

have been found it; so that as in the case of Spiti and other areas its exact age cannot be known; the only limits being Upper Silurian below and Lower Carboniferous above. It may therefore be of either of these ages, or it may be Devonian, or represent any two or all three of them".

The fossils now found are well preserved and occur in profusion though extraction is difficult. We have identified the trilobite *Phacops rana* Green; the brachiopods *Athyris spiriferoides* (Eaton), *Meristella atoka* Girty, and *Spirifer* sp.; a gastropod as *Diaphorostoma* sp. and a lamelibranch as *Modiolomorpha* sp. This fauna indicates a Devonian age—thus proving the age of a part at least of the Quartzite.

Further work is in progress on both the new Silurian and Devonian faunas. *Note added in proof.* We have now learned that I. Strachan, J. W. A. Bodenhausen, T. de Booy and C. G. Egeler have announced (*Geol. en Mijnb.*, 43, 380; 1964) the finding of early Silurian graptolites in Nepal.

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## CRYSTALLOGRAPHY

### Electron Diffraction Study of Evaporated Beryllia

WHEN beryllia flakes, supported on thin carbon films to form electron microscope specimens, are strongly irradiated with an electron beam, they disintegrate and small crystals condense on the surrounding carbon film. Willis, Austerman and Dearborn<sup>1</sup> reported that the condensed material gives electron diffraction ring patterns which they identify as being those of the high-temperature  $\beta$ -BeO phase examined by Smith, Cline and Frechette<sup>2</sup>. These latter authors suggest that the  $\beta$ -phase is cubic,  $a_0 = 4.76 \text{ \AA}$ , with a non-trivial structure. According to Austerman<sup>3</sup>, more recent work has suggested that the structure may be hexagonal or tetragonal.

The ring patterns of Willis *et al.* contain rings attributable to both the  $\beta$ -phase and the low-temperature  $\alpha$ -phase. The absence of the (002) ring on  $\alpha$ -BeO could be assumed to result from preferred orientations of the crystals.

In the course of an investigation of the disintegration of BeO crystals under electron irradiation in our *JEM-6A* electron microscope we have made observations on the crystals condensed on the supporting film which parallel those of Willis *et al.* However, we have found that under certain ill-defined conditions of electron irradiation, the condensed crystals take the form of comparatively large, thin crystal plates (linear dimensions of a few thousand  $\text{\AA}$ ) from which we have obtained fragmentary single-crystal patterns by selected-area diffraction methods.

From some areas we have obtained almost complete rotation patterns, given by a crystal or a set of parallel crystals bent around one axis.

Interpretation of these patterns shows clearly that the predominating ring pattern comes from a single substance rather than from a mixture of the  $\alpha$  and  $\beta$  phases. The rotation pattern is readily interpreted in terms of a hexagonal unit cell with  $a_0 = 5.40 \text{ \AA}$  and  $c_0 = 4.62 \text{ \AA}$ , the

accuracy of determination being in each case about 0.5 per cent. The rotation is about the  $c$ -axis. On the zero layer line,  $l = 0$ , the  $hk0$  arcs are present only for both  $h$  and  $k$  even. The same may apply for  $l = 2n$  because weak spots with  $h$  or  $k$  odd on layer lines with  $l = \pm 2$  may be due to secondary scattering. Because the  $a$  dimension is very close on twice that for  $\alpha$ -BeO (2.70  $\text{\AA}$ ) and the  $c$ -dimension is very nearly equal to the (100) spacing (4.68  $\text{\AA}$ ) the principal  $\alpha$ -BeO rings appear to be present in the ring patterns (apart from the 002), and the rings not attributable to  $\alpha$ -BeO have radii showing simple arithmetic relationships which could suggest a cubic structure.

The relationship between this hexagonal phase and the high-temperature  $\beta$ -BeO phase of Smith *et al.* remains obscure. The strong preferred orientation thought to be present in the high-temperature phase could possibly limit the pattern of the hexagonal phase to lines which could be indexed as cubic, and the report that the high-temperature phase could be hexagonal is suggestive. An identification of this sort would remove doubts that the observed hexagonal phase is actually BeO, since the possibility must be considered that it results from reaction of the BeO with the gases present or the carbon supporting film.

