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A preliminary study of precipitation in Ti^{4+}-doped polycrystalline alumina

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Precipitation processes in two titanium-doped aluminas (0.14 and 0.60 cation % titanium) have been examined using a variety of analytical electron microscopy techniques. The results strongly suggest that, for an ageing temperature of 1573 K, rutile is the only precipitate formed in the 0.14 cation % titanium material. However, evidence for the precipitation of both rutile and β-Al_2TiO_5 (the latter at triple junctions) was obtained in the 0.60 cation % titanium sample.

1. Introduction

The interest in the nature and distribution of second phase precipitates in polycrystalline alumina stems from the suggestion that Ti^{3+}-doped polycrystalline alumina should exhibit general plasticity, by a process of dislocation flow, at temperatures above 1700° C. The suggestion follows from the observation that Ti^{3+} softens the secondary slip systems while hardening the primary (basal) slip system [1–3]. Ageing studies of highly strained Ti^{3+}-doped single crystals subsequently oxidized to Ti^{4+} in the solution treatment temperature range, have shown that rutile nucleates and grows preferentially on dislocations, resulting in a high density of small precipitates, increasing both hardness and toughness relative to material which was not deformed to ageing [4, 5]. These results suggest that thermomechanically treated Ti^{3+}-doped polycrystalline alumina may demonstrate superior mechanical properties by promoting intragranular precipitation of rutile, thereby reducing the propensity for intergranular precipitation (and in particular of β-Al_2TiO_5).

Previous studies have shown that intragranular precipitates in star sapphire (Ti^{4+}-doped single crystal alumina) exhibit a needle-like morphology and lie in the basal plane parallel to the $\langle 10\bar{1}0\rangle$ directions [6]. In addition, Phillips *et al.* [7] determined that these precipitates were rutile and reported as well a spherical precipitate phase proposed to be β-Al_2TiO_5 [6]. Clarke *et al.* [8] also observed needle-like intragranular precipitates in Ti^{4+}-doped polycrystalline alumina but found that intergranular precipitation of β-Al_2TiO_5 (particularly at triple junctions) always preceded intragranular precipitation. In view of the fact that the above studies, particularly those of polycrystalline alumina, employed light microscopy and X-ray diffraction to detect the second phase precipitates, the present investigation is concerned with an examination of the early stage of precipitation in Ti^{4+}-doped polycrystalline alumina using analytical electron microscopy techniques.

2. Experimental procedures

Details of the specimen materials, together with their heat treatment schedule are given in Table I. The titanium content of material A is close to that of the single crystals examined in earlier studies [4], while material B contained a higher percentage of titanium (in order to increase the volume fraction of the precipitate phase). Both materials were fired at very low oxygen pressures, P_{O_2} (monitored with a carefully calibrated oxygen sensor on the inlet and outlet ports of a graphite resistance furnace) in order to provide a very high Ti^{3+} to Ti^{4+} ratio in the starting materials. After this treatment the samples exhibited a characteristic dark ruby colour indicative of a high Ti^{3+} content in solution in Al_2O_3. Material A was deformed to ~5.3% apparent permanent strain in compression at 1700° C at a very low P_{O_2} in order to attempt to generate a high dislocation density. Both materials

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TABLE I Composition and heat treatment history of the two materials investigated

Material A	Material B
0.14 cation % Ti as Ti_2O_3 in Linde A Al_2O_3	0.60 cation % Ti as TiO_2 (rutile) in Linde A Al_2O_3
Vacuum hot-pressed, 1600° C, 15 min	Pre-sintered air, 1400° C, 24 h
Reduced $P_{O_2} < 10^{-20}$ atm, 1700° C, 2 h	Reduced $P_{O_2} < 10^{-20}$ atm, 1800° C, 6 h
Deformed 5.3% permanent strain, 1700° C, $P_{O_2} < 10^{-15}$ atm	
Oxidized air, 1600° C, 24 h	Oxidized air, 1600° C, 24 h
Aged* air, 1300° C, 17 h	Aged* air, 1300° C, 13 days

*Ageing times correspond to optimum times (maxima in microhardness against ageing time curve [4]) for deformed and undeformed sapphire filaments.

were then oxidized at 1600° C to convert Ti^{3+} to Ti^{4+} *in solution* since both compositions are well within the solubility limit of Ti^{4+} in Al_2O_3 at 1600° C [9]. The ageing treatments at 1300° C correspond to the heterogeneous and general nucleation microhardness maxima, respectively, in the ageing curves for single crystals [4].

