

9. J. P. ROBERTS, J. HUTCHINGS, and C. WHEELER, "Sintering and Diffusion Studies of Zinc Oxide". *Trans. Brit. Ceram. Soc.* **55** (1956) 75.
10. J. P. ROBERTS and C. WHEELER, "Diffusion of Zinc in Zinc Oxide". *Phil. Mag.* **2** (1957) 708.
11. D. G. THOMAS, "Interstitial Zinc in Zinc Oxide". *Phys. Chem. Solids* **3** (1957) 229.
12. H. LAMATSCH, (in German) diploma project, Univ. of Erlangen, Germany (1958).
13. W. J. MOORE, "Parabolic Rate Constants and Diffusion Mechanisms in Oxides and Sulphides". *Z. Elektrochem.* **63** (1958) 794.
14. E. L. WILLIAMS, "Diffusion of Zinc and Oxygen in Single Crystals of Zinc Oxide". Thesis, Indiana University, *Diss. Abs.* **20** (1959) 1200; or see W. J. MOORE and E. L. WILLIAMS, "Diffusion of Zinc and Oxygen in Zinc Oxide". *Discuss. Faraday Soc.* **28** (1959) 86.
15. R. POHL, "The Diffusion of Surplus Zinc into Single Crystals of Zinc Oxide". *Z. Physik.* **155** (1959) 120.
16. J. P. ROBERTS and C. WHEELER, "Diffusion of Zinc in Polycrystalline Zinc Oxide". *Trans. Faraday Soc.* **56** (1960) 570.
17. E. A. SECCO, "Gas-solid Exchange Reactions, Zinc Vapour and Polycrystalline Zinc Oxide". Reactivity of Solids, International Conference (Amsterdam, May, 1960) Proceedings (edited by J. H. de Boer) (Elsevier, Amsterdam, 1961) p. 188. Preliminary work in *Discuss. Faraday Soc.* **28** (1959) 94.
18. *Idem*, "Diffusion of Zn in ZnO". *Can. J. Chem.* **39** (1961) 1544.
19. R. LINDNER, "Selbstdiffusion in Oxidsystemen" (in German). *Zeit. Naturforsch.* **10A** (1955) 1027.
2. J. DEBUIGNE and P. LEHR, "The Determination of Oxygen Diffusion Coefficient in the Zirconium-Oxygen System" (in French). *Compt. rend.* **256** (1963) 1136; or see "Dry Corrosion of Non-Alloyed Zirconium" (in French). IAEA, Corrosion of Reactor Materials Conference (Salzburg, June, 1962) Proceedings (IAEA, Vienna, 1962) Vol. 2, p. 105.
3. D. L. DOUGLASS, "Diffusion of Oxygen in Columbian Pentoxide and Zirconium Dioxide". IAEA, Corrosion of Reactor Materials Conference (Salzburg, June, 1962) Proceedings (IAEA, Vienna, 1962) Vol. 2, p. 223.
4. L. A. MCCLAIN, "Thermodynamic and Kinetic Studies for a Refractory Materials Program". USA Report ASD/TDR/62/204, Part II (April, 1962) p. 54.
5. P. KOFSTAD and D. J. RUZICKA, "On the Defect Structure of ZrO_2 and HfO_2 ". *J. Electrochem. Soc.* **110** (1963) 181.
6. T. SMITH, "Diffusion Coefficients and Anion Vacancy Concentrations for the Zirconia-Zirconium Dioxide System". *Ibid.* **112** (1965) 560.
7. B. COX and C. ROY, "Transport of Oxygen in Oxide Films on Zirconium Determined by the Nuclear Reaction O^{17} (He^3, α) O^{17} ". Canadian Report, AECL-2350 (October, 1965) and *Electrochem. Tech.* **4** (1966) 121.
8. L. A. SIMPSON and R. E. CARTER, "Oxygen Exchange and Diffusion in Calcia-Stabilised Zirconia". *J. Amer. Ceram. Soc.* **49** (1966) 139.
9. A. W. SMITH, F. W. MESZAROS, and C. D. AMATA, "Permeability of Zirconia, Hafnia and Thoria to Oxygen". *Ibid.* p. 240.
10. W. H. RHODES and R. E. CARTER, "Cationic Self-Diffusion in Calcia Stabilised Zirconia". *Ibid.* p. 244.
11. L. A. MCCLAIN and C. P. COPPEL, "Electrical Conductivity of Tetragonal Zirconia". *J. Electrochem. Soc.* **113** (1966) 80.

Zirconium Oxide

1. W. D. KINGERY, J. PAPPIS, M. E. DOTY, and D. C. HILL, "Oxygen Ion Mobility in Cubic $Zr_{0.85}Ca_{0.15}O_{1.85}$ ". *J. Amer. Ceram. Soc.* **42** (1959) 393.

