

# KINETICS OF FORMATION OF ANODIC OXIDE FILMS ON BISMUTH

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## ABSTRACT

The steady-state and transient kinetics of formation of thin insulating anodic oxide films on bismuth have been investigated. The thickness of the films was determined by the spectrophotometric method. No dependence on the crystal face of the substrate was detected (sensitivity better than 1% with thicker films). The transient behavior was found to be somewhat different from that of tantalum. The activation distances were found to be unusually large. The dielectric properties were also investigated.

## INTRODUCTION

Anodic polarization of bismuth electrodes immersed, for example, in dilute sodium hydroxide solution produces uniform, insulating oxide films which show bright interference colors, and which behave, in many ways, analogously with anodic oxide films on tantalum, aluminum, titanium, and similar more reactive metals (1, 2). Bismuth was chosen for the present study because it was thought that the comparison of the behavior of bismuth with that of materials which are so different in most other respects might be expected to help to show which aspects of the kinetics of anodic film growth are essentially characteristic of the process and which are special to the particular metal. In addition there is, of course, the possibility that some application may be found for the films, particularly since there have been only two or three papers on the subject since the exploratory work of Güntherschulze and Betz in 1931. Bismuth is obtainable in rather pure state, single crystals are easily grown, and, though this technique was not used, it is of interest, in view of recent trends, that thin layers of the metal are easily fabricated by evaporation.

## EXPERIMENTAL PROCEDURES

The metal was obtained from the Consolidated Mining and Smelting Co. of Canada and was of 99.999% purity. Spherical single crystals about 2 cm in diameter were grown for us by K. G. Davis of the Physical Metallurgy Department of the University of British Columbia. Faces corresponding to (100), (110), and (111) on the pseudocubic description were prepared. These were abraded with metallurgical papers down to 4X0 paper and were then electropolished in a bath due to Hare and Mallon (3) containing 10 volumes ethanol, 10 volumes orthophosphoric acid (S.G. 1.75), and 3 volumes concentrated hydrochloric acid (S.G. 1.19) at a current density of approximately 100 ma cm<sup>-2</sup> and cell voltage of around 2.5 volt using a tubular tantalum cathode. The bath was stirred. It was at an initial temperature of about 20° C. The specimens were washed in ethanol and water. They were then dipped into a 1:4 mixture by volume of concentrated hydrochloric acid and water and, finally, washed again in water before placing in the cell. Anodic oxide films were removed in the above acid solution and the specimens were reused several times before repolishing.

Electrical contact to the specimens was made with a metal rod screwed into the bismuth crystals and insulated with apiezon-type waxes or epoxy resin. Various other stopping-off materials were tried in preliminary work. The technique was also tried of using a tantalum rod as connector, anodized to provide insulation and screwed in tightly either with or without a Teflon gasket.

Various cells were used. The kinetic work reported here was obtained with a cell similar to that used previously with tantalum (4). The reference electrode in the work quoted was a hydrogen electrode in the same solution. The whole cell was immersed in a water thermostat. It was not practical to bring the tip of the Luggin capillary very close to the specimen. In some experiments no capillary was used. In most of the

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work the ohmic drop of potential in the solution did not matter since it was independent of the thickness of the film at constant current and was eliminated in calculating such quantities as  $\Delta V/\Delta D$ . When it was necessary to correct for it, the electrolyte resistance  $R_e$  between anode and cathode was determined by extrapolating plots of series equivalent resistance against reciprocal frequency to infinite frequency; the ohmic fall was then taken as  $IR_e$ , where  $I$  denotes the total current.

The electrolyte used in the work quoted was 0.1  $M$  sodium hydroxide in distilled water. The specimen was immersed for 5 minutes before starting formation in order to let it take up the temperature of the bath. The solution was circulated rapidly during formation.

The formation was at constant current and was controlled using the automatic electronic device used previously for tantalum (e.g., ref. 4). This terminates the current when a preset voltage is reached with respect to the reference electrode, and exhibits the times required to traverse successive 1- or 10-volt intervals during formation. Other equipment, such as the a-c. bridge and the spectrophotometric apparatus, were also as previously described.

## RESULTS

### *General Behavior*

The initial questions to which answers should be sought were clear from previous work on tantalum (e.g., refs. 4-8). The difficulty is, of course, that bismuth does not behave as ideally as does tantalum. With tantalum, for example, the current efficiency for the production of oxide is very close to 100% over a wide range of current density and temperature in a wide variety of solutions. With bismuth, oxygen evolution occurs more readily. However, under favorable conditions, the reduction in current efficiency due to this side reaction is not excessive. Numerical values are given later. Another difference from tantalum is that the film material is appreciably soluble. The films are also shown to be unstable by increases in the dielectric losses with time on standing in the solution. Possibly, as with aluminum (9), a non-aqueous or partly non-aqueous solution could be found that would give more ideal behavior, but experiments made with various common non-aqueous solvents that have been used for anodizing did not uncover any preferable alternative. In preliminary experiments various forms of non-ideal behavior were encountered. In the final experiments, quoted here, the behavior was very reasonably reproducible. The chief limitation was that we were able to obtain accurate kinetic data only over a rather limited range of temperature.

The field in the oxide required to produce a given ionic current density of the order of a few  $\text{ma cm}^{-2}$  is roughly of the order of one sixth of the value for tantalum. In other words, films formed at a few  $\text{ma cm}^{-2}$  to 10 volt on bismuth are of the same order of thickness as films formed to 60 volt on tantalum. However, the total maximum thickness that can be produced before breakdown occurs is of the same order as with tantalum. This is perhaps not without significance. Under the conditions of the present experiments the current efficiency fell off quickly at a little over 50 volt, more or less, according to whether the current density was higher or lower.

Except following breakdown, the films were structureless under the light microscope. They can be removed by attaching adhesive tape and pulling.

The experimental results to be presented are as follows. First, the dielectric properties of the film are discussed. The determination of thickness and derived quantities is then reviewed. The kinetic results are then described, first for steady-state conditions and then for transient conditions. The significance of the results in deciding the mechanism of the process is dealt with in the discussion section.

### *Dielectric Properties of the Oxide Film*

Since the size of the specimens used for the kinetic studies gave capacitances that were too high for the accurate measurement of their frequency dependence, measurements were made with a smaller polycrystalline specimen of 99.999% material, about  $0.86 \text{ cm}^2$

in area, of dimensions about 6 mm  $\times$  3 mm  $\times$  3 mm. This was stopped off with picien wax and etched in 70% nitric acid. It was immersed symmetrically in a large platinum tube electrode.