Thin foils for transmission electron microscopy (TEM) examination were prepared by mechanical grinding and polishing followed by argon ion milling in a commercial ion-beam thinner. The samples were carbon coated prior to examination in either a Philips EM300 TEM operating at 100 kV or in a Philips EM400 TEM/STEM operating at 120 kV.

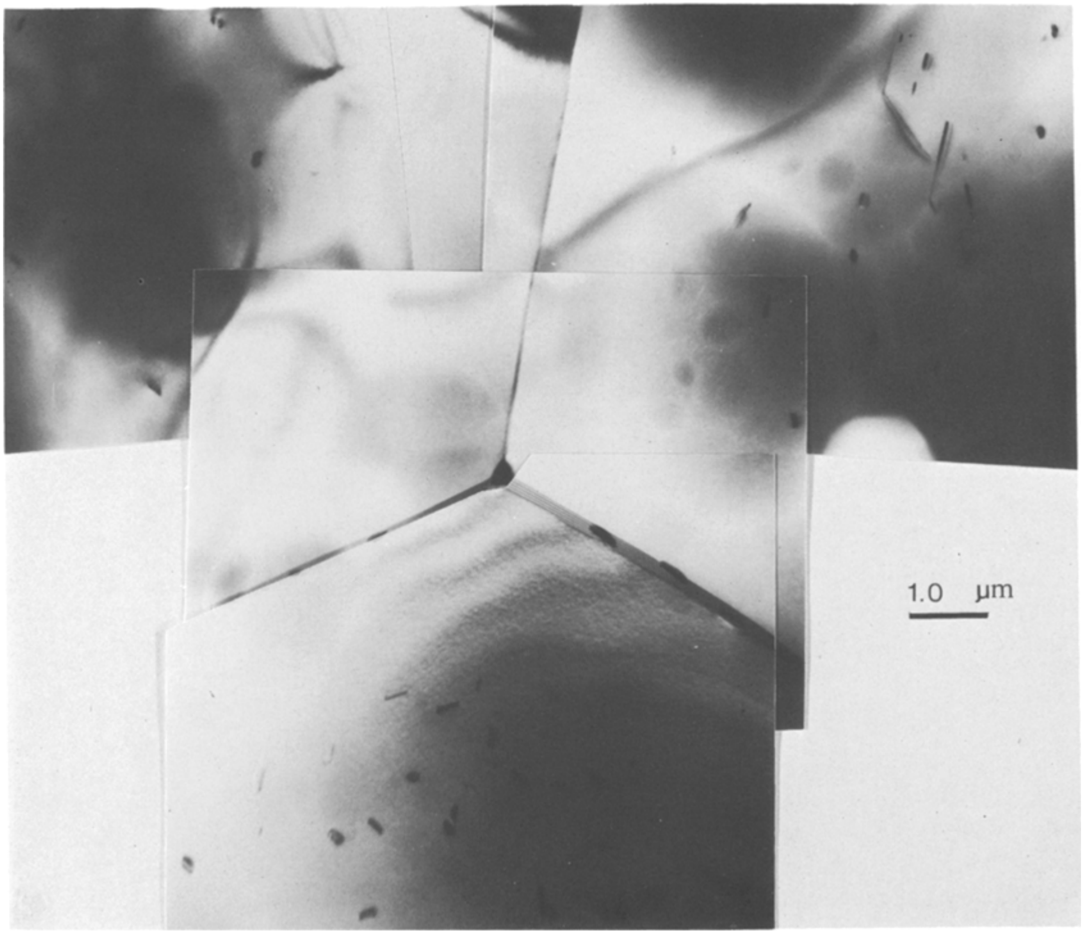
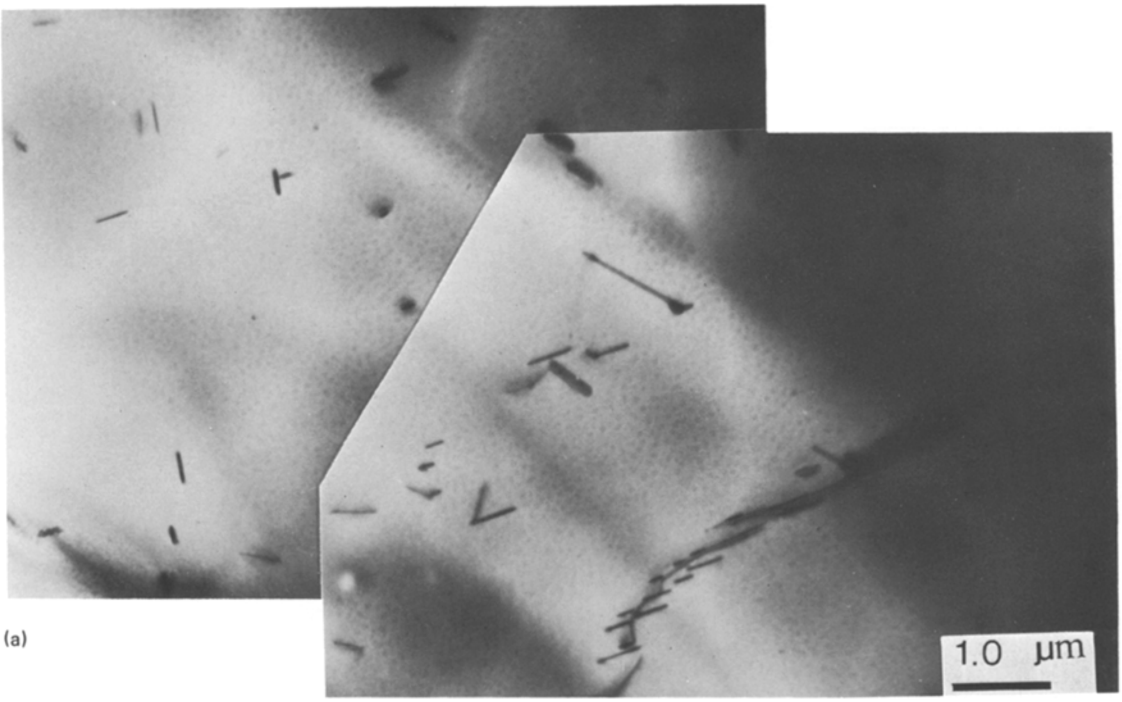