Letters

The Influence of Microporosity on the Ductility of Al/Al₂O₃ Alloys

Generally, the ductility of Al/Al₂O₃ (SAP) alloys decreases with increasing temperature and with decreasing deformation speed. Examples are given in figs. 1a and b. Electron micrographs [1] and density measurements [2] have indicated that this may be connected with the formation of microcracks.

This note presents first results of a systematic study on the influence of temperature on crack-formation in SAP alloys during tensile tests and creep.

Samples of 1.5 g were taken from the rupture zones of SAP specimens, of 10 mm diameter, broken in tensile and accelerated creep tests at temperatures between 20 and 620° C. The density of the samples was determined by the immersion technique; the precision was better than ± 0.002 g/cm³. SAP alloys with various fabrication histories and different oxide contents were investigated.

Typical results of density measurements of samples taken from tensile specimens of SAP with different Al₂O₃ contents (4, 7, 14 wt % Al₂O₃) are shown in fig. 1b. All alloys show the same behaviour. The density decreases slowly

with increasing test temperature up to 250° C, and decreases more markedly afterwards, especially at temperatures above 450° C. The density values show that, in all three alloys, void volume at 620° C is approximately 3%, which indicates the creation of many micropores during the tensile deformation.

The dashed line in fig. 1b indicates the density of samples of the 7% alloy taken from the zone of uniform elongation after rupture. Up to 250° C, the density does not change; above 450° C, there is a marked decrease. However, it is evident that void volume is far higher in the necked-down zone than in the zone of uniform elongation.

In fig. 2, the corresponding results of accelerated creep tests of an SAP 7% (with different fabrication history) are shown. Total elongation (fig. 2a) and density in the zones of rupture and uniform elongation (fig. 2b) are

presented as functions of time-to-rupture. Two regions can be distinguished clearly.

(a) In the first zone, elongation decreases with increasing time-to-rupture; density increases rapidly from a minimum of 2.705 g/cm³, at a lifetime of 10 min, to values of approximately 2.733 g/cm³ for 100 min.

(b) In the second zone, at lifetimes of 2 h approximately, both density and elongation show an asymptotic behaviour and assume values close to those of the zones of uniform elongation in the tensile test.

Our results show clearly that the degree of void formation in SAP is very high at elevated temperatures and almost negligible at room temperature. We suppose that this determines the elongation behaviour of SAP by the following mechanisms.

On the basis of Guyot and Ruedl's [3] theory, we think that, at low temperatures, the

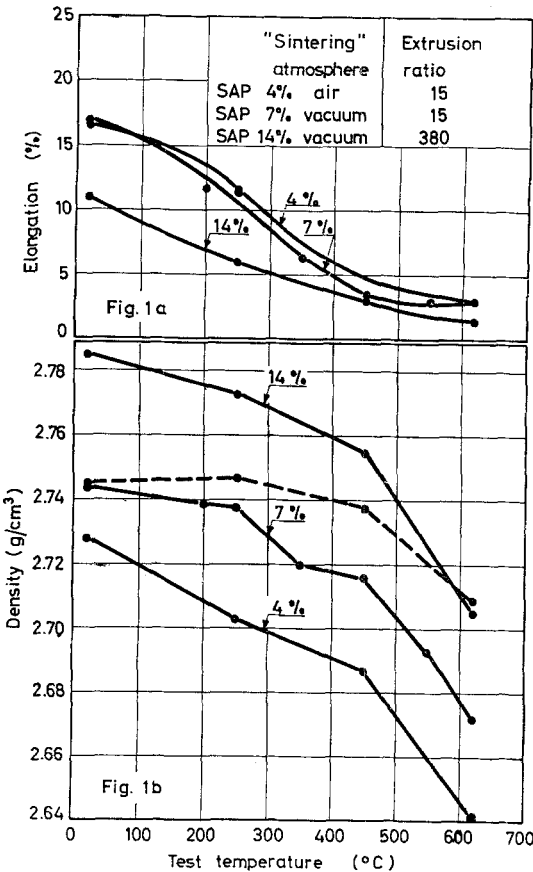


Figure 1 (a) Tensile elongation of SAP alloys as a function of test temperature. (b) Density of broken samples (— in the necked zone; - - - - in the zone of uniform elongation).

