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# The effect of rare earth dopants on grain boundary cohesion in alumina

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**Abstract**

The effect of rare earth (RE) grain boundary segregation on mode of fracture in alumina has been investigated. In order to isolate the effects of microstructure (i.e. grain size and residual porosity) from those due to grain boundary chemistry, the fracture behaviour of virtually pore-free (i.e. nearly transparent) undoped alumina has also been studied. This showed that mode of fracture becomes increasingly transgranular as grain size is reduced, a trend which has been explained by thermal expansion anisotropy effects.

The addition of RE (i.e. Yb, Gd or La) dopants to alumina resulted in a substantial increase in the proportion of intergranular fracture relative to the undoped material of similar grain size. This can be explained by the significant reduction in the free surface energy that results from RE segregation at grain boundaries, which reduces the work of fracture for intergranular failure. This is expected to lead to a reduction in strength compared to undoped aluminas with equivalent microstructures, although this is often more than offset by the improved microstructures that using a RE dopant can provide.


*Keywords:* Grain boundaries; Fracture; $Al_2O_3$; Rare earth dopants

## 1. Introduction

The presence of segregated dopants at grain boundaries in ceramics can have a large effect on mechanical properties such as creep and fracture behaviour. In the case of rare earth (RE)-doped alumina, the RE segregates very strongly to grain boundaries and a number of studies have shown a large (typically two to three order of magnitude) increase in creep resistance.[1–4] The effect of RE segregation on the fracture properties has received less attention, although studies examining fracture energy and strength have reported that RE dopants increase grain boundary cohesion.[5] The main difficulty encountered in these studies is, however, isolating the effect of grain boundary chemistry from the much larger effect of RE dopant on microstructural evolution during sintering. The presence of RE cations at grain boundaries is well known to reduce both the grain growth kinetics and densification rate for a given temperature and consequently results in materials with very different microstructures (i.e. grain size and porosity distributions). The effect of grain size on fracture behaviour is particularly pronounced in alumina because of the effects of thermal expansion anisotropy between neighbouring grains. In the literature, the effect of grain size on fracture behaviour is often obscured by porosity, the amount, size and location of which are inevitably affected by grain growth.

In this study, the effect of grain size on fracture behaviour in high purity alumina with low pore contents (indicated by their near-transparency) is determined. This is subsequently compared with similarly produced RE-doped alumina samples with a range of grain sizes, RE dopants and dopant contents, all with low pore contents. From these experiments, the effects of RE dopants on fracture behaviour has been elucidated.

## 2. Experimental procedures

Fully dense alumina samples were prepared from Taimicron TM-DAR (Taimei Chemicals, Japan) powders. Rare earth dopants (La, Gd and Yb) were introduced by dissolving the appropriate hydrated RE nitrate, e.g. 99.99% ytterbium(III) nitrate pentahydrate (Aldrich Chemicals, UK), in IPA and mixing with an alumina/IPA slurry. The slurry was dried at room temperature and used without further processing to minimise possible contamination. For comparative purposes, a similar

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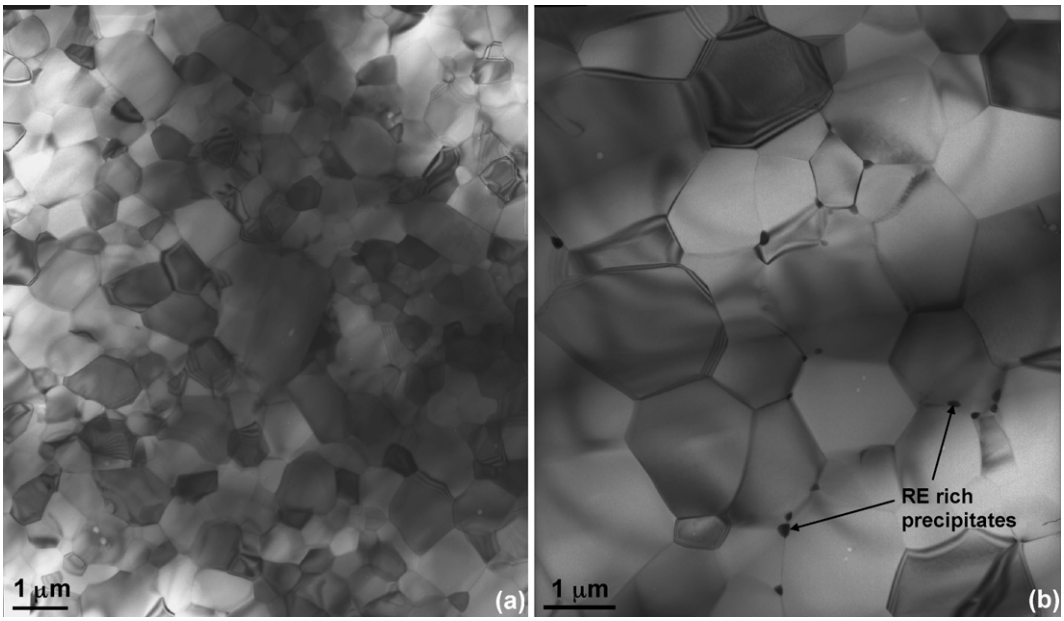