Figure 1 Bright-field electron micrograph of material B. Precipitation is observed within the matrix, on grain boundaries and at the triple junction. Note the precipitate-free zones adjacent to all the boundaries.



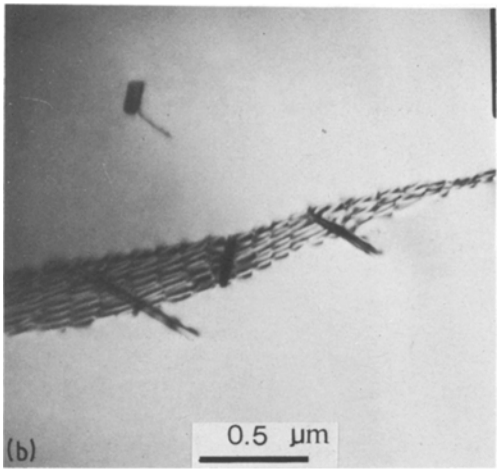


Figure 2 Examples of rutile precipitates within the matrix and on sub-boundaries in material A. The precipitates exhibit a characteristic needle-like morphology.

3. Results

Fig. 1 is a transmission electron micrograph of material B and serves to illustrate the major features characteristic of both materials in the aged condition. Precipitation is observed at the triple junctions, on grain boundaries and within the matrix; the latter being rod- or needle-like. It is also interesting to note that a precipitate-free zone is observed in the vicinity of the grain boundaries*.

In the low cation % titanium material, the results were consistent with earlier findings [6, 7] in that the precipitates were needle-like and oriented in specific crystallographic directions. Figs. 2a and b are examples of rutile precipitates, both on isolated dislocations and on sub-boundaries. Sub-boundaries were frequently observed and may result from polygonization during the ageing treatment.

The more highly doped specimen material (B), showed a wider variety of precipitate morphologies than material A, precipitation at triple junctions occurred more frequently, and the precipitates were, in general, larger. Figs. 3a and b are dark-field images of one particular region illustrating a large triple junction precipitate (Fig. 3a) together with intragranular needle-like precipitates and a faceted precipitate which is associated with an intragranular pore (Fig. 3b). Diffraction analysis of the triple point precipitate showed that it corresponded to the β-Al_2TiO_5 structure and Fig.

