1963.

Subjects suggested for this symposium are: classical stress corrosion; hydrogen embrittlement as a factor in stress-corrosion cracking; brittle fracture as affected by environmental conditions; and the application of modern concepts of solidstate physics to stress corrosion.

Papers giving data to support or disprove one of the current theories of the mechanism of stress-corrosion cracking would be considered under the classification of classical stress corrosion. Papers merely summarizing data on a particular alloy or group of alloys are not considered to have a place in the symposium.

Inasmuch as results of center or edge notch tests on very highstrength alloys are reported to be highly sensitive to the test environment, the Chairmen feel that papers giving results and particularly suggested mechanisms for these phenomena should be included.

Metal physics is an increasingly important field and papers in which the modern concepts of solid-state physics are applied to the theory of stress-corrosion cracking would be desirable.

Additional information on plans for the symposium can be obtained from one of the Co-Chairmen: E. H. Phelps, Applied Research Lab., U.S. Steel Corp., Monroeville, Pa., and Hugh L. Logan, National Bureau of Standards, Washington, D. C.

## Section News

#### **Chicago Section**

The January meeting of the Chicago Section was held on Wednesday, the 24th, rather than on the second Thursday of the month as is usual, to permit the scheduling as speaker of Society President Henry B. Linford.

The largest turnout of the year was a fitting tribute to this fine speaker, astute scientist, and one of the very best salesmen for the Society. His subjects: "Electrokinetics of Electrodeposition" and, of course, "Various Aspects of Society Affairs."

The stimulus of Dr. Linford's visit resulted in another fine turnout on February 8 to hear a paper on the "Electron Microscope Study of Surface Films on Metals" by Raymond K. Hart of the Argonne National Lab. Dr. Hart proved to be an outstanding authority on the electron microscope and on the growth and structure of corrosion product films on metals.

G. H. Timmings, Secretary

#### Indianapolis Section

The Indianapolis Section was host to Dr. Henry B. Linford at its January 26 meeting. President Linford discussed Society affairs and recent actions of the Board, after which he presented the paper "Cleaning for Electroplating." The presentation

<sup>\*</sup> No paper will be placed on the program unless one of the authors, or a qualified person designated by the authors, has agreed to present it in person.

covered the various tests on oxide films, adhesion, and charging curves for clean and soiled cathodes. The description of the meticulous care and exacting work required on this A.E.S.-sponsored research project was most interesting and informative.

M. L. Whitehurst, Sec.-Treas.

#### **Pittsburgh Section**

The Pittsburgh Section was honored to play host to the Society's President, Henry B. Linford, on January 22. At a meeting sponsored jointly with the Physical-Inorganic Group of the Pittsburgh Section of the American Chemical Society, Dr. Linford discussed his work on "The Effect of Soils on the Electrodeposition Process." At a dinner preceding the meeting, Dr. Linford talked about Society history, present activities, and plans for the future.

The Pittsburgh Section recently sent announcements to all local colleges and universities, inviting entries for the annual award in electrochemistry sponsored by the Section.

R. P. Frankenthal, Sec.-Treas.

#### San Francisco Section

The January meeting of the San Francisco Section was held at the Men's Faculty Club at the University of California in Berkeley. Following dinner, a short business meeting was held, the primary topic concerning the publication of an additional magazine by the Society. A number of opinions were expressed again, but no formal action was taken.

Dr. James J. McMullen spoke on epitaxial deposition, describing work done in the silicon system. The speaker reviewed the reasons for

#### Unpaid Members Off Mailing List April 1

According to the Constitution of the Society, Article III, Section 9, the names of all members whose dues for 1961 are not paid by April 1 must be removed from the mailing list, and will not receive the May issue of the JOURNAL. To avoid delay in receipt of JOURNALS as published, all members who have not yet sent in 1962 payments are urged to do so immediately.

Please be sure to use the new address of the Society, 30 East 42 St., New York 17, N. Y. the semiconductor industry's interest in epitaxial deposition. A brief review of the methods for the vapor deposition of silicon followed. Dr. McMullen described some of the problems encountered in such deposition in relation to semiconductors, and some of the practices used to solve the problems.

F. J. Bowen, Vice-Chairman

#### Washington-Baltimore Section

The third meeting of the 1961-1962 season was held at the National Bureau of Standards on January 18. Dr. Sigmund Schuldiner of the Naval Research Lab. was Chairman. Following a brief business session, the speaker, C. K. McLane, of the Heat Div., National Bureau of Standards, was introduced by the Program Chairman, Dr. Blanton C. Duncan.

Dr. McLane's topic was "Some Properties of the Gaseous Plasma." He gave an interesting general discussion of gaseous plasmas and their properties, as well as touching on a number of specific items. The latter included discussion of a plasma as a thermionic generator and as a magnetohydrodynamic generator; elucidation of thermal, nonthermal. and magnetic plasmas; and a discussion of temperature-density relations for different plasmas, e.g., solar and thermonuclear. He closed the discussion by drawing parallels between electrical effects that occur in plasmas with those that occur in electrolytic systems.

V. A. Lamb, Secretary

## Electronics Division Enlarged Abstract Booklet—1962 (Vol. 11, No. 1) Optical Masers, Semiconductors, Luminescence

The 1962 edition of the Enlarged Abstracts booklet will contain 1000-word abstracts of the papers to be presented before the Electronics Division at the Los Angeles Spring Meeting of The Electrochemical Society (May 6-10).

The booklet will contain about 300 pages and will include approximately 15 papers on Optical Masers, 52 papers on Semiconductors, and 27 papers on Luminescence.

The booklet will be mailed about four weeks prior to the meeting.

The price will be \$4.00 per copy with a discount of \$0.50 (net \$3.50 each) for orders accompanied by payment and requiring no invoicing. Orders requiring invoicing will be charged full price, even though payment does accompany the order.

In order to insure obtaining your copy, please fill in the order form below, enclose your check, and return to me as soon as possible. Make checks payable to: *Electronics Division, Electrochemical Society*, and mail to me at the address shown on the form.

Austin E. Hardy, Secretary-Treasurer

Please enter my order for copies of the Spring 1962 Enlarged Abstract Booklet, Vol. 11, No. 1.			
Bill later, \$4.00 each			
(Make checks payable to: Electronics Division, Electrochemical Society) (Mail order to: Austin E. Hardy, c/o Radio Corp. of America, Lan- caster, Pa.)			
Ship booklet to:			

## New Members

In March 1962, the following were elected to membership in The Electrochemical Society by the Admissions Committee:

#### Active Members

- J. C. K. Abrahami, Leesona Moos Labs.; Mail add: 138-32 90th Ave., Jamaica 35, N. Y. (Electro-Organic, Theoretical Electrochemistry)
- Daniel Berg, Westinghouse Research Labs., Pittsburgh 35, Pa. (Electric Insulation)
- C. J. Beuscher, International Telephone & Telegraph Corp., 3700
  E. Pontiac, Fort Wayne, Ind. (Electrodeposition)
- P. S. Blickensderfer, Champion Paper & Fibre Co., Knightsbridge, Hamilton, Ohio (Electrodeposition)
- P. L. Bourgault, Johnson Matthey & Mallory Ltd., 110 Industry St., Toronto 15, Ont., Canada (Theoretical Electrochemistry)
- A. V. Clack, Kaiser Aluminum & Chemical Corp., P. O. Box 6217, Hillyard Station, Spokane 28, Wash. (Electrothermics & Metallurgy)
- F. C. Collins, Shockley Transistor Corp., Stanford Industrial Park, Palo Alto, Calif. (Electronics— Semiconductors)
- J. M. Dessureault, Canadian Carborundum Co.; Mail add: 1472 8th Ave., Grand Mere, Que., Canada (Electrothermics & Metallurgy)
- P. F. Duby, Henry Krumb School of Mines, Columbia University, New

By action of the Board of Directors of the Society, all prospective members must include first year's dues with their applications for membership.

