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Modifications to the Zener Formula for Limitation of Grain Size

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An experimental investigation of the ratio of grain boundary curvature to grain size is reported, from which it is deduced that the terminal grain size determined by inclusions should be about an order of magnitude less than that predicted by the Zener formula in its usual form. It is demonstrated that the Zener formula does not necessarily include the condition that each boundary is impeded by an inclusion, and a supplementary condition is derived to cover this possibility.

1. Introduction

Zener's formula for the limiting grain size set by the presence of second-phase inclusions is derived [1] by equating the pressure tending to move a grain boundary towards its centre of curvature, caused by its surface energy and curvature, to the product of the retarding force produced by a second-phase particle and the number of such particles intersected by unit area of the boundary. The resulting equation is:

$$\bar{R} = 4r/3f \qquad (1)$$

where $\bar{R}$ is the average radius of curvature of the grain boundaries when growth stops, r is the radius of the (spherical) particles of the second phase, and f is the volume fraction of the second phase. It is usually assumed, following Smith [2], that the limiting radius of curvature of a grain boundary will be of the order of the grain size, so that the Zener formula is often quoted in the form

$$\bar{D} \sim r/f$$

where $\bar{D}$ is the final average grain diameter.

There are two features of this theory which appear to warrant further investigation: (i) the assumed near-equality between average grain boundary radius of curvature and grain radius, and (ii) the tacit assumption that the areas of the grain boundaries are sufficiently large for each boundary to intersect at least one second-phase particle.

The present paper reports the results of an investigation into the validity of these assumptions.

2. Studies of Grain Boundary Curvature

Specimens of fully-dense magnesia prepared by our colleague Mr E. Smethurst were used for this study. (This material was produced with the aid of lithium fluoride additions, by the method of Rice, but it is believed that very little of the additive remains in the densified specimens [3].) This material was chosen because it exhibits a microstructure typical of polycrystalline materials of uniform grain boundary energies, i.e. of uniform, equiaxed grains [4], and was therefore felt to be of a well-understood type of general applicability to polycrystalline materials. The relationship between grain boundary curvature and grain size for this material should be of general validity.

It has been shown by one of us [5] that the average radius of curvature $\bar{R}$ of a three-dimensional grain is related to the radius of curvature $\bar{p}$ observed in a random section by

$$\bar{R} = 4\bar{p}/\pi$$

The radii of curvature of 300 grain boundaries were measured on photomicrographs by comparison with a set of standard circular arcs, and corrected to true radii of curvature by the above formula. The mean grain size was determined

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*Current address: Atomic Energy Establishment, Cairo, UAR from the same photographs, using the relationship

$$\bar{D} = 2.239(\bar{A})^{\frac{1}{2}}$$

where $\bar{A}$ is the average sectional area of the grains. This relationship gives the diameter of a sphere of the same volume as the grain of average section area if the grain shape is a truncated octahedron [5]. This particular definition was used because the work formed part of a larger programme in which it was desired not to use any of the usual techniques which are strictly applicable only to spherical grains. As a body-centred cubic stacking of truncated octahedra is capable of filling space, and represents reasonably well the geometry of a set of equal-energy grain boundaries, the truncated octahedron is a suitable grain shape to choose, even though it is not a good approximation to the shape of grains actually observed [4]. The results are, in any case, not particularly sensitive to the method of measurement of grain size which is used.

The ratio of $\bar{R}$, the mean radius of curvature of the grain boundaries, to $\bar{D}$ the mean grain diameter, was found to be 9. Inserting this value in equation 1 gives:

$$\bar{D} = 0.15r/f \qquad (2)$$

The predicted value of terminal grain size is thus about an order of magnitude less than the unmodified Zener equation.

3. The Number of Inclusions per Boundary

For a random distribution of second-phase particles of volume fraction f and radius r the number intersected by 1 cm^2 of interface is $3f/2\pi r^2$ [1].

To determine the number of particles per grain boundary, the average area of a boundary must be determined. In order to do this, the assumption was again made that the grain shape is a truncated octahedron, although it will be shown that the exact shape is not very important.