Fig. 1. TEM micrographs of an La-doped (500 ppm) alumina hot pressed at 1450 °C (a), and a Gd-doped (500 ppm) alumina hot pressed at 1500 °C (b).

processing route was also employed for undoped powders. All powders were hot-pressed in a graphite die at temperatures between 1400 and 1550 °C with a dwell time of 10 min and a pressure of 30 MPa. Dopant levels of 500 and 2000 ppm (RE:Al cation ratio) were used, although grain boundary concentration was also dependent on grain size and hence sintering temperature. All 500 ppm samples with an average grain size >1 μm (i.e. ≥1500 °C) contained precipitates, suggesting saturation of grain boundary segregants. The distribution of these precipitates was examined using SEM (Leo 1530 VP FEG) and found to be uniform in the 500 ppm samples but less so in those doped at the higher level (2000 ppm).

Fracture sections were lightly coated with either Au/Pd or carbon and examined using a FEG SEM primarily with the secondary electron detector. The coating procedure could be avoided by working at low voltages or in the variable pressure (VP) mode but this was found to be less convenient. The percentage of transgranular fracture (PTF) was measured quantitatively from fractographs (each containing at least 200 grains) taken in at least six randomly chosen areas for each sample. SEM was also used to determine grain size from thermally etched (at 1200 °C for 2 h) polished sections. The grain size was taken as the average equivalent circle diameter multiplied by 1.225, which is a geometric correction factor. At least 300 grains were used for each material. The method has the advantage that it also enables grain size distributions to be established, which is important since certain mechanical properties of these materials can be dictated by the largest grains in the distribution. Grain boundary structure and segregation characteristics were examined using a (S)TEM (Philips Tecnai F20 FEG) as has been described in detail previously.[7] Samples were prepared using conventional grinding and polishing procedures followed by ion milling to electron transparency using a Gatan PIPS (Model 691). In STEM, a high angular annular dark field (HAADF) detector (Model 3000, Fischione Instruments) was used to produce atomic number ($Z$) contrast images that clearly displayed the RE distribution within the microstructure.

## 3. Results and discussion

### 3.1. Microstructural characterisation

TEM micrographs of typical alumina samples are shown in Fig. 1. The samples possess a microstructure containing very low pore content, which is consistent with the transparent appearance of the material.[8] All samples examined possessed a normal grain size distribution (Fig. 2) and, as expected, the addition of a RE dopant retarded grain growth for each sintering temperature. The magnitude of the retardation was dependent on the particular RE species, and increased with increasing ionic radius of cation (Yb < Gd < La). This dependence is consistent with the RE cations blocking $Al^{3+}$ diffusion pathways at grain