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*An approximate diffusivity for titanium can be calculated from the relationship $1.5L = (Dt)^{1/2}$. Taking $L = 1.9 \times 10^{-4}$ cm and $t = 1.1 \times 10^{6}$ sec, gives an effective diffusivity of $D = 1.8 \times 10^{-14}$ cm^2 sec^{-1} which is in good agreement with that determined by Nagai *et al.* [10] for titanium diffusion in sapphire at 1300° C.

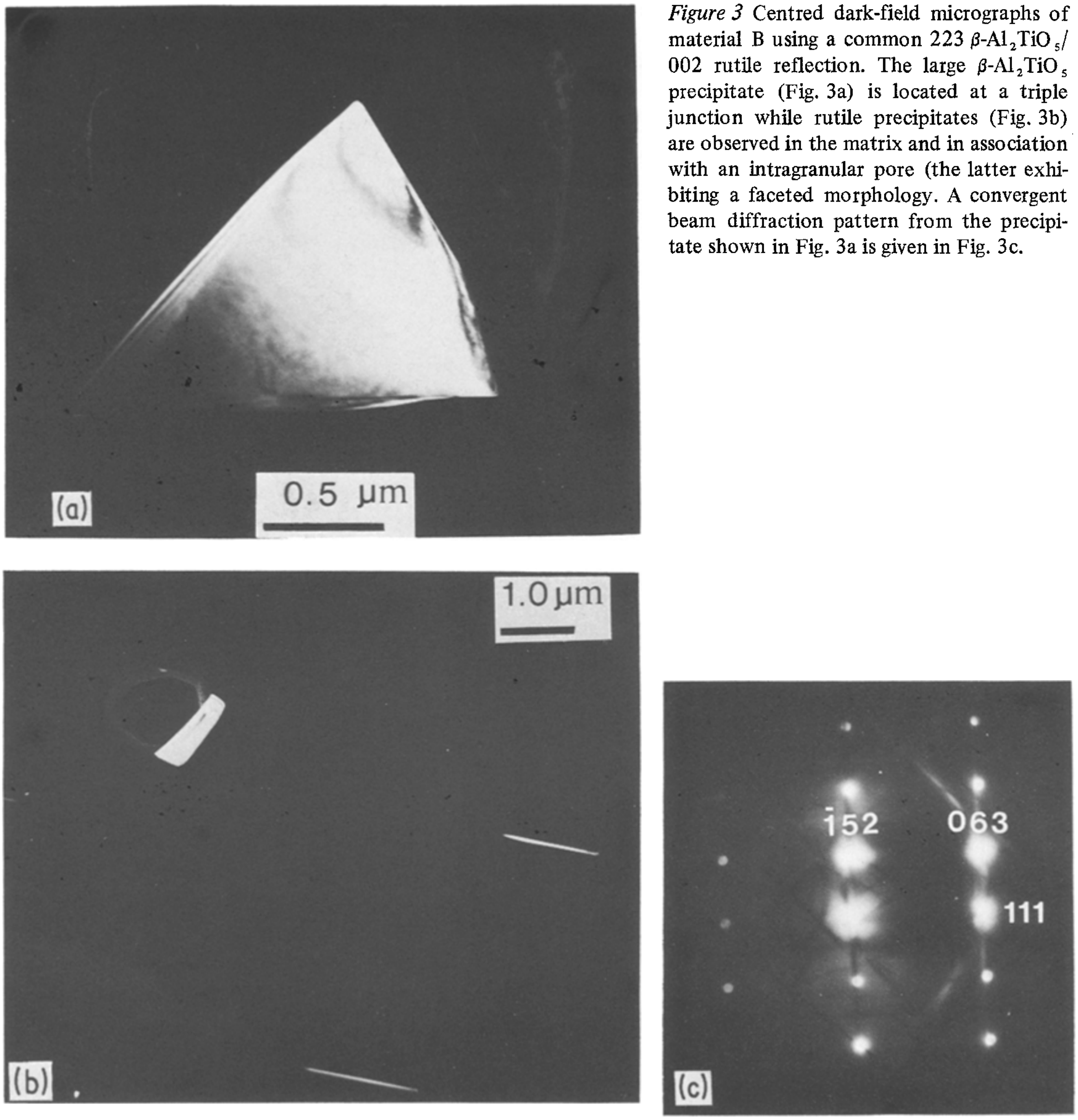

Figure 3 Centred dark-field micrographs of material B using a common 223 β-Al_2TiO_5/002 rutile reflection. The large β-Al_2TiO_5 precipitate (Fig. 3a) is located at a triple junction while rutile precipitates (Fig. 3b) are observed in the matrix and in association with an intragranular pore (the latter exhibiting a faceted morphology. A convergent beam diffraction pattern from the precipitate shown in Fig. 3a is given in Fig. 3c.