Also, please note that, if sponsors sign the application form itself, processing can be expedited considerably.

York 27, N. Y. (Battery, Electrothermics & Metallurgy, Industrial Electrolytic)

- R. E. Ewing, Shockley Transistor Corp.; Mail add: 2475 Burnham Way, Palo Alto, Calif. (Electronics—Semiconductors)
- Harold Field, Mallory Battery Co.; Mail add: 40 Edgewood Rd., Peekskill, N. Y. (Battery, Corrosion, Electrodeposition, Electrothermics & Metallurgy)
- R. J. Flannery, American Oil Co.; Mail add: 108 26th St., Park Forest, Ill. (Battery, Electro-Organic, Theoretical Electrochemistry)
- R. L. Graves, Sprague Electric Co., Concord, N. H. (Electronics— Semiconductors)
- Werner Herrmann, Robert Bosch GmbH.; Mail add: Heiligenbergstr. 65, Stuttgart-Feuerbach, Germany (Battery)
- P. A. Hersch, Beckman Instruments, Inc., 2500 Harbor Blvd., Fullerton, Calif. (Battery, Corrosion)
- E. D. Jungbluth, General Telephone & Electronics Labs., Willets Point Blvd., Bayside, N. Y. (Electronics —Semiconductors, Electrothermics & Metallurgy)
- S. J. Krumbein, DECO, General Electric Co., 950 Western

Ave., West Lynn 3, Mass. (Battery, Electrodeposition, Theoretical Electrochemistry)

- H. D. Kerfman, General American Transportation Corp.; Mail add: 739 N. Wells St., Chicago 10, Ill. (Corrosion, Electrodeposition)
- Jean Laroche, ONIA, Route d'Espagne, Toulouse, France
- J. F. Laurent, S.A.F.T.; Mail add: 19 Ave. Victor Hugo, Pavillonssous-Bois, Seine, France (Battery, Corrosion, Electrodeposition, Electro-Organic, Electrothermics & Metallurgy, Industrial Electrolytic, Theoretical Electrochemistry)
- S. C. Lawrence, Jr., Transport Div., Boeing Airplane Co.; Mail add: 1814 S. 142 Place, Seattle 88, Wash. (Corrosion, Electrodeposition, Electrothermics & Metallurgy, Theoretical Electrochemistry)
- S. M. Lee, Chemical Research Dept., Electro-Optical Systems, Inc., 125 N. Vinedo, Pasadena, Calif. (Electro-Organic)
- D. J. Levy, Lockheed Missiles & Space Div.; Mail add: 1540 Meadow Lane, Mountain View, Calif. (Corrosion, Electrodeposition, Theoretical Electrochemistry)
- W. H. Long, National Carbon Co.; Mail add: 5422 Elm Dr., Lewiston, N. Y. (Electrothermics & Metallurgy, Industrial Electrolytic)
- E. F. Moorman, International Harvester Co., 7 S. 600 County Line Rd., Hinsdale, Ill.
- R. P. Morgan, Youngstown Sheet & Tube Co., Youngstown 2, Ohio (Corrosion, Electrodeposi-

# Manuscripts and Abstracts for Fall 1962 Meeting

Papers are now being solicited for the Fall Meeting of the Society, to be held at the Statler-Hilton Hotel in Boston, Mass., September 16, 17, 18, 19, and 20, 1962. Technical sessions will be scheduled on: Batteries (General Sessions on primary and secondary batteries, and fuel cells), Battery—Theoretical Electrochemistry Joint Symposium on Porous Electrodes, Corrosion, Corrosion—Electronics Joint Symposium on Phenomena at Interfaces, Electrodeposition (including a Symposium on Alloy Electrodeposition), Electrodeposition—Electronics Joint Symposium on Electrochemical Processes for Semiconductor Devices, Electronics-Semiconductors (including a Symposium on Semiconductor Phenomena), Electrothermics and Metallurgy (including a Symposium on Hot Pressing), Electrothermics and Metallurgy—Corrosion Joint Symposium on High-Temperature Corrosion.

To be considered for this meeting, triplicate copies of abstracts (not exceeding 75 words in length) must be received at Society Headquarters, 30 East 42 St., New York 17, N. Y., not later than May 15, 1962. Please indicate on abstract for which Division's symposium the paper is to be scheduled and underline the name of the author who will present the paper. No paper will be placed on the program unless one of the authors, or a qualified person designated by the authors, has agreed to present it in person. An author who wishes his paper considered for publication in the JOUNNAL should send triplicate copies of the manuscript to the Managing Editor of the JOUNNAL, 30 East 42 St., New York 17, N. Y.

Presentation of a paper at a technical meeting of the Society does not guarantee publication in the JOURNAL. However, all papers so presented become the property of The Electrochemical Society, and may not be published elsewhere, either in whole or in part, unless permission for release is requested of and granted by the Editor. Papers already published elsewhere, or submitted for publication elsewhere, are not acceptable for oral presentation except on invitation by a Divisional program Chairman. tion, Electrothermics & Metallurgy, Industrial Electrolytic)

- Arthur Moskowitz, Crucible Steel Co. of America, 234 Atwood St., Pittsburgh 13, Pa. (Corrosion)
- E. B. Oldenburg, AMP Inc.; Mail add: 66 Hillside Dr., Carlisle, Pa. (Electrodeposition)
- J. N. Ong, Jr., Aeronutronic Div., Ford Motor Co.; Mail add: 20361 S.W. Birch St., Santa Ana, Calif. (Corrosion)
- R. M. Paine, Brush Beryllium Co.; Mail add: 1647 Northland Ave., Lakewood 7, Ohio (Electrothermics & Metallurgy)
- J. G. Peace, Aerovox Corp., 740 Belleville Ave., New Bedford, Mass. (Electric Insulation)
- C. F. Pihl, Sprague Electric Co.; Mail add: Box 155, Henniker, N. H. (Electrodeposition, Electronics— Semiconductors, Electrothermics & Metallurgy)
- Curtis Randolph, Texas Instruments, Inc., Box 5012, Dallas 22, Texas (Electronics—Semiconductors)
- G. H. Richter, Bell Telephone Labs., Inc.; Mail add: 200 W. 18 St., New York 11, N. Y. (Battery)
- J. M. Ross, Columbian Carbon Co., Box 975, Princeton, N. J. (Battery)
- S. D. Ross, Sprague Electric Co.; Mail add: 142 Main St., Williamstown, Mass. (Electro-Organic)
- Emil Rubes, Popov Research Institute for Radiocommunications; Mail add: 195 Smetanova, Prague, Czechoslovakia (Electronics-Semiconductors & Luminescence, Electro-Organic, Electrothermics & Metallurgy)
- D. P. Sanders, Philco Corp.; Mail add: 1152 Boyd Ave., Lansdale MR2, Pa. (Electronics—Semiconductors)
- G. T. Sermon, United Carbon Products Co.; Mail add: P. O. Box 747, Bay City, Mich. (Electrothermics & Metallurgy)
- P. J. Shipe, Delco Moraine Div., General Motors Corp., 1420 Wisconsin Blvd., Dayton 1, Ohio (Electrodeposition)
- G. W. Stackhouse, P. R. Mallory & Co., Inc.; Mail add: 640 N. Gray St., Indianapolis 1, Ind. (Battery, Electrodeposition)
- J. E. Steinhelper, Jr., Bendix Corp.; Mail add: 16151 Fielding Ave., Detroit 19, Mich. (Electronics— Semiconductors)
- Edwin Sterling, Bell Telephone Labs., Inc., 2D418, Murray Hill, N. J. (Electronics—Semiconductors, Electrothermics & Metallurgy)
- S. G. Taseos, Solid State Products Inc.; Mail Add: 24 Princeton Rd., Burlington, Mass. (Electronics— Semiconductors)