Figure 1 shows the reciprocal of the series equivalent capacity  $C_s$  (normalized to unity at 1 kc/s), and the loss tangent ( $\tan \delta$ ) plotted against the logarithm of the frequency  $f$

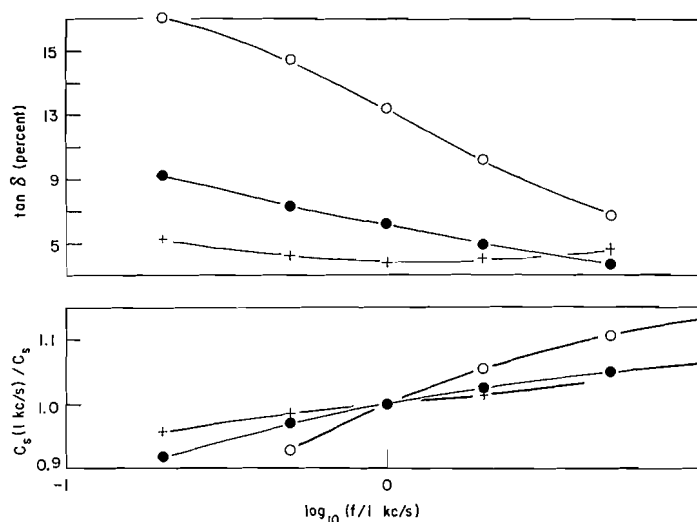


FIG. 1. Loss tangent ( $\tan \delta$ ) and reciprocal series equivalent capacity (normalized) for three thicknesses of oxide (formed to voltages of 30 v (O), 10 v (●), and 3 v (+) at 2 ma  $\text{cm}^{-2}$  and 1.4° C) as function of frequency  $f$  of measurement.

for a series of films formed to 3, 10, and 30 volt respectively at 2.0 ma  $\text{cm}^{-2}$  and 1.4° C. To eliminate the time dependence, the measurements at the various frequencies were made first in order of increasing frequency and then back. The plotted values are the means. The figure shows that the dielectric losses are very much larger than would be found with non-porous films on tantalum or aluminum. The losses increase with increasing thickness of oxide.

Similar high dielectric losses with anodic oxide films on zirconium (10) may satisfactorily be explained by assuming that the films contain a comparatively high density of microfissures. The alternative would be that the dielectric losses of the flawless film material were unusually high. The electrolyte solution is supposed to penetrate into these cracks and to provide a parallel leakage conductance. The theory may be tested by varying the conductivity of the electrolyte. Figure 2 shows the effects with bismuth of reducing the concentration of the solution. The losses were, as expected, markedly decreased.

The increase in the losses with increasing thickness is also typical of films on zirconium and other metals. It appears that as the film thickens, stresses accumulate which cause cracking.

#### *Reciprocal Capacity and Formation Potential*

Figure 3 shows the reciprocal capacity at 1 kc/s plotted against the successive potentials to which the specimen was formed at the indicated current densities. The film was removed after each separate formation (see Experimental Procedure), and the next film then formed starting from the "bare" metal. The significance of such plots is as follows.

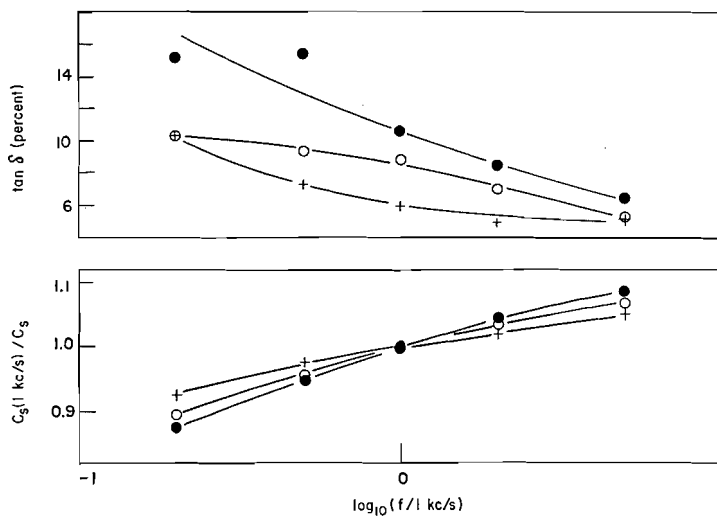


FIG. 2. Loss tangent and reciprocal capacity for a single film measured in 0.1 *M* NaOH (○), in 0.01 *M* NaOH (+), and remeasured in 0.1 *M* NaOH (●).

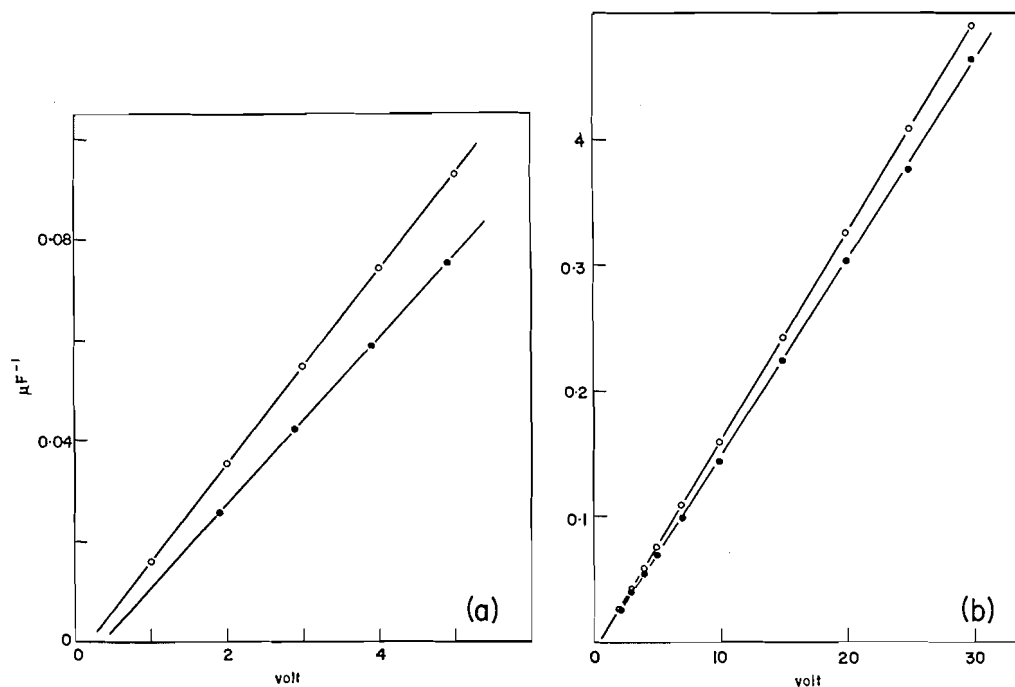


FIG. 3. (a) Reciprocal series equivalent capacity at 1 kc/s versus potential against hydrogen electrode in same solution to which the specimen was formed in 0.1 *M* NaOH at 0° C with current densities 0.2 ma cm<sup>-2</sup> (○) and 2 ma cm<sup>-2</sup> (●).  
(b) Reciprocal capacity at 100 c.p.s. (●) and at 1 kc/s (○) versus potential (larger scale than (a)), for film formed at 2 ma cm<sup>-2</sup> and 0° C.