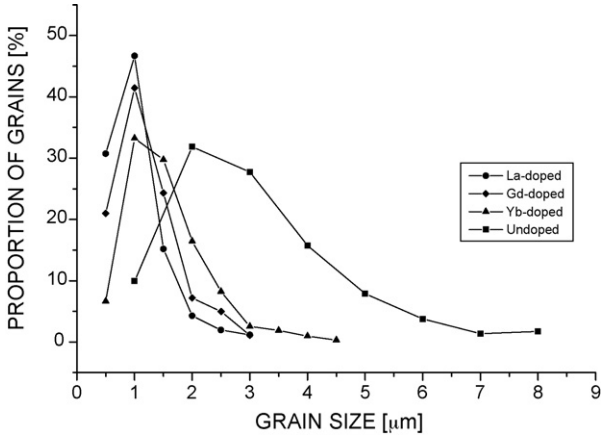


Fig. 2. A graph comparing the grain size distributions of undoped and RE-doped (500 ppm) samples hot pressed at 1500 °C.

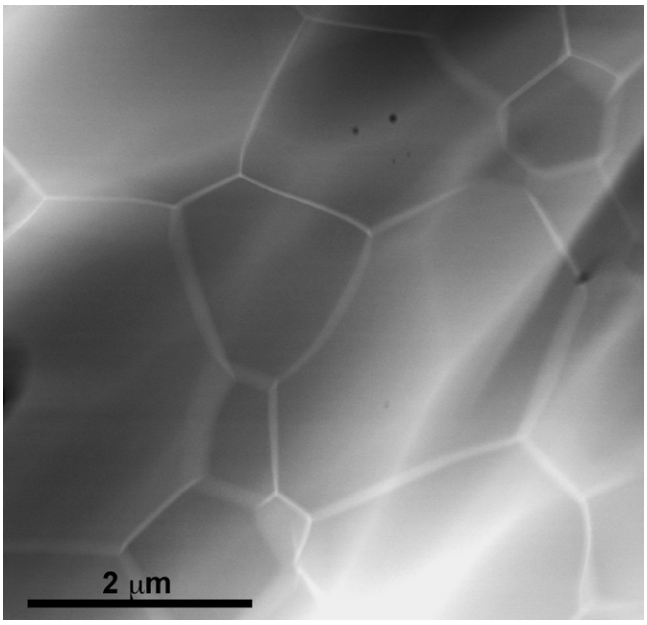


Fig. 3. A HAADF STEM micrograph of Gd-doped alumina hot pressed at 1500 °C.

boundaries, which has also been used to explain the tensile creep behaviour of similar materials.[3]

A variety of techniques have been used to study the segregation behaviour of RE-doped alumina.[7] TEM based techniques are particularly powerful as they can provide a measure of both the thickness of the segregated grain boundary layer and the concentration profile of RE dopants across them. Fig. 3 shows a HAADF STEM image of a Gd-doped alumina. The increase in image intensity at the grain boundary can be linked directly with the segregation of the high atomic number of RE dopants. This technique can provide an accurate profile of grain boundary segregation and when used in conjunction with analytical techniques such as EDS and PEELS can provide the grain boundary composition gradients.[7] These techniques have shown that RE grain boundary concentration is relatively uniform in general grain boundaries (special low energy grain boundaries have been shown to account for only a very small fraction of the grain boundary total).

### 3.2. Mode of fracture in alumina

Fracture sections of undoped and RE-doped aluminas with various grain sizes are compared in Figs. 4 and 5. Such fractographs were used to calculate the proportion of transgranular fracture (PTF) in each sample. Fig. 6 shows that in all cases RE doping results in an increased proportion of intergranular fracture relative to the undoped material of similar grain size. Explanations for this fracture behaviour in undoped and RE-doped aluminas are discussed below.

#### 3.2.1. Mode of fracture in undoped alumina

Fig. 6 shows that in undoped alumina, the proportion of transgranular fracture increases as grain size is reduced. This can be attributed to the microstresses that occur between adjacent grains with different orientations due to thermal expansion anisotropy. This promotes intergranular fracture and at large grain size or high thermal stress can lead to spontaneous grain boundary cracking. The magnitude of these microstresses reduces with