- Angelo Tulumello, School of Electrical Engineering, Purdue University, West Lafayette, Ind. (Electrodeposition, Electronics— Semiconductors, Electrothermics & Metallurgy)
- Haig Vartanian, National Research Corp.; Mail add: 297 Bellevue St., Newton 58, Mass. (Theoretical Electrochemistry)
- L. E. Q. Walker, Marconi's Wireless Telegraph Co. Ltd., Baddow Research Labs., West Hanningfield Rd., Great Baddow, Chelmsford, Essex, England (Electrodeposition, Theoretical Electrochemistry)
- J. H. Weaver, Aeronautical Systems Div., WPAFB; Mail add: 2340 W. Skyview Dr., Dayton 32, Ohio (Electrodeposition)
- J. R. Williams, Crystlonics, Inc.; Mail add: 156 Cottage St., Natick, Mass. (Electronics—Semiconductors)
- O. W. Wilson, Central Research Labs., Texas Instruments, Inc., 13500 N. Central Expressway, Dallas, Texas (Electronics—Semiconductors)

#### Associate Members

- S. D. Axelrod, Tyco, Inc.; Mail add: 51 Carey Ave., Watertown, Mass. (Electronics—Semiconductors)
- Martha Chin, Lockheed Missiles & Space Div.; Mail add: 344 E. Englewood Ave., Sunnyvale, Calif. (Electrodeposition, Electronics, Electro-Organic)
- D. O. Fegenbush, Sr., Electra Mfg. Co., 800 N. 21 St., Independence,

Kansas (Electrodeposition, Electronics)

- M. C. McKinnon, Bendix Research Labs., 10½ Mile & Northwestern, Southfield, Mich. (Electronics-Semiconductors)
- Fred Schulenburg, Jr., Fairchild Semiconductor Corp.; Mail add: 3239 Waverly St., Palo Alto, Calif. (Electronics)

#### Reinstatements to Active Membership

- W. G. Hennessey, Union Carbide Consumer Products Co.; Mail add: 2245 Riverside Dr., Lakewood 7, Ohio (Battery)
- J. C. La Plante, Alloys Unlimited, Inc., 21-01 43rd Ave., Long Island City 1, N.Y. (Electronics—Semiconductors, Electrothermics & Metallurgy)

#### Transfers from Student to Active Membership

- Harlow Freitag, IBM Corp.; Mail add: 2043 Crompond Rd., Yorktown Heights, N. Y. (Theoretical Electrochemistry)
- D. R. Rhodes, California Research Corp., Box 1627, Richmond, Calif. (Theoretical Electrochemistry)
- R. L. South, Geneva College; Mail add: 806 12th St., New Brighton, Pa. (Theoretical Electrochemistry)

## Personals

**R. Porter Bailey** has left Eldorado Mining & Refining Ltd., Ottawa, Canada, to join the Dept. of Mines

# Papers Solicited for New ECS Magazine to be Published in 1963

As announced in the February issue of the JOURNAL (page 37C), The Electrochemical Society will publish a new magazine under a name and cover design yet to be adopted. The first issue will be published in January-February 1963. Initially, the new publication will be issued bimonthly. It will become a monthly publication as soon as enough papers are received to justify such a step.

The new magazine will cover electroprocesses in areas of technology, engineering, design, devices, economics, and appropriate reviews. The same review procedures which apply to the present JOURNAL will also obtain with regard to the new magazine.

A. C. Loonam, Editor, is now soliciting papers for publication in the new magazine. All members and others concerned, who are engaged in the applied areas of electroprocesses, who can submit papers on timely subjects are urged to do so as soon as possible.

Triplicate copies of each manuscript, prepared in accordance with the Instructions to Authors of Papers published on pp. 31C-32C of the January 1962 JOURNAL, should be submitted to the Editor of the new magazine, A. C. Loonam, The Electrochemical Society, Inc., 30 East 42 St., New York 17, N. Y.

Manuscripts so submitted become the property of The Electrochemical Society and may not be published elsewhere, in whole or in part, unless permission is requested of and granted by the Editor. & Technical Surveys, Ottawa, as a metallurgist in the Mineral Processing Div.

Myron E. Browning has joined the Research & Development Div. of American Machine & Foundry Co., Alexandria, Va., as project manager in the Advanced Research Dept. His responsibilities will include project direction in applied electrochemistry, alloy electrodeposition, vapor deposition, and high-temperature intermetallic coatings. Mr. Browning formerly was associated with the Fort Worth Div. of General Dynamics Corp.

M. C. Carosella has been appointed director of development in the Technology Dept. of Union Carbide Metals Co., Niagara Falls, N. Y. Mr. Carosella has been with the company since 1943. Prior to his new appointment, he served as assistant director of development since 1957.

John E. Currey has been named to the newly created position of manager-electrochemical development in the corporate enginering department of Hooker Chemical Corp., Niagara Falls, N. Y. In this capacity, he will be in charge of Hooker cell sales and licensing, and of the IBM computer section of corporate engineering. For the past year, he had been a senior engineer-electrochemical development.

George A. Cypher, formerly technical director with the Natvar Corp., Woodbridge, N. J., is now technical director with the Spaulding Fibre Co., Tonawanda, N. Y.

Edward F. Duffek has joined the Research and Development Dept. of Fairchild Semiconductor, Palo Alto, Calif., where he will be in charge of electrochemistry and plating activities. Previously, he was with Stanford Research Institute, Menlo Park.

George E. Fitzgibbon, formerly with P. R. Mallory & Co., Indianapolis, Ind., has taken a position as engineer with the Philco Corp., Lansdale, Pa. He will work on advanced device development in the area of diffusion technology of silicon.

**R. Leigh Glover** has been appointed vice-president-technology of Union Carbide Consumer Products Co., New York City. Mr. Glover, who joined the Union Carbide Corp. in 1935, had been general managertechnology for Union Carbide Consumer Products Co. since 1959.

**Rolf R. Haberecht** recently joined the staff of Texas Instruments Inc., Corporate Research and Engineering, Dallas, Texas. He had been with P. R. Mallory & Co., in Burlington, Mass.

Henry F. Ivey has been named research and engineering consultant, Lamp Div., Westinghouse Electric Coro., Bloomfield, N. J. Except for a short period, Dr. Ivey has been employed in the Lamp Div. of Westinghouse since 1946. During this time, he has engaged in research on electronic tubes and, later, lamp problems. Since 1956, he has served in the capacity of phosphor section manager.