The E.M.F. which causes the electrochemical formation of oxide is the oxide overpotential, defined as the actual potential of the electrode with respect to some reference electrode less the reversible potential for the oxide-producing reaction (in this case

assumed to be  $2\text{Bi} + 3\text{H}_2\text{O} = \text{Bi}_2\text{O}_3 + 3\text{H}_2$ ,  $E^0 = 0.37$  volt). The overpotential  $V$  may formally be considered to be made up of a possible contribution  $V_1$  from the interfaces oxide/metal and oxide/solution plus a term  $ED$ , where  $E$  is the mean overfield in the oxide (defined analogously with the overpotential) and  $D$  is the thickness of the film. The interfacial contribution will be expected to be independent of  $D$  but possibly to be dependent on the current density and the temperature. Thus

$$\begin{aligned} V &= ED + V_1 \\ &= E\epsilon A/4\pi C + V_1, \end{aligned}$$

where  $\epsilon$  is the dielectric constant,  $A$  is the area, and  $C$  is the capacity. Thus the slope of the plots is a measure of the field  $E$  and its constancy indicates either that  $\epsilon$  and  $E$  are inversely correlated, or, more probably, that  $\epsilon$  and  $E$  are independent of  $D$ . The deviation of the intercept on the voltage axis at zero  $1/C$  from the calculated reversible potential is a measure of  $V_1$ . Clearly,  $V_1$  was of the same order as the experimental error, the observed deviation being within about 0.2 volt. Thus we expect differential measures of the field strength (of the form  $\Delta V/\Delta D$ ) to equal integral measures (of the form  $V/D$ ).

#### *Thickness, Dielectric Constant, and Related Quantities*

##### *Principles of Method*

There are several types of measurement that purport to give a measure of the thickness of the films. Each type involves one or more parameters, such as the density of the oxide, the refractive index, or the dielectric constant. By comparing the data from the various types of measurement, first a check is obtained that thickness is indeed being measured and that the films are uniform, and, secondly, various relations are obtained among the parameters. If sufficient of these may be taken as known, the values of the others may be deduced. The charge to form an increment of thickness  $x$  is expected to be

$$[1] \quad Q = xA\rho 6F/M,$$

where  $A$  denotes true area;  $\rho$ , the density;  $F$ , the Faraday;  $M$ , the molecular weight (the oxide being presumed to be  $\text{Bi}_2\text{O}_3$ ). The consequent change in reciprocal capacity is expected to be

$$[2] \quad \Delta(1/C) = x4\pi/\epsilon A,$$

where  $\epsilon$  denotes the dielectric constant. Minima in the specular reflectivity at a wavelength  $\lambda$  are expected to occur with successive increments of thickness,

$$[3] \quad x = \lambda/2n \cos \theta,$$

where  $n$  is the refractive index, assumed constant, and  $\theta$  is the angle of refraction. In previous work with tantalum and niobium, it was shown that it was not necessary to assume that the true area is equal to the measured macroscopic area, since the area may be eliminated between [1] and [2]. With bismuth, however, it seemed preferable to assume that the true area was equal to the apparent area. The calculation was done by first determining the field strength at various temperatures and current densities in terms of the optical thickness (involving  $n$ ). Values of the fields were also obtained with the thickness calculated from the charge to form the films, using a method by which it was hoped to allow for current efficiencies below 100%. Comparison gave  $n/\rho$ . A similar procedure using the capacity to estimate the thickness gave  $\epsilon n$ . The refractive index here was for  $\lambda = 4000 \text{ \AA}$ . By also determining the field at one current density and temperature only in terms of  $n$  for  $\lambda = 5890 \text{ \AA}$ , the ratio of the refractive indices at these two

wavelengths was determined. Finally, a value of the index in sodium light was assumed. Corresponding numerical values for  $\epsilon$ ,  $\rho$ , and the field strengths could then be deduced. If a preferable value of any of these should later become available, it would be a simple matter to recalculate the data given here to fit the new value.

#### *Optical Thickness*

Figure 4 shows tracings of the spectrophotometer records of the minima in reflectivity, shown as maxima in "optical density," for specimens giving destructive interference at

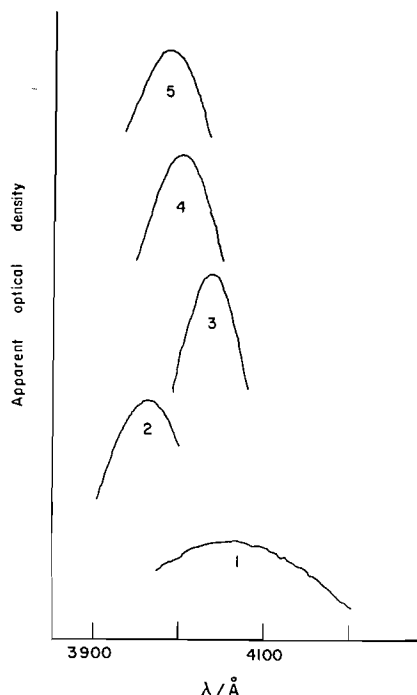


FIG. 4. Tracings of spectrophotometer recordings (apparent optical density) of minima in specular reflectivity (maximum in optical density) at near-normal incidence for films giving minima near 4000 Å in successive orders of interference.

successive orders at wavelengths near 4000 Å. The peaks are flattest in the first order, but are then the most sensitive to the thickness of oxide (cf. Fig. 5). The wavelength ( $\lambda$ ) of the peak may be determined (excluding calibration errors of the instrument) to about 10 Å with thin films and 5 Å with thick films, giving a thickness ( $D$ ) sensitivity of a few Å of oxide (see Table IV for  $dD/d\lambda$ ).

Figure 5 shows plots of the wavelengths of the peaks versus voltage for specimens formed at a given current density and temperature. Such plots were interpolated to obtain estimates of the potentials corresponding to the thicknesses giving interference in successive orders at precisely 4000 Å for each current density and temperature. Numerical data are given in Table I. In all such experiments, each film was formed on "bare" metal, the previous film being first dissolved away.