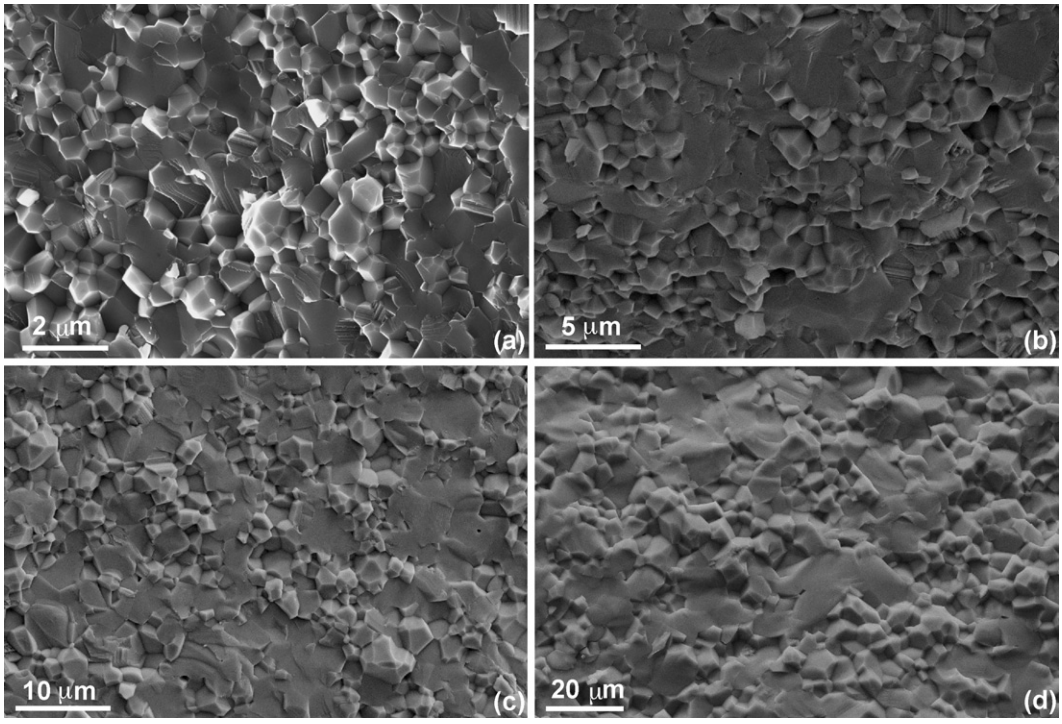


Fig. 4. SEM fractographs of undoped aluminas with a range of grain sizes.