3c is a convergent beam electron diffraction (CBED) pattern of this particular precipitate (beam direction: $[1 1 \bar{2}]$ β-Al_2TiO_5). In contrast, precipitates associated with the intragranular pores could, in general, be indexed in terms of the rutile structure. Fig. 4a is a centred dark-field image of one such precipitate and Fig. 4b is the energy dispersive X-ray spectrum from this precipitate. The presence of only one cation (i.e. titanium) is consistent with the diffraction analysis that the precipitate is rutile (the small copper peak observed in the spectrum of Fig. 4b originates from the support grid).

For both materials, the grain boundary precipitates were, in general, rod-like and frequently twinned. Fig. 5 shows a bright-field micrograph of a twinned rutile precipitate together with the centred dark-field micrographs of the twinned regions. The X-ray spectrum from the precipitate contained a strong titanium peak together with a very weak aluminium peak. The aluminium peak most probably arises from interaction between the electron probe and the aluminium-rich matrix.

4. Results and conclusions

In summary, rutile appears to be the only precipitate phase formed in the 0.14 cation % titanium material after ageing for 17h at 1300° C, while both rutile and β-Al_2TiO_5 (the latter at triple junctions) was observed in the 0.6 cation %

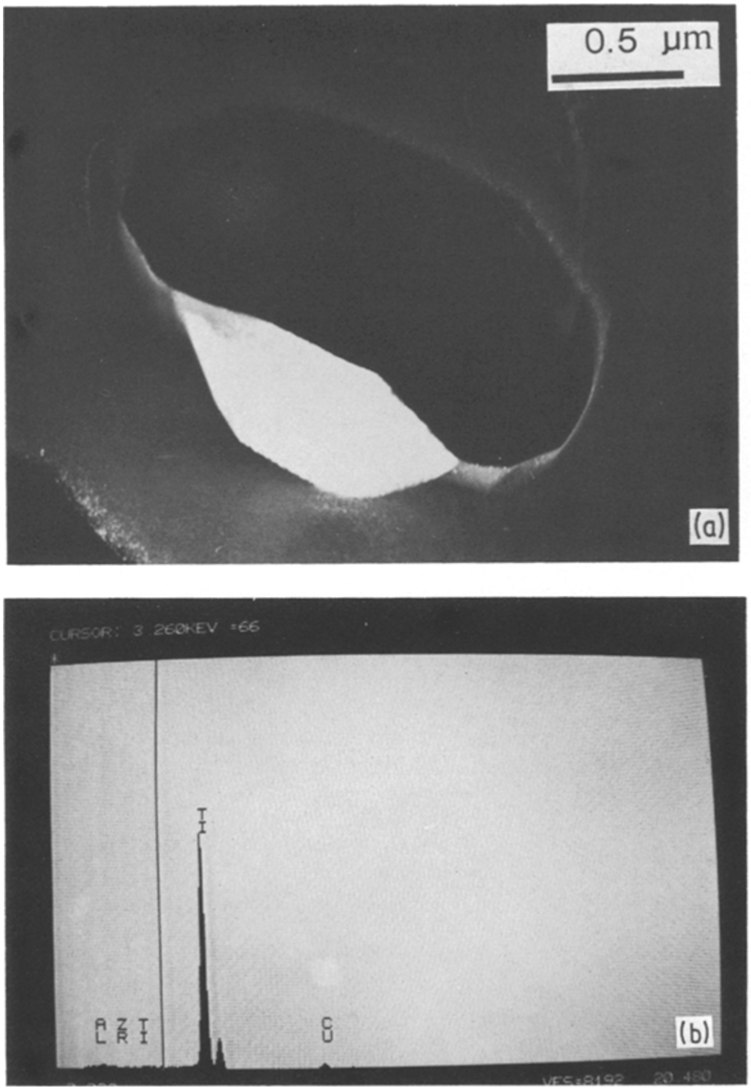

Figure 4 (a) Centred dark-field micrograph of a precipitate in association with an intragranular pore. (b) The energy dispersive X-ray spectrum for the precipitate shown in Fig. 4a. The presence of titanium as the only significant cation shows that the precipitate is rutile.

titanium material after ageing for 13 days at 1300° C. These results can be interpreted in two ways.