Figure 6 shows the voltages giving interference at successive orders at 4000 Å plotted against order of interference (i.e., thickness in units of  $\lambda/2n \cos \theta$  with arbitrary zero) for formation at a given current density and temperature. The plot is linear. This was

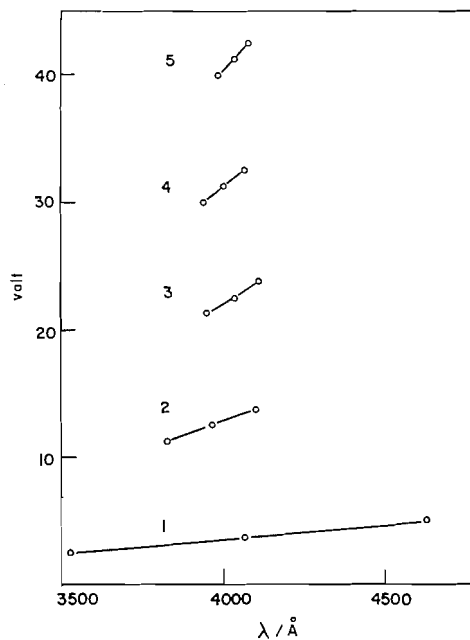


FIG. 5. Potential (against hydrogen electrode in the same solution) to which film was formed at  $2 \text{ ma cm}^{-2}$  and  $25^\circ \text{C}$  plotted against wavelength of interference for films giving interference at wavelengths close to  $4000 \text{ \AA}$  in successive orders.

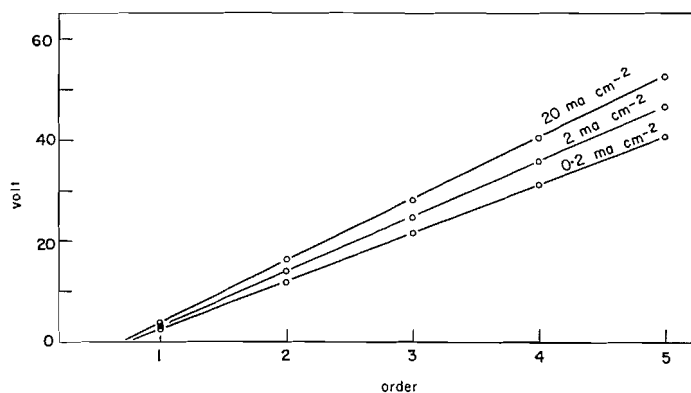


FIG. 6. Oxide overpotential (formation at 0.2, 2, and  $20 \text{ ma cm}^{-2}$  and  $0^\circ \text{C}$ ) for films giving interference at  $4000 \text{ \AA}$  in successive orders plotted against order of interference (i.e., thickness in arbitrary units with arbitrary zero).

typical and indicates the absence of detectable variation of field with thickness at constant current.\* The slope of such plots, estimated graphically, was taken as a measure of the field strength for the conditions of the plot.

To obtain the dispersion of the refractive index between  $4000 \text{ \AA}$  and  $5890 \text{ \AA}$ , the slopes of two such plots were compared, one plot for each wavelength of interference. The ratio of the refractive indices was  $n(4000 \text{ \AA})/n(5890 \text{ \AA}) = 1.19$  (estimated accuracy,  $\pm 0.02$ ). Thus if the (rather old) published (11) value of the index for white light is assumed as

\*The unlikely alternative is that compensation occurs in that the various methods suggest constant field but that parameters such as the refractive index vary to compensate for an actual change in field.

TABLE IA

Potentials (in volts) against hydrogen electrode in the same solution (ohmic p.d. eliminated) corresponding to the thicknesses  $D_1, D_2, \dots$  giving interference at  $4000 \text{ \AA}$  in successive order for various current densities and temperatures

$D$	Total current density (ma cm <sup>-2</sup> ):					
	0.2	0.63	2.0	6.3	20.0	20.9
At 0° C						
1	3.0		3.6		4.4	
2	12.4		14.3		16.7	
3	21.9		25.3		29.0	
4	31.5		36.3		40.9	
5	40.9		47.0		52.8	
At 25° C						
1	2.5	2.6	2.8	3.0	3.5	
2	10.1	10.8	12.2	13.0	14.3	
3	17.7	19.0	21.5	23.2	24.0	
4	25.7	27.7	30.9	32.9	35.5	
5	33.5	36.4	40.2	42.7	46.0	
At 50° C						
1						2.8
2						12.1
3						21.6
4						30.9
5						40.2

TABLE IB

Increases (rounded to nearest 0.1 volt) in potential corresponding to increase in thickness from  $D_1$  to  $D_2, D_2$  to  $D_3$ , etc. (i.e., by  $\lambda/2n \cos \theta$ ) for various current densities and temperatures (this is a measure of the field in the oxide)

$D$	Total current density (ma cm <sup>-2</sup> ):					
	0.2	0.63	2.0	6.3	20.0	20.9
At 0° C						
2-1	9.3		10.8		12.2	
3-2	9.5		11.0		12.2	
4-3	9.6		11.0		12.0	
5-4	9.4		10.8		12.0	
At 25° C						
2-1	7.6	8.2	9.4	10.0	10.8	
3-2	7.6	8.2	9.3	10.1	10.8	
4-3	8.0	8.8	9.4	9.7	10.4	
5-4	7.8	8.7	9.3	9.9	10.6	
At 50° C						
2-1						9.4
3-2						9.5
4-3						9.3
5-4						9.2

$n(5890 \text{ \AA}) = 1.91$ , we have  $n(4000 \text{ \AA}) = 2.27$ . The value 1.91 was obtained using a prism of metal converted to oxide by heating in air and cannot be considered reliable though it is the same as the mean of one pair of values tabulated by Larsen (12) for bismite. It is assumed quite arbitrarily and all the other numerical values of field, etc. are derived from this value. Furthermore, it is assumed that the refractive index is independent of the current density and temperature of formation.

Data on the capacities at 1 kc/s of films formed at 2 ma cm<sup>-2</sup> at 0° C gave  $\epsilon n = 140$ , i.e.  $\epsilon = 62$  for  $n(4000 \text{ \AA}) = 2.27$ .



*The Charge to Form the Films*

Figure 7 shows statistical plots illustrating the variations of the charge required to increase the potential by 1 volt during formation at a given current density and temperature. The individual values are grouped into successive 5-volt ranges. The plots are of the