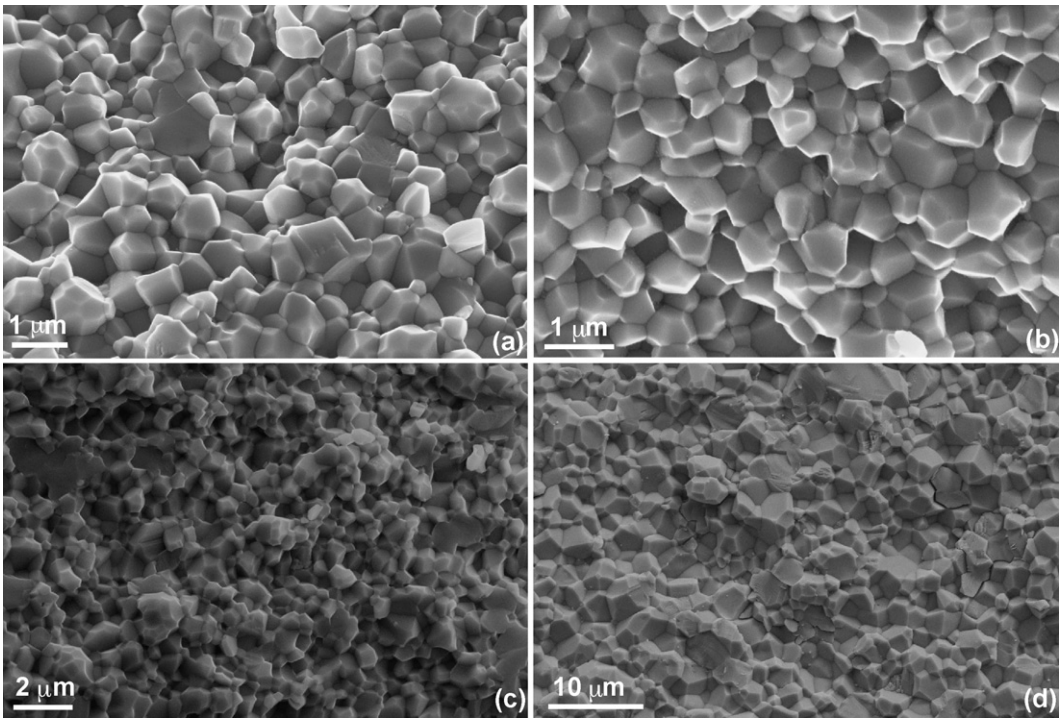


Fig. 5. SEM fractographs of various RE-doped alumina: (a) Gd 1450 °C (500 ppm), (b) La 1450 °C (2000 ppm), (c) La 1450 °C (500 ppm) and (d) Yb 1550 °C (500 ppm).

decreasing grain size, which is consistent with the observed fracture behaviour in undoped alumina.

In the literature, the effect of grain size on the mode of fracture in alumina is often over-shadowed by secondary effects such as porosity (e.g.[9]) and impurity segregation at grain boundaries (e.g.[10]). For example, the change in fracture mode with grain size was recently examined for pressureless sintered alumina, and a transition from intergranular to transgranular was observed as the grain size was increased.[9] Although this behaviour was considered to be an intrinsic grain size effect, an alternative explanation could be due to the changes that the significant pore content, which varied from 4% (for fine grained samples) to 0.6%, has on fracture.

Although these effects have been minimised here by hot pressing to full density (i.e. near-transparency), and the use of a powder with very low impurity content, residual porosity could still have a slight effect on the measured PTFs. The effect of RE segregation (an intentionally added impurity) on mode of fracture and grain boundary cohesion is discussed in detail in the succeeding section.

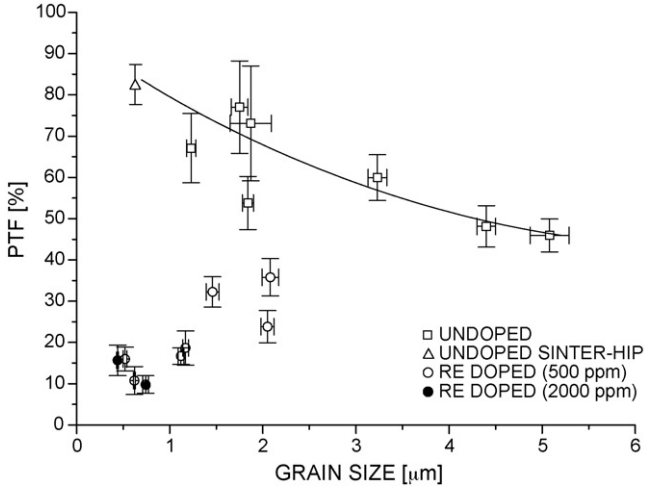


Fig. 6. A graph showing the percentage of transgranular fracture (PTF) against grain size for undoped and RE (La, Gd and Yb)-doped aluminas. It was not possible to hot press very fine-grained (i.e. grain size <0.8 μm) undoped samples to near-transparency so a sinter-HIP sample prepared from the same powder was used instead.

### 3.2.2. *Mode of fracture in RE-doped alumina*

RE-doped alumina was found to have a substantially lower transgranular component of fracture relative to undoped aluminas of comparable grain size for all of the RE dopants (La, Yb and Gd), dopant concentrations and grain sizes examined. As grain size increases, the proportion of transgranular fracture increases slightly. This is unlikely to be an intrinsic grain size effect since the reverse trend was observed in the undoped material. However, as grain size increases above 1 μm the grain boundary volume is insufficient to accommodate all the RE dopant and grain boundary precipitation starts to occur (Fig. 1b). Precipitates are likely to have a different effect on fracture than grain boundary segregants, and in addition can deplete the local concentration of the grain boundary segregant. Also in samples where excessive grain growth has occurred (this is not significant in the samples considered here) precipitates can be formed in intragranular locations, which is likely to strongly promote transgranular fracture.