Henry Mahlstedt, electroplating pioneer, recently announced his retirement from Metal & Thermit Corp., New York City. Mr. Mahlstedt has been closely connected with chromium plating since its initial introduction and has been responsible for a number of developments for which patents have been issued. In 1927, he joined United Chromium Inc. in Waterbury, Conn., one of the first companies to commercialize the chromium plating process. He became sales manager of that company's Plating Div. in 1948. In 1956, United Chromium was merged into Metal & Thermit Corp. Mr. Mahlstedt subsequently became M&T's plating products manager.

T. F. Nagey, director of research at the Allison Div. of General Motors Corp., Indianapolis, Ind., has been appointed to the combustion and propulsion panel of the Advisory Group for Aeronautical Research and Development. AGARD is a North Atlantic Treaty Organization instrument for the exchange of technical information.

Fred P. Peters recently was elected to the newly created position of executive vice-president of Reinhold Publishing Corp., New York City. Mr. Peters has been with Reinhold for 25 years. Since 1949, he had been a vice-president and director of the company and general manager of its Book Div., a position which he will continue to fill along with the new one. He joined the company in 1936 as assistant editor of Materials in Design Engineering magazine (then known as Metals and Alloys) and was successively associate editor and managing editor, becoming editor-in-chief in 1943. In 1948, he was made assistant general manager of the Book Div. and, in 1949, he was elected an officer and director of the company and placed in charge of its book publishing activities as general manager of the Reinhold Book Div. He also was the initial publisher of Reinhold's magazine Automatic Control, and for several years was secretary of the corporation.

**Robert F. Shurtz** has been elected a vice-president of Basic Inc., Cleveland, Ohio. Mr. Shurtz will be in charge of Basic's subsidiaries, responsible for expanding their operations into new areas and for coordinating their activities. With Basic since 1956 as assistant vicepresident-technical, Mr. Shurtz most recently headed the company's research and development program.

#### **Benjamin F. Freeberg**

Benjamin F. Freeberg, of Chicago, Ill., died on February 1, 1962 at the age of 57.

Mr. Freeberg was born on March 8, 1905 in Colorado. At the time of his death, he was employed as a chemist and metallurgist at the Vapor Heating Corp. in Chicago. He had been with the company for approximately 15 years. Prior to that, he had been affiliated with the Commonwealth Edison Co. for 22 years and with Scientific Control Labs. for 2 years.

He was an active member of The Electrochemical Society, which he joined in March 1941, both on the national and the local level. He was a Past Chairman of the Chicago Section.

He also was a member of the American Society for Metals and the Chemical Arts Forum.

## **Book Reviews**

- Wave Mechanics and Valency, by J. W. Linnett. Published by Methuen & Co., London, and John Wiley & Sons, Inc., New York City, 1960. XII + 184 pages; \$3.00.
- An Introduction to Spin-Spin Splitting in High Resolution Nuclear Magnetic Resonance Spectra, by John D. Roberts. Published by W. A. Benjamin, Inc., New York City, 1961. vii + 116 pages; \$4.95.
- Molecular Orbital Theory for Organic Chemists, by Andrew Streitwieser. Published by John

Wiley & Sons, Inc., New York City, 1961. xvi + 489 pages; \$14.50.

Time was, an organic chemist made organic chemicals and let the physical chemist worry about quantum mechanics. Not now. Today's organic chemist differs from the physical chemist only in considering physical chemistry and chemical physics as tools rather than objects of primary interest. Illustrative of the trend are these three books, each on a different aspect of wave mechanics as applied to organic chemistry.

"Wave Mechanics and Valency" by J. W. Linnett is an excellent introductory monograph. It gives the derivation of the basic Schrödinger equation and some of the applications. Topics covered are the particle in a box, in a ring, and on a sphere, the hydrogen atom and molecule, the helium atom, polyelectronic molecules, and inorganic polyatomic molecules and ions. The mathematics is given without rigor but with clear and definite statements of all assumptions and their implications and of the limitations of the solutions. The writing is clear and straightforward and the author takes pains to point out at least qualitatively all of the basic principles and ideas involved. This reviewer would recommend this book both as an introductory text and as a review outline for those who have long been away from the subject.

"An Introduction to Spin-Spin Splitting in High Resolution Nuclear Magnetic Resonance Spectra" by John D. Roberts is essentially a "how-to---" manual for making quantum mechanical computations in NMR spectroscopy. The author gives a brief qualitative introduction to spin-spin splitting, and follows by showing how to formulate nuclear spin states and how to compute their energies and the probabilities of transitions between states. In this book also, the mathematics is nonrigorous. The treatment is, as the author puts it, illustrative rather than comprehensive. Many exercises and problems have been included but there is. unfortunately, no way for the reader to check the answers. The production job is very good and the charts and graphs are clear and helpful. The book would be of value to anyone working in the field of NMR and also would be helpful to students learning how to make quantum mechanical calculations.

"Molecular Orbital Theory for Organic Chemists" by Andrew Streitwieser is a critical review of the literature through 1960, and a report of original contributions and interpretations by the author. It purports as well to be a textbook for the interested student. With this last, this reviewer must disagree. It is, rather, a review volume for those already familiar with at least the outlines of the field. The introductory part covers simple molecular orbital theory with stress on the Hückel approximation method. The body of the main part covers the application of the theory to molecular properties such as dipole moments, ionization and redox potentials, spectra, resonance energy, and aromaticity to reactions, including aromatic substitution, carbanion and carbonium ion and radical reactions, and four center reactions. The book would be of value to the theoretical physical or organic chemist or chemical physicist as a literature survey and review book. There is, however, much too much advanced material for the student who does not have a thorough background in quantum mechanics.

In the conclusion to his monograph, Linnett observes that it has not been possible to treat exactly any electronic system which contains more than one electron, and it is not yet possible to calculate quantities such as heats of dissociation or energies of activation with a reliability sufficient to make them valuable. Such calculations are still at the point where they are useful chiefly as a guide to further development, to new ideas, and fresh interrelationships between experimental data.

> H. W. Salzberg City College

#### The Proton in Chemistry, by R. P. Bell. Published by the Cornell University Press, Ithaca, N. Y., 1959. vii + 223 pages; \$4.75. (Includes a preface, table of contents, author index, and subject index.)

This book is a sequel to the author's "Acid-Base Catalysis" (1941) and deals with the material Bell discussed in his George Fisher Baker Lectures in 1958. (This reviewer attended these interesting and informative lectures, and now finds the amplified published version most welcome.) Those interested in proton transfer reactions are thus provided with an opportunity to consider carefully the arguments supporting Bell's concepts and interpretations, which in some instances are still being debated, and to study closely the large amount of quantitative material which is incorporated in the text.

In the introduction, Bell briefly outlines the reasons for assigning a special role to the positive ion of hydrogen. In the ten chapters which follow, he amply supports this treatment by analyzing the nature of acids and bases, the effect of the solvent on proton transfer reactions, the relation between acid-base strength and molecular structure, the rates of acid-base reactions, and the catalytic functions possessed by acids and bases. He also discusses in some detail the definition of the terms acidbase, restricting them to the Brönsted formulation, and the measurement of acid-base strengths in aqueous solutions. The thermodynamic functions which provide quantitative measures of acid-base equilibria, the properties of concentrated solutions, and the magnitudes of isotope effects in acid-base reactions have been presented with clarity.

Bell's style is easy to read; his sentences are straightforward. He holds the reader's interest in the subject by allusions to the historical development of the concepts and by critical analyses of them. References to the literature are copious, a few being as recent as 1959. The reader of this book in 1962 will, of course, have to supplement the few references to proton magnetic resonance

## **December 1962 Discussion Section**

A Discussion Section, covering papers published in the January-June 1962 JOURNALS, is scheduled for publication in the December 1962 issue. Any discussion which did not reach the Editor in time for inclusion in the June 1962 Discussion Section will be included in the December 1962 issue.