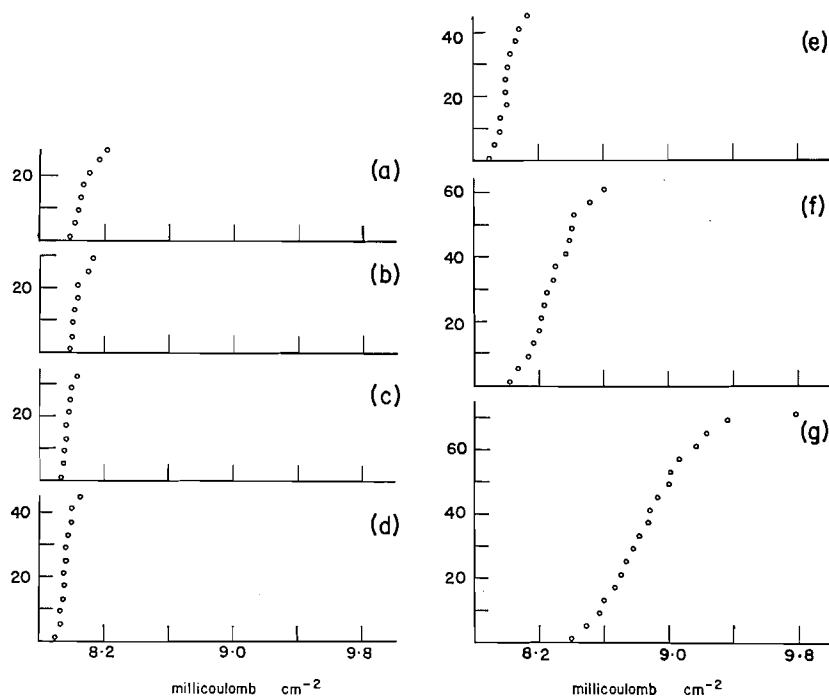


FIG. 7. The ordinate shows the number of specimen trials in which less than the charge/cm<sup>2</sup> indicated in the abscissa was required to form through 1 volt in the voltage intervals indicated at 2 ma cm<sup>-2</sup> and 25° C. The abscissa scale is common to the whole set of plots. (a) 31–36 v, (b) 26–31 v, (c) 21–26 v, (d) 16–21 v, (e) 11–16 v, (f) 6–11 v, (g) 1–6 v.

integrated type (13) instead of the usual distribution function type. The number of specimen trials which required less than a given amount of charge is plotted against the charge.

To use these plots, we rely on the principle that the charge can never be less than corresponds to 100% current efficiency\* but that it can exceed this amount without limitations. Thus the estimated values of the charge can be less than the theoretical minimum only by the small measuring error.

To obtain an estimate of the theoretical charge, the plots of Fig. 7 are extrapolated to zero specimens and the intercept on the charge axis is taken as the required value. This gives an estimate of

$$\frac{dQ}{dV} = \frac{dQ}{dD} \cdot \frac{dD}{dV} = \frac{(A\rho 6F)}{M} \frac{1}{E}$$

\*To avoid misunderstandings, we note that references are occasionally made in the literature to current efficiencies greater than 100%. Such statements usually mean that the actual reaction was not that being assumed. In some cases the experimental result was really that the weight increase had been found to be greater than expected. This can occur, for example, if components of the solution have been absorbed by the oxide.

Figure 8 shows how the results tended to vary with the potential. The charge was in all cases high at the beginning of the formation, then decreased as the thickness increased,

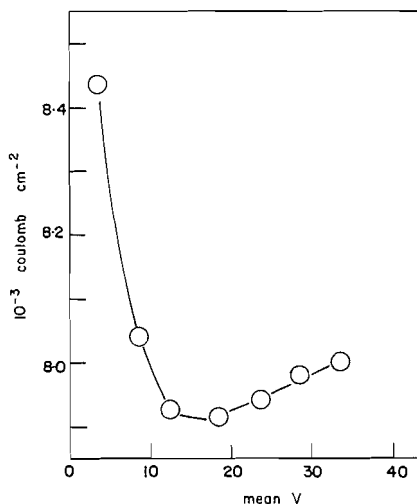


FIG. 8. Estimated minimum charge/cm<sup>2</sup> to form through 1 volt at 2 ma cm<sup>-2</sup> and 25° C plotted against mean voltage (from intercepts in Fig. 7).

and finally rose slowly with further increase in thickness. Since the field calculated from the optical thickness showed no such variation over the same range of thickness, these variations appear to be without significance. A mean was taken of the values for each current density and temperature, excluding the values for voltages less than 10. The scatter of the data was least for the conditions of Fig. 8, i.e., 2 ma cm<sup>-2</sup> and 25° C. Other data are given in Fig. 9.

Together with the fields from the optical thickness, the data gave an overall mean value of  $n/\rho = 0.333$  (accuracy believed to be a few percent). With  $n(4000 \text{ \AA}) = 2.27$ , this gives  $\rho = 6.8 \text{ g cm}^{-3}$ . Published values of the bulk density fall in the range 8.2–8.9 g cm<sup>-3</sup>. Evidently if the assumed index is correct, the films differ somewhat in properties from chemically prepared Bi<sub>2</sub>O<sub>3</sub>.

#### Current Efficiency

The field strengths obtained from the optical thickness refer to total applied current density. To estimate the ionic current density a mean was taken of the times required to traverse the last 1 volt (or 10 volt at the highest current density) before the current was terminated for all the specimens in the various orders of interference which were used to determine the field at a given applied current and temperature. This gave a mean  $dV/dt$  for these conditions. The ionic current density  $i$  was calculated from

$$i = \frac{1}{E} \frac{dV}{dt} \frac{6F\rho}{M},$$

where  $E$  was the optically determined field. A value of  $n/\rho$  is required and the value determined above was used. A value of  $n$  itself is not required. This gave the results for the current efficiency reproduced in Table II.

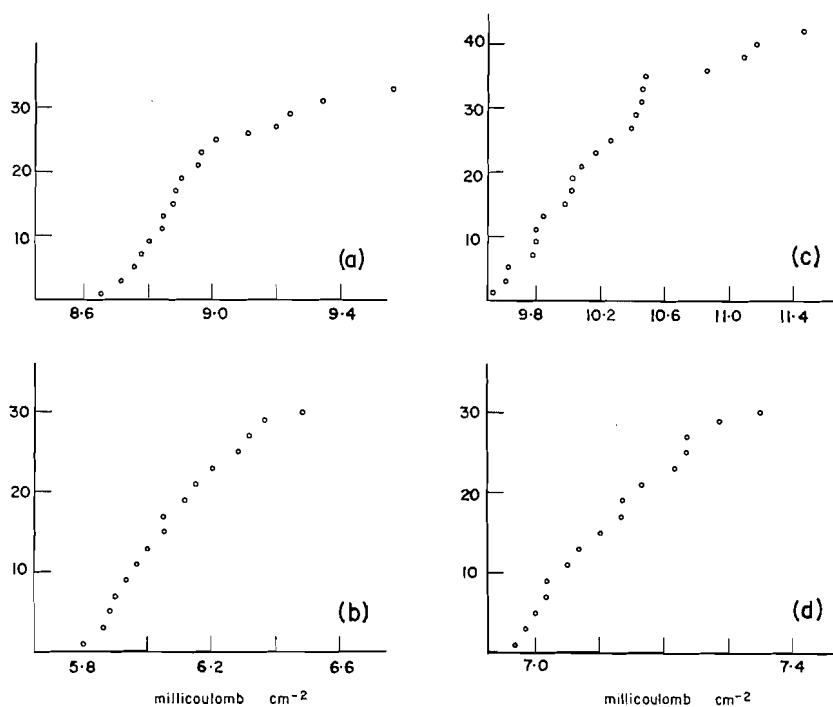


FIG. 9. Similar data to Fig. 7 for conditions shown. (a)  $0.2 \text{ ma cm}^{-2}$ ,  $0^\circ \text{ C}$ , 11–16 v; (b)  $20 \text{ ma cm}^{-2}$ ,  $0^\circ \text{ C}$ , 4–55 v; (c)  $0.2 \text{ ma cm}^{-2}$ ,  $25^\circ \text{ C}$ , 11–16 v; (d)  $20 \text{ ma cm}^{-2}$ ,  $25^\circ \text{ C}$ , 2–48 v.