1. Al_2TiO_5 is not stable at 1300° C in material A;

2. Al_2TiO_5 is a stable phase at 1300° C in material A and will precipitate after prolonged holding at 1300° C.

If Al_2TiO_5 is not stable at 1300° C, its presence in material B could be a reflection of the fabrication process, most likely the 1400° C pre-sintering treatment in air (material A was synthesized from Ti^{3+} and was fired at very low P_{O_2}'s). If this interpretation is correct, then the phase diagram of Lejus *et al.* [11] would require alteration to show Al_2TiO_5 with a lower stability limit above 1300° C instead of ~1150° C. The results of Clarke *et al.* [8] (who invariably found Al_2TiO_5 precipitation preceding nucleation of rutile) could then be explained in terms of a "relic" of the fabrication route employed prior to ageing.

The second hypothesis, that Al_2TiO_5 will form at longer ageing times than material A experienced, is consistent with the fact that the energy of the Al_2TiO_5/Al_2O_3 interface is likely to be higher than the energy of the TiO_2/Al_2O_3 interface. Hence, it is to be expected that the incubation time for the onset of the Al_2TiO_5 reaction would be longer than that required for the nucleation of rutile. This reasoning is also consistent with the observation that Al_2TiO_5 is only formed at triple junctions in material B.

Clearly, further work is necessary to resolve the uncertainties in interpretation. However, if the

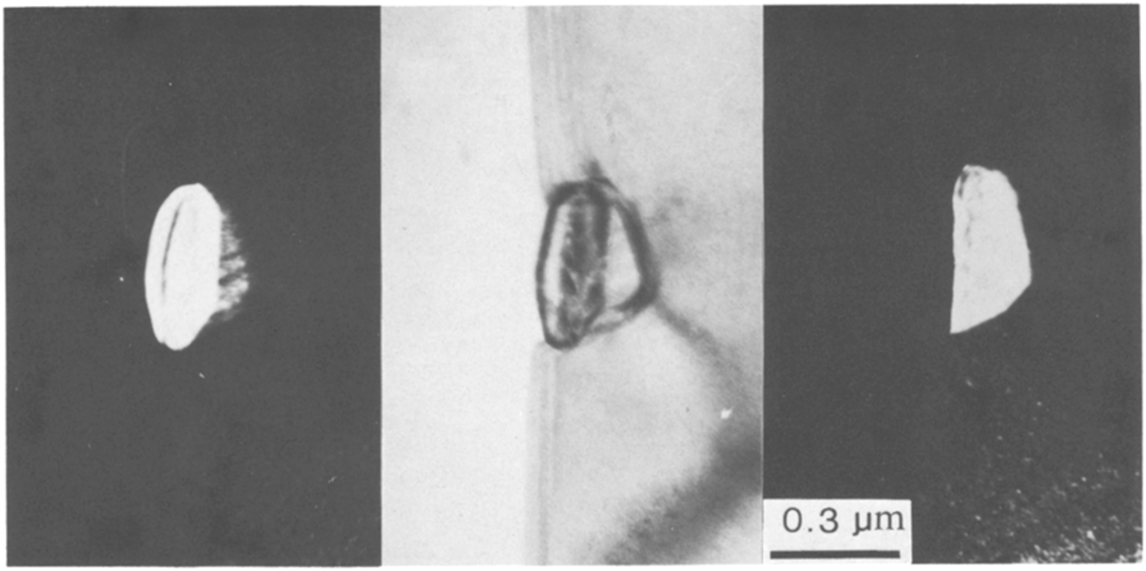

Figure 5 Bright-field and dark-field images of an internally twinned grain boundary rutile precipitate.

former case is the accurate picture, there is a very good possibility of precipitation hardening and toughening titanium-doped polycrystalline alumina, as found for titanium-doped sapphire; provided the starting materials are carefully chosen and the firing is performed at very low P_{O_2}'s in order to retain titanium in the 3+ state and in solution in the alumina prior to the oxidation and ageing heat treatments.

Acknowledgements

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