Those who plan to contribute remarks for this Discussion Section should submit their comments or questions in triplicate to the Managing Editor of the JOURNAL, 30 East 42 St., New York 17, N. Y. not later than September 3, 1962. All discussion will be forwarded to the author(s) for reply before being printed in the JOURNAL.

studies as applied to proton transfer reactions by referring to one of several recent books on this subject. Further, the chapter on rates of acidbase reactions could be amplified considerably at present and, in a few instances, work which has now been proven erroneous could be corrected. Some revision is in order regarding the assembled evidence for existence of the species H<sub>3</sub>O<sup>+</sup>, in the first part of Chapter III. After calling attention to the various physical measurements which argue for this entity in solid acid hydrates, the author points out that it is "much more difficult to get clear evidence for the existence of a recognizable H<sub>3</sub>O<sup>+</sup> ion in aqueous solutions." However, current kinetic data strongly favor H<sub>0</sub>O<sub>4</sub><sup>+</sup> as the unit. Mass spectral data indicate that this ion has a relatively high stability even in the gas phase.

The typography and paper of the book are of good quality, as is the binding.

> S. H. Bauer Cornell University

## News Items

#### Second International Symposium on Passivity

The Second International Symposium on Passivity will be held at the University of Toronto, Ontario, Canada, during the week of September 3-7, 1962, sponsored by The Electrochemical Society, the American Society for Testing and Materials, the Deutsche Bunsen Gesellschaft, and the Faraday Society. The preliminary program indicates that papers will be presented by scientists from England, Germany, U.S.A., Canada, Russia, Japan, and some other countries. They cover all aspects of the passive phenomenon, ranging from optical measurements of passive film thickness, to reaction kinetics on passive metal surfaces and the nature of passivity in alloys. All papers will be published in a special issue of the JOURNAL of The Electrochemical Society scheduled to appear soon after the Symposium date.

Those who are actively carrying out research in the field of passivity are invited to write for further information to members of the Organizing Committee. Dr. T. P. Hoar, Dept. of Metallurgy, University of Cambridge, Cambridge, England, represents the Faraday Society; Professor Helmuth Fischer, Institut für Physikalische Chemie und Elektrochemie der Technischen Hochschule Karlsruhe, Karlsruhe, West Germany, represents the Deutsche Bunsen Gesellschaft; and The Electrochemical Society is represented by Dr. Morris Cohen, National Research Council, Ottawa, Canada; Professor Norman Hackerman, University of Texas, Austin, Texas; and Professor H. H. Uhlig, Massachusetts Institute of Technology, Cambridge, Mass.

## 1962 National Electronics Conference

The 1962 National Electronics Conference will be held at Chicago's magnificent new exposition hall, McCormick Place, on October 8, 9, and 10. It is expected that 100 technical papers will be presented.

The American Institute of Electrical Engineers will be conducting its Fall General Meeting in Chicago during the NEC period. A convenient joint registration procedure has been arranged.

For further information, contact the National Electronics Conference, Inc., 228 N. LaSalle St., Chicago 1, Ill.

#### 45th Canadian Chemical Conference

Upward of 800 delegates are expected to attend the 45th Canadian Chemical Conference and Exhibition of The Chemical Institute of Canada in Edmonton, Alberta, May 27-30, according to O. A. Greiner, general conference chairman. Mr. Greiner is plant manager, Canadian Chemical Co. Ltd., Edmonton, Alberta.

The technical sessions and the Exhibition of New Chemicals and Equipment will be held at the Physical Sciences Centre of the University of Alberta, while social events will be centered at the Macdonald Hotel.

#### Pacific Regional Meeting for Applied Spectroscopy and Analytical Chemistry

The First Annual Pacific Regional Meeting for Applied Spectroscopy and Analytical Chemistry will be held October 18-19, 1962 at the Huntington-Sheraton Hotel, Pasadena, Calif. Sponsor for the meeting is the Los Angeles Chapter of the Society for Applied Spectroscopy, in cooperation with the San Diego and San Francisco Chapters and the Southern California Section of the American Chemical Society.

The two-day meeting program includes four technical sessions of one half day each, a banquet meeting, and an instrument exhibit where manufacturers will demonstrate the latest in scientific equipment.

Those interested in submitting papers for the meeting should forward abstracts of not less than 150 words to the program chairman: Arthur A. Chodos, Div. of Geological Sciences, California Institute of Technology, Pasadena, Calif.

An instrument exhibit will be conducted in the hotel on the same floor with the meeting rooms. Exhibitors should contact Mr. P. Evans at Braun Chemical Co., 1363 S. Bonnie Beach Place, Los Angeles, regarding space and other information.

Additional information can be obtained from the meeting chairman: Dr. W. F. Ulrich, Scientific and Process Instruments Div., Beckman Instruments, Fullerton, Calif.

#### **Conference of Metallurgists**

A Conference of Metallurgists, arranged by the Metallurgy Division of The Canadian Institute of Mining and Metallurgy, will be held at McMaster University in Hamilton, Ont., Canada, on September 5, 6, and 7, 1962.

Dr. John Convey, director of the Mines Branch, Dept. of Mines and Technical Surveys, Ottawa, is general chairman. The program will cover the fields of mineral dressing, extractive metallurgy, iron and steel, physical metallurgy, and metal physics. Plant tours to Hamilton's metallurgical industries are also being arranged.

#### Seventh Annual Appalachian Underground Corrosion Short Course

The Seventh Annual Appalachian Underground Corrosion Short Course will be held June 12, 13, and 14, 1962 at West Virginia University, School of Mines, Morgantown, W. Va. It will cover basic, intermediate, and advanced education of corrosion control practices as related to underground pipe, cable, and water systems. Approximately 64 papers are scheduled, plus field demonstrations.

Additional information can be obtained by contacting Mr. W. E. Cook, Jr., publicity chairman, Pipe Line Service Corp., P. O. Box 465, Glenwillard, Pa.

#### Motorola Forms New Division

Motorola Inc., Chicago, has announced the formation of a new company division to be known as the Solid State Systems Division, with headquarters in the company's facility at 3102 N. 56 St. Phoenix, Ariz.

The new division, under the leadership of Dr. H. William Welch, Jr., joins the Communications, Military Electronics, and Semiconductor Products technically oriented divisions reporting to Daniel E. Noble, executive vice-president and director of the corporation. Dr. Noble has explained that the advancement of the Solid State Systems group to full divisional status reflects the degree of maturity attained by this group since its beginning three years ago and will better identify the organization in terms of its dual mission of solid state research and industrial products development and manufacture.

#### New Unified Scale Adopted for Atomic Weights

The International Union of Pure and Applied Chemistry has adopted a new basis for the expression of atomic weights—the exact number 12 as the assigned atomic (nuclidic) mass of the principal isotope of carbon—carbon 12. This action, taken in August 1961, parallels the 1960 action of the International Union of Pure and Applied Physics.

Prior to about 1930, both physicists and chemists had used natural oxygen with an atomic weight of 16 as the basis for fixing the scale of atomic weights. However, the discovery that natural oxygen is a mixture of three isotopes, and a slightly variable mixture at that, led physicists to assign the number 16 as the atomic mass of oxygen isotope 16, whereas chemists continued to use 16 as the atomic weight of natural oxygen.