TABLE II

Current efficiency for the formation of oxide calculated from rate of rise of potential (see text)

Total current density ( $\text{ma cm}^{-2}$ )	Temperature ( $^\circ \text{C}$ ):		
	0	25	50
20	97	99	101
2	97	96	—
0.2	86	92	—

#### Zero of Thickness

Unless values of the optical constants of the metal are assumed, the spectrophotometric method gives a measure of increments of thickness rather than of absolute thickness. Three methods may be used to obtain a zero point. First, as shown above, the plots of reciprocal capacity versus potential (Fig. 3) suggest that if a plot is made of thickness with unknown zero against oxide overpotential (for a given current density and temperature), the intercept at zero overpotential would indicate the zero of thickness. Thus, in Fig. 6, this would give the thickness  $D_1$  (say) of the film giving first-order interference at  $4000 \text{ \AA}$  as a fraction  $0.29 (\pm 10\%)$  of the increment between orders (i.e., of  $\lambda/2n \cos \theta = 884 \text{ \AA}$  if  $n(4000 \text{ \AA}) = 2.27$ ). This gives  $D_1 = 255 (\pm 10\% \text{ or more}) \text{ \AA}$ . The second method is to plot the charge-to-form against the order of interference. This neglects the film present before anodization (with tantalum the thickness of this pre-existing film can be estimated from the charge-to-form, with certain assumptions). The

plot shown in Fig. 10 is for  $2 \text{ ma cm}^{-2}$  at  $25^\circ \text{C}$  and, clearly, gave good agreement within the accuracy of the data. Thirdly, the increase in voltage that is required to produce a

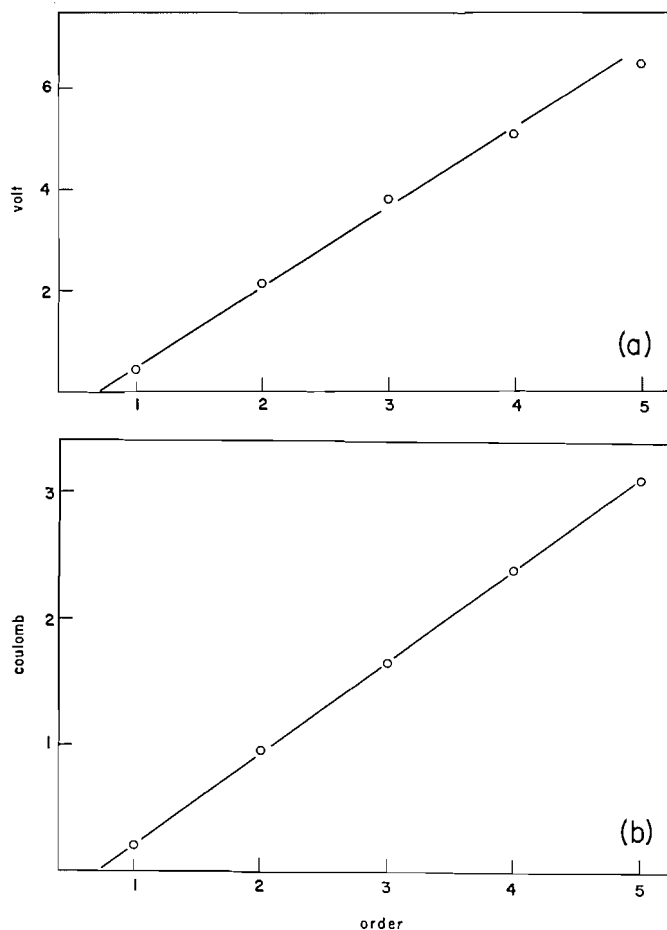


FIG. 10. (a) Increase in potential required to increase steady-state current density at  $25^\circ \text{C}$  by a factor of 10 plotted against order of interference. Mean values using all points available at each thickness. (b) Total charge required to form at  $2 \text{ ma cm}^{-2}$  and  $25^\circ \text{C}$  to thicknesses giving destructive interference at  $4000 \text{ \AA}$  in successive orders plotted against order of interference.

10-fold increase in current may also be plotted against the order of interference, as shown in Fig. 10. In drawing the line shown, the zero has been taken in agreement with that given by the above methods. This method involves fewer assumptions but is less precise.

#### *Steady-State Kinetics*

Figure 11 shows data on the field from the optical thickness versus  $\log_{10}$  (ionic current density). The field and the ionic current density were determined as explained in previous sections. The difference between the total and the ionic current density is quite small on the logarithmic plot. The plots are linear within experimental error, but it is perhaps doubtful whether small deviations from linearity of the type observed with tantalum would have been detected, the accuracy being less than with tantalum.

With tantalum and niobium a mean value of  $dE/d \log_e i$  (the equivalent of the Tafel slope in the kinetics of non-film-forming electrode processes) over a fixed range of  $i$  has

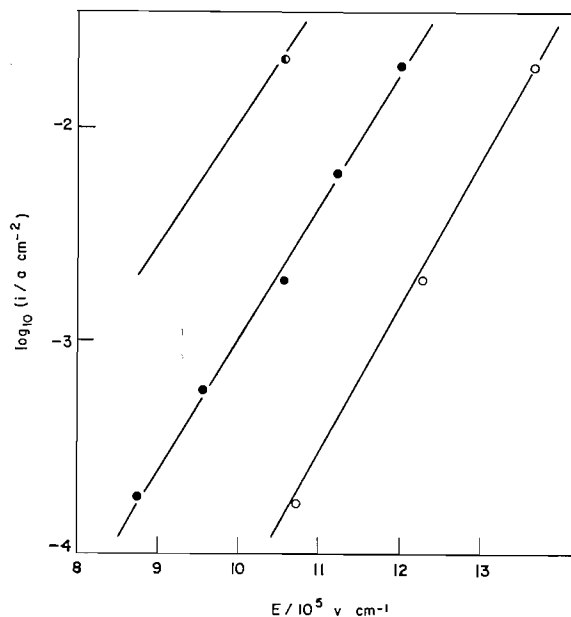


FIG. 11.  $\log_{10}$  (ionic current density) versus field strength at 0° C (○), 25° C (●), and 50° C (◐) in 0.1 *M* NaOH. The points are experimental, the continuous lines are calculated from the fitted equation (see text). The ionic current density was derived from  $dV/dt$ . The fields are differential values ( $\Delta V/\Delta D$ ) derived from the slopes of plots such as Fig. 6.

been found to be nearly independent of temperature instead of proportional to temperature as expected on simple theory. With bismuth, as with aluminum, it has not proved possible to obtain accurate results over a wide enough range of temperature to obtain a real test of the temperature dependence of  $dE/d \log_e i$ . We, therefore, have chosen to fit the data with the expression  $i = i_0 \exp \{-(W - qaE)/kT\}$ . The constants are given with the number of digits needed to reproduce closely the experimental data. They are, of course, individually known to much lower accuracy. The values are  $\log_{10} (i_0/a \text{ cm}^{-2}) = 10.09$ ,  $W = 1.14 \text{ eV}$ , and  $a = 12.2 \text{ \AA}$ ,  $q$  being assumed to be  $3e$ , where  $e$  is the charge on the proton. The lines in Fig. 10 are calculated from the above expression with these values of the constants.