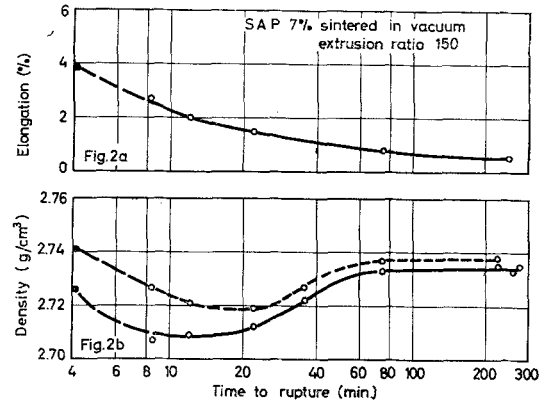


Figure 2 (a) Elongation of SAP in creep test at 450° C as a function of time-to-rupture. (b) Density of samples ruptured in creep (— in the necked zone; - - - - in the zone of uniform elongation). The values from a tensile test are shown for comparison (●).

movement of glide dislocations is hindered mainly by forest dislocations, whereas, at high temperatures, the density of the forest decreases, and blocking of the dislocations is taken over to a large extent by the oxide particles.

According to the Griffith criterion, cracks can be created by piled-up glissile dislocations. Forest dislocations cannot give rise to effective pile-ups [4]. Accordingly, crack nucleation in SAP should be easier at high temperatures, where the oxide particles are rate-controlling and block the glide dislocations. The mechanism of the formation of micropores by cracking at

dispersed particles has been described by Ashby [5]. These cracks have a decisive influence on the elongation. If we suppose that necking of a specimen starts at a given void volume and that void formation is favoured by higher temperatures, then uniform elongation must decrease with rising temperature. This corresponds to the experimental findings.

Further deformation will be controlled by creation of new cracks, by growth of existing ones, and, mainly, by necking-down of aluminium zones: these zones are now separated from the oxide particles by the cracks spreading from the oxide particles and are hence free to deform, which leads to local ductile fracture. Elongation before and after necking are therefore controlled by different mechanisms. The final brittle fracture is composed of a multitude of microscopic ductile fracture zones.

This mechanism, proposed for tensile deformation, apparently cannot be transferred completely to the creep test. In this case, cracks should grow slowly (as shown for other materials [6]) and should give rise to microscopic necking and elongation similar to that in tensile testing. Fig. 2 showed, however, that, after creep tests of more than 1 h, void volume is lower than after tensile testing. Probably there is some phenomenon which stops crack-growth in long-time tests. This could, in part, be explained by the following hypothesis.

Owing to the complex fabrication schedule, it is most probable that, in SAP, there are inclusions of air trapped by the oxide particles, as has been found for many powder metallurgy materials [7]. Activation analysis has shown [8] that, in the 7% alloy, there is 10 ppm argon

which, if it came mainly from included air, would indicate a high initial air content of 0.1 wt %. When a crack starts at a particle where an air bubble is trapped, the gas may enter into the cavity, and internal surfaces of oxides and nitrides will be formed which should hinder the further growth of the crack. In this way, most of the cracks should remain small and could, therefore, not liberate the extensive aluminium zones which could give rise to appreciable elongation.

Such a mechanism of gas-transport and oxidation must be a time-dependent process. This hypothesis can explain the findings of fig. 2b, that fast testing leads to high void volumes and slow testing to low void volumes.

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References

1. A. GIARDA and M. PAGANELLI, *Mem. Sci. Rev. Met.* **62** (1965) 921.
2. H. KELLERER, G. SAUR, and H. BORCHERS, Euratom Report EUR 3497 (1967).
3. P. GUYOT and E. RUEDL, *J. Matls. Sci.* **2** (1967) 221.
4. A. KOCHENDÖRFER, *Z. angew. Phys.* **14** (1962) 129.
5. M. F. ASHBY, *Phil. Mag.* **14** (1966) 1157.
6. R. C. BOETTNER and W. D. ROBERTSON, *Trans. AIME* **221** (1961) 613.
7. I. JENKINS, *Powder Met.* **7** (1964) 68.
8. F. GIRARDI (Euratom, Ispra), private communication.

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The Growth of Strain-Free $Y_3Al_5O_{12}$ Single Crystals

Vertically pulled single crystals of yttrium aluminium garnet ($Y_3Al_5O_{12}$) characteristically exhibit a central core of elastically strained material which is associated with the formation of {211} type facets, (fig. 1), on the solid/liquid interface during growth. Because this defect impairs the crystalline and optical perfection of the material, high quality laser rods can only be cut from the outer regions of such crystals [1, 2].

In this laboratory, recent studies of mixed

rare-earth aluminium garnets [3] have shown that if such crystals can be grown with a flat solid/liquid interface, faceting does not occur, and the optical quality is greatly improved. The results of these studies have been successfully applied to the growth of $Y_3Al_5O_{12}$ single crystals, and it is now possible to grow crystals of this material entirely free from the strained central core. The technique employed is simply to reduce the temperature gradients across the interface by rotating the crystal at high speed. Hitherto, crystals have been grown at rotation speeds in the range 10 to 50 rev/min when the solid/liquid interface is approximately conical