The observed increase in intergranular fracture in RE-doped alumina has important implication on the strength and fracture toughness of these materials. According to the Griffith energy-balance concept, the mode of fracture in brittle materials is determined by the relative values for the work of fracture for cleavage ($G_C$) and intergranular failure ($G_{GB}$),

$$G_C = 2\gamma_c$$

$$G_{GB} = 2\gamma_s - \gamma_b$$

where $\gamma_c$ is the surface energy of the cleavage plane, $\gamma_s$ the specific surface energy of each grain exposed by fracture (here a symmetrical fracture is assumed) and $\gamma_b$ is the grain boundary free energy per unit area.

In undoped alumina, since a mixed fracture mode was observed, $G_C$ and $G_{GB}$ must be similar. However, the transition to predominantly intergranular fracture in RE-doped samples shows that in these samples $G_{GB} < G_C$. Since $\gamma_c$ is unaffected by grain boundary segregation it follows that RE dopants cause the work of fracture for intergranular failure to decrease. It is well known from the extensive work on metal embrittlement, that impurity grain boundary segregation causes a large reduction in the absolute surface free energies.[11] This is partially offset by a reduction in grain boundary free energy, but since $\gamma_b$ is typically only one-sixth of $2\gamma_s$, the reduction in surface free energy is dominant. A reduction in the work of fracture for intergranular failure reduces grain boundary cohesion and hence the strength of the material.

This energy-balance model is, however, over-simplistic for the following reasons; firstly, for monolayer grain boundary segregation, the segregant atoms will be divided between the two intergranular fracture surfaces (each with energy $< \gamma_s$, corresponding to non-equilibrium surface segregation)[12] and, secondly, the value of $G_{GB}$ does not include the influence of non-planar crack paths and a contribution from crack deflection/grain boundary frictional sliding during crack propagation. However, the energy balance, represented by $2\gamma_s - \gamma_b$, may be approached for multilayer segregation coupled with a symmetrical fracture path. Further, the presence of segregant atoms on the new fracture surfaces could possibly facilitate instantaneous relaxation of surface atoms, even at low temperatures, and hence further reduce the value of $\gamma_s$ from the pure surface state. Consequently, although the link between RE grain boundary segregation and enhanced intergranular fracture is unquestionable, the underlying mechanism remains unresolved.

It should be noted that this paper is in apparent contradiction with much of the literature where RE segregation has been reported to increase grain boundary strength in similar materials. These studies are based on fracture energy[5] and strength[13] studies that used pressureless sintered aluminas that were not corrected for grain size and had a significant (and variable) pore content. It is therefore likely that the effect the dopants have upon sintering behaviour and hence microstructure completely outweighed any variation in grain boundary properties.

There are, however, also a number of studies, which provide indirect support for the observed reduced grain boundary cohesion due to RE grain boundary segregation in alumina. For example, in wear studies, increased grain pullout is observed in Y-doped compared with undoped alumina, which is indicative of reduced grain boundary cohesion.[2] Also, in a study on hot pressed alumina/SiC composites,[14] it was found that the addition of RE dopants caused fracture to become intergranular, although because of the earlier work on the fracture of RE-doped alumina, this was attributed to a combined effect of the RE and Si at the grain boundary.

It should also be noted that the reduced grain boundary cohesion of RE-doped aluminas does not have such a catastrophic effect on fracture toughness as in the case of metal embrittlement where the transition is from ductile to brittle. Indeed, the reduced grain boundary cohesion in RE-doped alumina is expected to have only a modest effect on fracture toughness. This is because the reduced grain boundary cohesion is offset by the increase in fracture surface area due to the more tortuous crack path that is followed in intergranular failure.[15]

## 4. Conclusions

In undoped alumina, the proportion of transgranular fracture increases as grain size is reduced. This can be explained by microstresses caused by thermal expansion anisotropy reducing as grain size decreases. In RE-doped aluminas, a substantially higher proportion of intergranular fracture is observed relative to the analogous (i.e. same grain size and residual pore content) undoped material. This is due to the RE dopant, which segregates strongly to grain boundaries, reducing grain boundary cohesion.

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