The International Commission on Atomic Weights took the first step toward unification in 1957 with the proposal that carbon 12 be adopted as a common reference species. Dr. Edward Wichers, associate director of the National Bureau of Standards, who was then president of the Commission, advocated the adoption of the new basis among chemists. Similar work was done among physicists by Dr. J. Mattauch, the leading figure in Germany in the field of mass spectroscopy. After considerable discussion by the organizations concerned, and by interested scientists, carbon 12, the most abundant natural isotope of carbon, was adopted as the reference species for a unified scale, with assigned mass of 12 exactly.

An official table of atomic weights, based on the new standard, was published by the IUPAC in October 1961, with the recommendation that it be placed in universal use as of January 1, 1962. Values in this table differ from those based on natural oxygen by about 40 ppm, and from those based on isotopic oxygen 16 by about 300 ppm. In addition to these systematic changes, many values were revised in light of the re-evaluation of experimental data by the Commission. No atomic weights are listed in the new table for most radioactive elements, as these elements have no fixed value. However, a more complete table, listing the mode of distintegration and mass numbers of selected isotopes, will be published with the proceedings of the 1961 IUPAC meeting.

#### Highly Enriched Stable Isotopes Available

Oak Ridge National Laboratory is now offering more highly enriched separated stable isotopes of the rare gases krypton, neon, and argon. Krypton-86, with a natural abundance of 17.37%, is enriched to 99.-97%; neon-22, from 8.82% to 99.95%; and argon-36, from 0.337% to 99.95%.

These highly enriched stable isotopes are the product of the Oak Ridge Isotopes Development Center at ORNL and reflect a constant effort to supply the nation's research programs with large quantities of highpurity isotope materials. These rare gas isotopes, produced by a thermal diffusion process are available at a cost of \$6.70 per cc for argon-36, \$7.55 per cc for neon-22, and \$7.50 per cc for krypton-86.

Oak Ridge National Lab., one of the nation's largest nuclear energy research and development laboratories and principal isotope center in the United States, is operated by Union Carbide Corp. for the U.S. Atomic Energy Commission.

#### Ruby Optical Maser Operated Continuously at Bell Labs.

A ruby optical maser emitting a coherent red beam has operated continuously at Bell Telephone Laboratories. It is the first solid-state optical maser to emit continuous coherent visible light. This advance has been made possible by development of a radically new way to excite the master crystal which gives a "pumping" intensity five times greater than has been possible from previous continuous optical maser pumps.

The new technique was described at a meeting of the American Phy-

## New 10-Year Index of ECS Journal

The new 10-Year Index of the JOURNAL of The Electrochemical Society, covering Volumes 99-108 for the years 1952-1961, will be published in the spring of 1962.

This publication will include Subject Index and Author Index, the latter with title of paper following each author's name. This will be an invaluable addition to your library.

Price to ECS Members	\$12.50
Price to Subscribers and Nonmembers	
prepublication (until April 1, 1962)	12.50
postpublication (after April 1, 1962)	15.00

If you have not yet ordered your copy of the new 10-Year Index, the order form below may be used. Remittance, made payable to The Electrochemical Society, Inc., should accompany your order.

Purchasers located overseas should remit by New York Bank Draft or United States International Money Order.

THE ELECTROCHEMICAL SOCIETY, INC., 30 East 42 St., New York 17, N.Y.
Date
Please send me a copy of the 10-Year Index of the JOURNAL of The Electrochemical Society covering Vol. 99-108 (1952-1961).
Attached is remittance in the amount of \$
Name
Company
Street Address
City
Country
ECS Member Subscriber or Nonmember

sical Society by William S. Boyle and Donald F. Nelson. Besides proving that a ruby optical maser can operate continuously, the configuration provides a convenient geometry for conducting a number of physical experiments. The pumping technique will apply to masers using materials other than ruby. This new development is another step toward communications over optical carrier waves.

It has been only a little over a year since the first solid-state optical maser was made to operate on a pulsed basis. This was a ruby rod. with highly reflective ends, surrounded by a spiral flash lamp. The discharging lamp caused a beam of coherent, monochromatic light to emerge from the ends of the rod in an extremely narrow cone. Similar configurations using other maser materials have since resulted in a number of pulse-operated, solidstate masers. Recently, Bell Labs. announced continuous operation of a maser at infrared frequencies in a crystal of calcium tungstate containing a small amount of neodymium.

One of the most significant improvements in solid-state masers is in the lowering of the power requirements for the pumping source. Ruby originally needed over 1000 kw for pulsed operation; it now needs less than 1 kw to operate continuously. In the present ruby maser, action starts when the input power exceeds 850w, giving an output power in the maser beam of a few milliwatts.

The maser material consists of two separate materials grown by the Linde Co. as a special boule of one crystal. The maser crystal is shaped like a trumpet. Its "front" is pure aluminum oxide (sapphire) in the shape of a cone forming the "bell' of the trumpet. The face of the bell, approximately 60 mils in diameter, receives the pumping arc. The cone portion of the trumpet tapers down to meet a shank of chromium-doped aluminum oxide, or ruby, which has a diameter of approximately 24 mils. It is in this shank that maser action takes place, producing the intense red maser beam.

The image of the arc of the pumping lamp reaches the face of the trumpet at the same size and intensity as the arc itself. The cone of the trumpet acts as a "radiation condenser," making the arc light six times more intense as it enters the shank. The light then travels down the shank by a series of internal reflections. A silver coating at the end of the rod causes the pumping light to return and emerge at the original face. Since the pumping light travels a "double path" its intensity, already increased six times, is doubled, making it much greater than that in a conventional maser rod receiving light from the side. The result is a lower required power to the pumping lamp that produces the continuous maser action.

Initial results of the continuous operation of the ruby optical maser, as well as a full description of the new pumping arrangement, appeared in the March issue of the Journal of Applied Optics.

#### G. E. Awarded Navy Contract for Research on Thermionic Materials

The General Electric Co., Palo Alto, Calif., has been awarded a \$153,000 contract by the U.S. Navy Bureau of Ships for a one-year research and development program on thermionic materials. Signing of the contract was announced by Herman Miller, manager of G.E.'s Special Purpose Nuclear Systems Operation (SPNSO), which will have project responsibility. Mr. Miller indicated the program will contribute information of value in the development of reliable, long-lived thermionic power supplies for use in space, the underseas, and at remote land sites.

Development work will be conducted at the company's Vallecitos Atomic Lab. near Pleasanton under the direction of Dr. M. J. Sanderson, an authority on thermionic materials.

The program is designed to provide data not available at present on high-temperature thermionic materials, particularly those of importance for nuclear applications.

#### First Pound of Scandium Analyzed

Analysis of the first pound of scandium ever made indicates that the extremely rare metal has mechanical and physical properties very similar to yttrium and somewhat similar to titanium.

Conducted by Doyle Geiselman, of Union Carbide Metals Co., Div. of Union Carbide Corp., the tests concluded the second of two UCM contracts with the Materials Lab., Air Research and Development Command, and the Air Materiel Command of the United States Air Force at Wright Air Development Center. The first contract called for production of a pound of scandium, the largest quantity of the metal ever to exist in one place at one time.

In fulfilling the second contract, UCM for the first time measured the practically unknown metal's crystal structure, density, electrical resistivity, thermoelastic power, and thermal expansion, as well as its hardness, modulus of elasticity, tensile strength, compressive strength, corrosion resistance, and reaction with air, nitrogen, and oxygen. Conclusions indicated that scandium is more like yttrium and the rareearth metals than aluminum or titanium.