The existence of a structure derived from  $\alpha$ -BeO with commensurate unit cell dimensions (except for a 6 per cent increase in  $c$ -axis) is of particular interest in relation to the anisotropic expansion of the lattice of BeO irradiated in a nuclear reactor at moderate temperature<sup>4</sup>. The relatively great expansion in the  $c$ -direction commonly observed could be explained if a primary effect of irradiation was the formation of small nuclei of this hexagonal phase.

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## METALLURGY

### Effect of Grain Boundaries on the Diffusional Growth of Oxides on Metals

SEVERAL mechanisms<sup>1-3</sup> for the growth of thin films of oxides on metals have yielded equations of the form  $y^3 = kt$ , where  $y$  is the film thickness,  $k$  a rate constant, and  $t$ , time. However, none of these mechanisms can be satisfactorily extended to the case of thick films formed on such metals as titanium, zirconium and tantalum<sup>4</sup>. It is proposed that this so-called 'cubic' oxidation can result from a combination of diffusion along grain boundaries and normal bulk diffusion in relatively thick oxide films.

The usual high-temperature protective oxidation of metals obeys a parabolic kinetic law,  $y^2 = k't$ , and the mechanism universally accepted for this law is that proposed by Wagner<sup>5</sup>. The oxide is assumed to grow by the diffusion of defects across the film. Constant defect concentrations at the metal-oxide and oxide-gas interfaces provide a gradient of chemical potential inversely proportional to film thickness. It is assumed in this mechanism that diffusion occurs across the bulk of the oxide film and that grain boundaries in the oxide film can be safely ignored.

In laboratory determinations of diffusion coefficients the possibility of grain boundary effects, especially at moderate temperatures, is generally appreciated<sup>6</sup>. The significance of grain boundary effects can be examined by

two methods derived from the mathematical solutions of the equations appropriate to diffusion into a semi-infinite body from a planar source. The more usual method is to plot the logarithm of the concentration of the diffusing species as a function of the distance from the source. However, since growing oxide films have a constant concentration difference across them, this method is not applicable. The alternative is to determine the distance from the source at which a given concentration-level is found at successive times. For bulk diffusion the distance is proportional to  $t^{1/2}$ , but for grain boundary diffusion the function is  $t^{1/4}$  (refs. 7 and 8). It has been generally appreciated that these two laws ( $t^{1/2}$  and  $t^{1/4}$ ) are limiting cases. Hitherto it has not been possible to appreciate the intermediate kinetic behaviour when grain boundary diffusion is playing some part but is not completely dominant.

Two papers have recently been published<sup>9,10</sup> presenting results of the numerical integration of the differential equation governing diffusion from a constant planar source into a semi-infinite solid containing a grain boundary perpendicular to the surface. These permit a closer examination of this intermediate behaviour, which can conveniently be discussed in terms of the parameter

$$\beta = \frac{D'}{D} \frac{\delta}{2} \frac{1}{\sqrt{Dt}}$$

where  $D'$  is the diffusion coefficient in the

grain boundary of width  $\delta$ ,  $D$  the coefficient of bulk diffusion, and  $t$ , time. This parameter can be regarded as a measure of the relative significance of grain boundary to bulk diffusion. If  $\beta < 0.1$  grain boundary effects are negligible and the  $t^{1/2}$  law applies. When  $\beta > 10$  grain boundary effects are dominant and the law becomes  $t^{1/4}$ . By using the published results for  $\beta = 1$  and  $\beta = 5$  (ref. 9) it has been demonstrated that the exponent of  $t$  decreases smoothly, as might be expected from  $\frac{1}{2}$  to  $\frac{1}{4}$  as  $\beta$  increases from approximately 0.1 to 10 and that values close to  $\frac{1}{2}$  correspond to values of  $\beta$  between about 1 and 5, that is, when the effects of grain boundaries are comparable to those of bulk diffusion.