#### Transient Kinetics

As with other "valve metals," the system adjusts slowly to a sudden change in field or current. The field-current relations that have been reported above refer to the situation where a constant current has been applied for a long enough time to achieve steady-state conditions. Two types of experiment were made under transient conditions.

The first type of experiment consisted in applying a constant current until a steady state was set up and then suddenly changing the potential (i.e., the field). The current immediately after the change was determined by the method (4) described elsewhere (involving cathode ray oscilloscope photography). The "transient" Tafel slope defined as  $\Delta E/\Delta \log_e i$  was then calculated. Results are given in Fig. 12 and Table III.

In the second kind of experiment, the current was recorded during the period after the field had been suddenly increased to a new value. Tracings of photographs are given in Fig. 13, which also contains the result of a similar experiment with tantalum. With

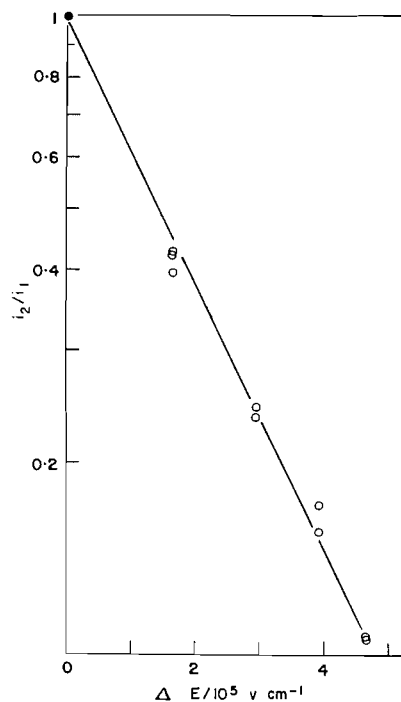


FIG. 12. Change in  $\log_{10} i$  (shown as ratio  $i_2/i_1$  of final to initial current with logarithmic scale) for sudden decrease  $\Delta E$  in field ( $50^\circ\text{C}$ , initial current  $i_1 = 20.9 \text{ ma cm}^{-2}$ ).

TABLE III

Transient Tafel slope and derived activation distance for mobility of ions ( $a_2$ )

Temperature ( $^\circ\text{C}$ )	Initial total current density ( $\text{ma cm}^{-2}$ )	$\Delta E/\Delta \log_e i$ ( $10^5 \text{ v cm}^{-1}$ )	$a_2$ ( $\text{\AA}$ )
0	2.0	2.34	3.35
0	20.9	2.19	3.59
50	20.9	2.08	4.46

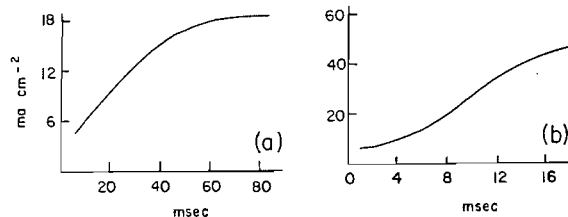


FIG. 13. (a) Tracing of oscilloscope photograph showing current versus time following sudden change as potential reached 20 volt from formation at constant current density ( $2 \text{ ma cm}^{-2}$ ) to formation at constant voltage (28 volt) for bismuth. Temperature  $4^\circ\text{C}$ . (b) Similar but not identical experiment with tantalum. Initial formation at  $4 \text{ ma cm}^{-2}$  to 90 volt. After 1 minute on open circuit, 100 volt was suddenly applied.

tantalum (4), the current (after its initial sudden jump) increased slowly at first and then more rapidly. With bismuth, the current increased rapidly at first and then more slowly. It would have been preferable to have been able to check this result by working at lower

fields with specimens with a very low initial concentration of mobile ions. This experiment, however, is difficult because of the lower current efficiencies at lower current densities.

#### *Dependence of Kinetics on Crystal Face*

With tantalum no variation with crystal face of the substrate metal in the field required to produce a given ionic current has been detected. Probably a variation of 1% would have been found. On the other hand, with indium antimonide a difference was found by Dewald (14), though only at the low end of the range of field studied. Differences occur with titanium (15) and with zirconium and hafnium (16, 17), but only under circumstances that are not fully established. Differences have been found with thin anodic films on cadmium (18), but these are probably a special case, since the oxide is crystalline and epitaxial.

With spherical single crystals of bismuth, no variation in interference color could be seen by eye. To obtain numerical data, films were prepared on a single crystal on which three contiguous faces ((100), (111), and (110)) had been prepared. The specimen was formed at  $0.2 \text{ ma cm}^{-2}$  in one set of experiments, and at  $20 \text{ ma cm}^{-2}$  in another set, to a series of potentials giving interference near  $4000 \text{ \AA}$  in successive orders. The wavelengths of the peaks were measured on the three crystal faces. The wavelengths of interference for the films on the three crystal faces were not entirely consistently in the same order but showed some tendency to be so. The maximum difference between any two faces at each formation voltage was calculated. The quantities  $dD/d\lambda$  (i.e., the variation in film thickness corresponding to unit change of wavelength) were determined from the data of Fig. 5 for the successive thicknesses (say  $D_1, D_2, D_3, D_4$ ) giving interference at  $4000 \text{ \AA}$ . From the differences in  $\lambda$  and the  $dD/d\lambda$ , the corresponding maximum variation in oxide thickness between any two faces was calculated. The results are given in Table IV. The

TABLE IV  
Test of possible variation of kinetics with crystal face of substrate metal

Order of interference	Maximum difference in $\lambda$ between any two faces ( $\text{\AA}$ )	$dD/d\lambda$	Maximum difference in $D$ ( $\text{\AA}$ )	$D$ ( $\text{\AA}$ )	Maximum percent variation in field
Formation at $20 \text{ ma cm}^{-2}$ and $25^\circ \text{ C}$					
1	67	0.18	12	250	5
2	19	0.66	12	1170	1
3	11	1.0	11	2080	0.5
4	7	1.4	10	2910	0.3
Formation at $0.2 \text{ ma cm}^{-2}$ and $25^\circ \text{ C}$					
1	19	0.17	3	190	2
2	28	0.67	19	990	2

maximum percentage change in field was about 5% at  $D_1$ , falling to 0.3% at  $D_4$ . Probably the small differences observed were due to slight variation between crystal faces in the ohmic potential fall in the solution. Variations in optical constants of the metal from face to face will not affect the above test.