"In fact," UCM's report said, "the research that has been conducted on yttrium might well be used as a guide to the behavior of scandium."

## Announcements from Publishers

- "Handbook of Semiconductor Electronics: A Practical Manual Covering the Physics, Technology, and Circuit Applications of Transistors, Diodes, and Photocells," Second Edition. Edited by Lloyd P. Hunter. Prepared by a staff of specialists. McGraw-Hill Handbook Series. Published by McGraw-Hill Book Co., New York City, 1962. 876 pages, plus index; 496 illustrations; \$18.50.
- "Protection of Refractory Metals for High-Temperature Service—Progress Report 3—January 1, 1961— Further Work on the Zinc-Base Coating for Niobium," G. Sandoz and others, U.S. Naval Research Lab., July 1961. Report AD 263 125,\* 37 pages; \$1.00.
- "Protection of Refractory Metals for High-Temperature Service—Progress Report 4—April 1, 1961— Final Quarterly Progress Report on the Zinc-Base Coating for Niobium," B. F. Brown and others, U.S. Naval Research Lab., Aug. 1961. Report AD 265 418,\* 18 pages; 50 cents.
- "Dislocation Relaxation Phenomena in Oxide Crystals," Sept. 1961. AEC Report NAA-SR-6222,\* 20 pages; 50 cents.
- "Oxygen Diffusion in Beryllium Oxide," Sept. 1961. AEC Report NAA-SR-6427,\* 24 pages; 50 cents.
- "Corrosion Investigations of High-Temperature Aluminum Alloys," Sept. 1961. AEC Report ANL-6204,\* 81 pages; \$2.00.
- "Corrosion and Activity Transfer in the SRE Primary Sodium System," Oct. 1961. AEC Report NAA-SR-5363,\* 42 pages; \$1.00.

\* Order from Office of Technical Services, Business and Defense Services Administration, U. S. Dept. of Commerce, Washington 25, D. C.

## Literature from Industry

Aluminum Bright-Dipping. Monsanto Chemical Co. has announced the preparation of a question and answer folder for the aluminum bright-dipping industry which gives information on easy, economical ways to control bright-dipping baths. For a free copy, write to NFB Sales Dept., Inorganic Chemicals Div., Monsanto Chemical Co., 800 N. Lindbergh Blvd., St. Louis 66, Mo.

Bright Nickel Process Manual. Hanson-Van Winkle-Munning Co. has made available a two-color, 16page brochure on its bright nickel process, Superlume. Superlume, an electroplating process for producing full bright, mirrorlike nickel deposits, is recommended where high leveling and rapid brightening ability, coupled with maximum brightness, are needed. For a copy of the Superlume manual, write to Hanson-Van Winkle-Munning Co., Church St., Matawan, N. J.

Aluminum Cleaner and Brightener, Metex M-618, designed to remove buffing compound quickly and effectively and to be compatible with bright dip solutions, is fully described in Product Data Sheet No. 108. It also is effective in removing shop oils, corrosion stains, most working inks, heat-treat scale, and smut. Data sheet is available from MacDermid Inc., Waterbury 20, Conn.

Metex Solder Stripper. Lead-tin plate now can be dissolved from printed circuit boards safely, rapidly, and economically by following information contained in Product Data Sheet No. 134. The product is used full strength at room temperature. Stripping rate of the fresh solution is approximately 6 mils/hr at 70°F. Data sheet is available from MacDermid Inc., Waterbury 20, Conn.

General-Purpose Soak Cleaner. Metex Cleaner TS-40A, a generalpurpose soak cleaner low in alkalinity and high in wetting agent content, is described in Product Data Sheet No. 45. It is designed especially as a non-etch soak cleaner for aluminum; it also is effective in cleaning copper, brass, zinc, lead, and ferrous metals. Data sheet is available from MacDermid Inc., Waterbury 20, Conn. **Chemicals Catalog.** Aceto Chemical Co., Inc., announces the availability of its Research Chemicals Div.'s new, 76-page catalog and price list, which includes more than 800 hard-to-find laboratory chemicals. Many compounds listed are also available in semicommercial quantities and are so indicated. Copies are available on request from Aceto Chemical Co., Inc., 40-40 Lawrence St., Flushing 54, N. Y.

**Neutron Activation Analysis.** Qualitative and quantitative chemical analysis through neutron activation is completely described in Technical Bulletin 10. This six-page publication contains graphs, tables, illustrations, and examples. It can be obtained from Nuclear-Chicago Corp., 359 E. Howard Ave., Des Plaines, Ill.

Acids and Anhydrides. A new 48page booklet describes the properties and uses of organic acids and anhydrides. Comprehensive data are given on acetic, propionic, butyric, 2-ethylbutyric, 2-ethylhexoic, acrylic, sorbic, valeric, and isodecanoic acids; acetic, propionic, and butyric anhydrides. Included is information on physical properties; constant-boiling mixtures; specification limits; test methods; storage, handling, and shipping; toxicological properties; and selected literature references.

The booklet is available from Union Carbide Chemicals Co., Div. of Union Carbide Corp., 270 Park Ave., New York 17, N. Y.

Conductivity Measurement and Control in High-Purity Water are discussed in a brochure written especially for users of distilled or demineralized water, nuclear power plant cooling water, semiconductor rinsing, and steam generation. Included are Wheatstone Bridge and nonbridge type circuits, instruments requiring manual balancing, and units providing continuous indication, meters, controllers, and recorders. Sections devoted to each instrument present their special characteristics and specifications.

Brochure 21644D is available from Industrial Instruments, Inc., 89 Commerce Rd., Cedar Grove, N. J.

## **New Products**

**Coleman Electrodes.** Coleman Instruments, Inc., 42 Madison St., Maywood, Ill., has introduced a com-

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pletely new line of 30 electrodes for pH measurement, millivolt measurement, and titrations in the chemical laboratory. The line includes glass, reference, metallic, and special-purpose electrodes to meet the full range of requirements for laboratory electrodes. In addition to the conventional capillary method for establishing a liquid junction, Coleman reference electrodes are available with a new method by which the liquid junction is established. The new method, incorporating precision-bore tubing and a precision-ground glass plunger, avoids problems of capillary blocking and the resultant loss of the liquid junction. The plunger permits almost instantaneous renewal of the liquid junction merely by lightly touching the exposed portion of the plunger.

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Experience should include evaluation, selection, specification, and use of materials of construction, both metallic and non-metallic, for process equipment and structures. This should include corrosion properties, fabrication procedures and inspection techniques.



## Guide for the Preparation and Publication of Synopses

Provided by United Nations Educational, Scientific, and Cultural Organization (UNESCO)

- 1. "Synopsis" is a term adopted by the Royal Society of London (in fulfillment of a recommendation of the Scientific Information Conference sponsored by the Society in 1948) and by the Unesco International Conference on Science Abstracting, 1949, to describe an author's summary of a scientific paper which is published simultaneously with the paper itself after editorial scrutiny by the editor of the journal in which it is published.
- 2. The purpose of a synopsis is not only to convenience the readers of the journal in which it is published, but also to reduce the cost and to expedite the work of the abstracting journals, and thus to contribute to the general improvement of informational services in the scientific field.
- 3. The synopsis should comprise a brief and factual summary of the contents and conclusions of the paper, a pointer to any new information which it may contain, and an indication of its relevance. It should enable the busy reader to decide more surely than he can from the mere title of the paper whether it merits his reading it.
- 4. The author of every paper is consequently requested to provide also a synopsis of it, in accordance with the following suggestions.