Since  $\beta$  is itself a function of time ( $\propto t^{-1/2}$ ) the value of the exponent of  $t$  for  $0.1 < \beta < 10$  is not strictly a constant. However, the exponent increases from  $\frac{1}{2}$  to  $\frac{1}{4}$  as  $\beta$  is varied by two orders of magnitude, and this corresponds to a variation of four orders of magnitude of time. Hence, in practice, where time-intervals rarely cover even two orders of magnitude, the variation will be small and could easily be obscured by the scatter of experimental results.

To apply the above kinetic behaviour to the growth of oxides on metals with the usual assumption of the Wagner oxidation mechanism (constant concentrations of the diffusing defects at the metal-oxide and the oxide-gas interfaces) the oxide thickness should be equated to the penetration from the surface to a constant concentration contour. The published figures<sup>9,10</sup> relate solely to the penetration at the grain boundary, whereas oxidation measurements, as usually determined by weight gain or volumetric methods, provide a mean thickness of oxide film. The difference between the mean thickness and maximum grain boundary penetration is seen<sup>9,10</sup> to depend on both  $\beta$  and the concentration difference. For fairly small values of  $\beta$  and for the small concentration differences associated with defects in oxides this discrepancy between penetration and mean thickness is not expected to be large. It should also be noted that the model for the mathematical analysis involves only a single grain boundary, and hence is strictly only applicable if the boundaries are sufficiently far apart to exert independent influence. Grain size in oxide layers is typically of the same order of magnitude as the thickness and therefore this condition does not apply. However, one effect of multiple boundaries will be to make the mean thickness closer to the grain boundary penetration. Mathematical analysis of the multiple grain boundary model has not been evaluated but to a first approximation the effect of multiple

boundaries will be to increase the concentration within the grains and that other boundaries will have relatively little effect on the penetration at a boundary itself. This lends some support to the application of the kinetics of grain boundary penetration to oxidation.

Since grain boundary diffusion kinetics arise from a combination of penetration along a boundary and lateral spreading away from the boundary some modification due to multiple boundaries is to be expected. In general terms it can be seen that the effect of material reaching the grains from more than one boundary will be to reduce the tendency of material to diffuse laterally away from grain boundaries. The magnitude of this effect is expected to increase as grain size is reduced, and in the limit of infinitely small grains diffusion would be characterized by the grain boundary diffusion coefficient alone. At this limit a parabolic law would again apply. The distance from a grain boundary enters the calculations as a reduced dimensionless parameter which incorporates  $t^{1/2}$  and therefore the effect of the grain boundary spacing in the multiple grain boundary model is also expected to be time-dependent. In the early stages with thin oxide films the boundaries are comparatively widely spaced and act independently with the kinetics of the mathematical model. However, the mean thickness will be comparatively less like the grain boundary penetration than in the later stages where the oxide thickness is similar to the grain size. At this stage, however, the mathematical model is inadequate. These two effects, the initial difference between mean thickness and grain boundary penetration and the later significance of grain boundary interaction, both act in the same sense to make oxidation behaviour somewhat closer to parabolic than the mathematical model of grain boundary diffusion indicates.

The boundary conditions used for the numerical integration correspond to a uniform concentration of diffusant over a planar source surface. For gaseous oxidation with growth proceeding by anion diffusion this should be appropriate provided the outer interface remains reasonably planar. For growth by cation movement this condition requires that the metal-oxide interface is planar and has high surface diffusion rates (with little surface diffusion at the gas-oxide interface). The boundary conditions would have to be modified if these assumptions do not apply.

To take account of grain boundaries the kinetic equation for the diffusional protective growth of oxides on metals has to be generalized to  $y^n = kt$ , where  $n$  takes the value 2 for negligible effect of boundaries but may be as high as 4 for complete dominance of grain boundary diffusion. The effect of grain boundaries may not be constant during oxide growth and the value of  $n$  may similarly change.

Not only does a consideration of grain boundaries in an oxide film provide a satisfactory mechanism for cubic and similar growth laws but it also suggests new possible mechanisms for the effect of alloy additions on oxidation characteristics and such phenomena as breakaway oxidation. It is hoped to explore these and give a more thorough analysis of the effect of grain boundary diffusion at a later date.

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