Although no appreciable change was detected between crystal faces, the kinetic data given here were, as a precaution, obtained for a specific face, (111). It should be mentioned that in preliminary work with polycrystalline material, different crystal faces were sometimes found to show different colors. The reason for this was not discovered—possibly the effect is due to some variation in the state of the surface produced during its preparation prior to anodization, perhaps because the etching process was sensitive to the crystal face.

## DISCUSSION

The discussion of the significance of the results as regards the fundamental mechanisms involved can only be tentative. The experimental results do not provide answers to all the questions that one would wish to ask and the possible alternative theories cannot be said to have been fully explored. Despite the recent intensive study of tantalum, the behavior even of this metal is not well understood.

As a preliminary point, we note that the evidence seems consistent with a uniform film though, of course, narrow transitional layers near the interfaces are not excluded.

The constancy of the field with thickness does not mean, as is sometimes stated, that there is no space charge present. It may mean either that the films are so thin and the space charge density so small that the change in field across the film is negligible or it may mean that the films are so thick that the space charge layers required to adjust the rate of entry of ions to the rate of passage through the oxide are complete and yet occupy only a small fraction of the total thickness. The second case means that we have the same conditions as with macroscopic-sized conductors. The first case is that dealt with by the theory of Cabrera and Mott. In this case, the field required to give a particular ionic current is entirely determined by the properties of the metal/oxide interface. It is not wholly certain but it appears likely that in this case the kinetics should depend to a detectable extent on the crystal face of the substrate metal. Since no such dependence was found and since, also, it is difficult to explain convincingly the transients on this theory, one is led to conclude that the results refer to the second case, that is to ionic conduction by an electrically neutral slab of oxide, the interfaces playing no part.

The most striking difference from tantalum, aluminum, zirconium, and similar metals is that the field strengths required to give the observable range of ionic currents are comparatively very low, though still sufficiently high to give "high-field conduction" (i.e., an exponential dependence of current on field). It has been suggested in connection with work on niobium (19) that an inverse correlation seems possible between the dielectric constant and the ionic resistivity. The present results are in accord with this idea.

One might expect that the lowness of the fields would lead to differences in mechanism, but this is no more than an expectation since the fields are low only because ionic movement is relatively easy, so that effects requiring high fields with tantalum might well be expected at lower fields with bismuth.

The best approach to the explanation of the transients involves the idea that the concentration of mobile ions is a function of the field but adjusts only slowly to a sudden change in the field. Since electroneutrality is being postulated, this must be taken to mean that a background of negative space charge is a function of the field and only adjusts slowly to change in the field. The concentration of mobile ions is supposed to be in itself variable, but to take up the value giving electroneutrality. It is perhaps difficult to envisage that electroneutrality should be maintained at all times, even after a sudden change in the field, but this simplifying assumption has been made in several recent papers and is difficult to avoid if one is to have a simple mathematical treatment of the model to be discussed. Space charge effects would be more in line with the usual, rather vague, explanations of similar effects with bulk materials.

An idea first proposed by Bean, Fisher, and Vermilyea (20) to account for certain reported features of the steady-state kinetics with tantalum was applied by Vermilyea (5) and by Dewald (6) to the transients with this and other metals with some initial success. The idea is that the high fields directly produce Frenkel defects. (A Frenkel



defect is the electrically neutral combination of vacant lattice site and interstitial metal ion.) The process is equivalent to the ordinary process of ionic mobility except that here the ion moves from a lattice to an interstitial site rather than from one interstitial site to the next. The interstitial ions are supposed to be mobile but (to avoid complications) the vacant sites are supposed to be immobile. The rate of production of defects was supposed to be given by the usual form of expression for ionic mobility,  $N\nu_1 \exp \{-(W_1 - qa_1E)/kT\}$ , where  $N$  = concentration of filled cation sites,  $\nu_1$  = vibration frequency,  $W_1$  = activation energy at zero field,  $q$  = charge on ions,  $a_1$  = activation distance, and the rate of destruction is given by  $i\sigma m$ , where  $i$  = current,  $\sigma$  = cross section for the capture of interstitial ions by vacant sites, and  $m$  = concentration of vacant lattice sites. Thus,

$$\begin{aligned} dm/dt &= N\nu_1 \exp \{-(W_1 - qa_1E)/kT\} - i\sigma m \\ i &= 2a_2\nu_2m \exp \{-(W_2 - qa_2E)/kT\}. \end{aligned}$$

Thus for a sudden increase in field,  $(\Delta E/\Delta \log_e i) = kT/qa_2$ , and for steady-state conditions,  $dE/d \log_e i = 2kT/q(a_2 + a_1)$ . Furthermore, on suddenly increasing the field, the current after the initial sudden change should increase rapidly at first and then more slowly. With tantalum (4), the current actually builds up slowly and then more rapidly, thus suggesting the existence of some sort of cascade process involving the production of Frenkel defects by the moving ions instead of by the field alone. With bismuth, on the other hand, the behavior found is qualitatively as expected.

With tantalum and niobium, which are the only metals which behave sufficiently ideally for it, so far, to have been proved possible to obtain unequivocal evidence on the point, the Tafel slope, for steady-state conditions, shows an unexpected form of temperature dependence. With tantalum the Tafel slope for transient conditions has been shown to exhibit a similar anomalous temperature dependence. According to the most recent work (4), which happens to be by one of us, the behavior may be explained by the necessity to include a higher power of the field, so that  $(\alpha - \beta E)$  replaces  $a$  in the above equations. With the lower fields with which we are here concerned one might anticipate that, if the explanation is correct, the simple form of temperature dependence would be shown. Unfortunately, we were not able to obtain experimental data over a wide enough range of temperature to settle the point. The data on the transient Tafel slope (Table III) obtained at 0° C and 50° C (with initial current about 20 ma cm<sup>-2</sup>) show the same absence of the expected temperature dependence as would be found with tantalum (with fixed initial current). The data are probably statistically significant on this point but we do not consider them to be decisive. Significant values of the steady-state Tafel slope could be obtained at 0° C and 25° C only. They were, as it happens, consistent with proportionality to temperature.

The values of the activation distances (obtained from the Tafel slopes, see earlier) are unusually large. Thus with tantalum  $a_2$  is of the order of 1 Å and  $a_1$  of the order 5 Å (varying with temperature and current density). With bismuth  $a_2$  is of the order 4 Å and  $a_1$  of the order 22 Å.

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