For a truncated octahedron with side l: total surface area, $A = 26.78\ l^2$; volume, $V = 11.31l^3$; and $V = \pi D^3/6$, where D is the diameter of the sphere of equal volume. From these relations, and the fact that the body has 14 faces it is easily derived that the average area of a face is $0.247\ D^2$. If the condition that there must be at least one particle per boundary is now imposed, and allowance is made for the fact that all boundaries are shared between two grains, the following condition results

$$D = 2.06\ r/f^{\frac{1}{2}}$$

The alternative assumption that the grain shape is a regular dodecahedron (which approximates more closely than the truncated octahedron to the shape of real grains, but does not stack to fill space) results in the factor 2.06 in equation 3 being replaced by 1.90, which makes no essential difference. It is therefore believed that the choice of grain shape is not critical, and that equation 3 predicts to within about 10% the value of the ratio D/r at which there will be one second-phase particle per grain boundary.

4. Discussion

Equations 2 and 3 are of different form, the modified Zener formula giving a ratio of grain size to inclusion size which depends directly on the volume fraction of additive, and the condition of one particle per boundary giving this ratio as dependent on the square root of the volume fraction of the additive. It is easily shown that the two formulae give the same value of the ratio D/r for a volume fraction of about 0.5% of second phase. For larger fractions of second phase than this, the modified Zener formula will give a lower value of D/r than the one-particle-per-boundary condition, that is to say the average boundary will be retarded before all the boundaries come into contact with a second-phase particle as growth proceeds. Complete inhibition of growth would not be expected under these conditions. For volume fractions below the critical value, inhibition by the Zener formula will take place when the average boundary intersects more than one second-phase particle, and the formula would thus be expected to apply.

The numerical values of the ratio of grain boundary radius to grain radius, and hence of the critical volume fraction of additive are not necessarily of precise universal validity as given here. Again, because the movement of an individual grain boundary in a polycrystalline material involves movement of other boundaries, the condition that all boundaries must encounter a second-phase particle for inhibition of grain growth is probably over-restrictive. Nevertheless, it is felt that the order of magnitude predicted here for the critical additive content is correct.

It is assumed in the derivations of equations 1, 2, and 3 that the inclusions are fixed in space and that their intersections with grain boundaries are purely random. The real situation is unlikely to be as simple as this, so that the numerical predictions are subject to an unknown degree of uncertainty. It would be expected that the equations would be affected equally by departures from the situation assumed, so that the general conclusion that some boundaries may be inhibited from movement while others are still relatively free remains valid, and is in fact more reliable than the numerical predictions.

Some observations of our own, to be reported elsewhere, on the effect of the particle size of magnesia additions on grain growth in dense alumina appear to support the idea that the number of second-phase particles per boundary is of some significance in grain growth phenomena, and it is hoped that other workers will find these ideas useful.

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References

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Letters

Anodising in a Gas and in Methyl Cyanide – an Analogy

The results of Jackson [1] on the gaseous anodisation of tantalum show a striking analogy to results obtained in attempts to anodise tantalum in electrolytes based on methyl cyanide.

The experiments were carried out in a conventional Hull cell, with a tantalum foil anode and a platinum gauze cathode. Methyl cyanide to which a few drops (per litre) of concentrated aqueous HCl had been added to increase the conductivity and serve as a source of oxygen, was used as the electrolyte. The tantalum foil was degreased with trichloroethylene, flushed with chromic-sulphuric acid solution and distilled water and dried, the anodising was carried out at room temperature at a constant voltage.

No change in the appearance of the tantalum foil was observed below ~10 V, even with anodising times of 2 h or more. The interference colours characteristic of anodic oxide films appeared at higher voltages, but the process was extremely slow and only a fraction of the surface was anodised even after 12 h. The current density was low (e.g. 0.02 mA per centimetre of *total* surface) and did not increase significantly when the electrolyte was stirred. Only the surface facing the cathode was oxidised at the part closest to the cathode. The back side of the tantalum foil remained unchanged in appearance. The appearance of the anodised part was uniform, except for a narrow band of different colour (i.e. of lower thickness) at the boundary between oxidised and non-oxidised surfaces. However, such uniformity was obtained only with carefully cleaned samples, and any traces of contamination (e.g. finger marks) prevented oxidation of the contaminated area.

The current efficiency, determined by measuring the weight increment, integrating the current and calculating on the basis of Faraday's laws, was of the order of 40%.

As in the case of anodising in a gas, the relatively low conductivity of the electrolyte interferes with the creation of a high field at the oxide. In addition, the low initial oxygen concentration in the electrolyte results in rapid depletion of the oxygen in the layer adjacent to the anode and slows down the oxidation process.

Thus, except for the fact that a high temperature is developed at the anode in gas anodising, an analogy is observed between the oxidation of tantalum in methyl cyanide and in a gas. The author believes that this analogy is due to the fact that both media are of relatively low conductivity and low oxygen content (in terms of the absolute amount of oxygen per unit volume).

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