#### Style of Writing

5. Use complete sentences rather than a mere list of headings. Any reference to the author of the article should be in the third person. Standard rather than proprietary terms should be used. Unnecessary contractions should be avoided. It should be presumed that the reader has some knowledge of the subject but has not read the paper. The synopsis should therefore be intelligible in itself without reference to the paper. (For example, it should not cite sections or illustrations by their numerical references in the text.)

#### Content

- 6. As the title of the paper is usually read as part of the synopsis, the opening sentence should be framed accordingly so as to avoid repetition of the title. If, however, the title is not sufficiently indicative, the opening sentence should indicate the subjects covered. Usually, the beginning of a synopsis should state the objects of the investigation.
- 7. It is sometimes valuable to indicate the treatment of the subject by words such as: brief, exhaustive, theoretical, etc.
- 8. The synopsis should indicate newly observed facts, conclusions of an experiment or argument, and, if possible, the essential parts of any new theory, treatment, apparatus, technique, etc.
- 9. It should contain the names of any new compound, mineral species, etc., and any new numerical data such as physical constants; if this is not possible, it should draw attention to them. It is important to refer to new items and observations, even though some may be incidental to the main purpose of the paper; such information may otherwise be hidden although in fact it might be very useful.
- 10. When giving experimental results the synopsis should indicate the methods used; for new methods the basic principle, range of operation, and degree of accuracy should be given.

#### **References**, Citations

- 11. If it is necessary to refer in the synopsis to earlier work, the reference should always be given in the same form as in the paper; otherwise, references should be omitted.
- 12. Citations to scientific journals should be made in conformity with the standard practice of the journal for which the paper is written. (The International Conference on Science Abstracting has recommended the standard proposed by the International Organization for Standardization, Technical Committee 46, names of journals being abbreviated as in the World List of Scientific Periodicals.)

#### Length

13. The synopsis should be as concise as possible. It should only in exceptional cases exceed 200 words, so as among other things—to permit it, when printed, to be cut out and mounted on a  $3 \times 5$  inch card.

#### Publication—Language and Format

- 14. The International Conference on Science Abstracting has recommended that synopses be published in one of the more widely used languages, no matter what the original language of the paper, in order to facilitate its international usefulness.
- 15. The International Conference on Science Abstracting also commended the practice of certain journals in which all the synopses appearing in a single issue are printed together either inside the cover or with advertisements on the back in such a way that they can be cut out and mounted on index cards for reference without mutilating pages of the journal itself. For this purpose the synopses should be not more than about 4 inches wide so as to be mounted on  $3 \times 5$  inch cards.

# Monographs of The Electrochemical Society

## **ECS Series**

The following are books developed and sponsored by The Electrochemical Society and published by John Wiley & Sons, Inc., 440 Fourth Ave., New York 16, N. Y. Members of The Electrochemical Society can receive a 33 1/3% discount by ordering volumes from Society Headquarters, 30 East 42 St., New York 17, N. Y. Book and invoice will be mailed by John Wiley & Sons. Nonmembers (including subscribers) should order direct from Wiley.

Corrosion Handbook. Edited by Herbert H. Uhlig. Published 1948, 1188 pages, \$16.00

Modern Electroplating. Edited by Allen G. Gray. Published 1953, 563 pages, **\$8.50** (Out of print; new edition to be published sometime in 1962)

Abstracts of the Literature on Semiconducting and Luminescent Materials and Their Applications. Compiled by Battelle Memorial Institute.

Vol. I, 1953 Issue—published 1955, 169 pages, \$5.00 (soft cover)

Vol. II, 1954 Issue-published 1955, 200 pages, \$5.00 (soft cover)

Vol. III, 1955 Issue-Edited by E. Paskell; published 1957, 322 pages, \$10.00 (hard cover)

Vol. IV, 1956 Issue-Edited by E. Paskell; published 1959, 456 pages, \$12.00 (hard cover)

Vol. V, 1957 Issue-Edited by C. S. Peet; published 1960, 449 pages, \$12.00 (hard cover)

Vol. VI, 1958 Issue-Edited by J. J. Bulloff and C. S. Peet; published 1961, 528 pages, \$14.00 (hard cover)

Electrochemistry in Biology and Medicine. Edited by Theodore Shedlovsky. Published 1955, 369 pages, \$11.50

Vapor Plating (The Formation of Metallic and Refractory Coatings by Vapor Deposition), by C. F. Powell, I. E. Campbell, and B. W. Gonser, Published 1955, 158 pages, \$6.00

High-Temperature Technology (Materials, Methods, and Measurements). Edited by I. E. Campbell. Published 1956, 526 pages, \$15.00 (Out of print; new edition to be published sometime in 1962)

Stress Corrosion Cracking and Embrittlement. Edited by W. D. Robertson. Published 1956, 202 pages, \$7.50

Arcs in Inert Atmospheres and Vacuum. Edited by W. E. Kuhn. Published 1956, 188 pages, \$7.50 (Papers Presented at the Symposium on Arcs in Inert Atmospheres and Vacuum of the Electrothermics and Metallurgy Division of The Electrochemical Society, April 30 and May 1, 1956, San Francisco, Calif.)

Technology of Columbium (Niobium). Edited by B. W. Gonser and E. M. Sherwood. Published 1958, 120 pages, \$7.00

(Papers Presented at the Symposium on Columbium-Niobium of the Electrothermics and Metallurgy Division of The Electrochemical Society, May 15 and 16, 1958, Washington, D. C.)

- The Structure of Electrolytic Solutions. Edited by Walter J. Hamer. Published 1959, 441 pages, \$18.50 (Based on a Symposium held in Washington, D. C., in May 1957, sponsored by The Electrochemical Society, New York, and The National Science Foundation, Washington, D. C.)
- Mechanical Properties of Intermetallic Compounds. Edited by J. H. Westbrook. Published 1959, 435 pages, \$9.50 (A Symposium, Sponsored by the Electrothermics and Metallurgy Division of The Electrochemical Society, May 4, 5, and 6, 1959, Philadelphia, Pa.)
- The Surface Chemistry of Metals and Semiconductors. Edited by Harry C. Gatos, with the assistance of J. W. Faust, Jr., and W. J. La Fleur. Published 1960, 526 pa ges, \$12.50 [Proceedings of an International Symposium Sponsored Jointly by the Office of Naval Research and The Elec-

trochemical Society, Inc. (Corrosion and Electronics Divisions), October 19, 20, and 21, 1959, Columbus, Ohio]

Transactions of the Symposium on Electrode Processes. Edited by Ernest Yeager. Published 1961, 374 pages, \$20.00

(The papers and discussions of the Symposium on Electrode Processes, sponsored jointly by the U. S. Air Force, Office of Scientific Research, and The Electrochemical Society, Inc., Philadelphia, Pa., May 1959)

Iodide Metals and Metal Iodides, by Robert F. Rolsten. Published 1961, 441 pages, \$17.50

#### Vacuum Metallurgy

Vacuum Metallurgy, third printing, 1958. Edited by J. M. Blocher, Jr.; 216 pages; \$5.00, less a 20% discount to ECS members only. Available from Electrochemical Society Headquarters, 30 East 42 St., New York 17, N. Y.

(Papers Presented at the Vacuum Metallurgy Symposium of the Electrothermics and Metallurgy Division of The Electrochemical Society held in Boston, Mass., October 6 and 7, 1954)

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