

Structure of Incoherent  $ZrO_2/Al_2O_3$  Interfaces

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High-resolution electron microscopy was used to image incoherent  $ZrO_2/Al_2O_3$  interfaces in  $ZrO_2$ -toughened  $Al_2O_3$  containing intragranular  $ZrO_2$ . These particles are generally spherical but are sometimes faceted. High-resolution electron micrographs provide atomic-level information on the interfacial structure. For spherical particles, both ledgelike images and misfit dislocation-like images accommodated the lattice misfit, depending on the orientation of the interface, while faceted particles imply at least one low-energy  $ZrO_2/Al_2O_3$  interface.

## I. Introduction

ZIRCONIA-TOUGHENED alumina (ZTA) is the most important member of the wide class of  $ZrO_2$ -containing dispersion-toughened ceramics.<sup>1</sup> Such materials typically consist of modest amounts of  $ZrO_2$  (up to 30 vol%) dispersed in a fine-grained  $Al_2O_3$  matrix. The  $ZrO_2$  particles can have tetragonal (*t*) or monoclinic (*m*) symmetry, are incoherent with the  $Al_2O_3$  matrix, and can be either intergranular or intragranular (Fig. 1).

In the present paper, we will show high-resolution electron micrographs which provide information on the nature of the incoherent  $ZrO_2/Al_2O_3$  interfaces on an atomic level, particularly for intragranular  $ZrO_2$  particles. Intergranular  $ZrO_2/Al_2O_3$  interfaces appear to be wetted by an amorphous grain-boundary phase;<sup>2</sup> these interfaces have also been imaged by high-resolution electron microscopy (HREM), but these results will be reported elsewhere.<sup>3</sup>

## II. Experimental Procedure

ZTA samples containing 3.8, 10, and 15 vol%  $ZrO_2$  have been studied using HREM; the fabrication or provenance of the samples is described elsewhere.<sup>2</sup> All microscopy was performed in a transmission electron microscope\* dedicated to HREM and fitted with a top entry  $\pm 10^\circ$  tilting stage; the TEM pole piece has a *C*<sub>s</sub> (spherical aberration constant) of 1.1 mm. This microscope routinely provides point-to-point resolution down to 0.236 nm.

Thin-foil HREM samples were prepared by ion beam thinning

using conventional means, except that the thinned foils were annealed at 1200°C for 15 min before HREM examination. This annealing induced the (reverse) *m*  $\rightarrow$  *t* transformation in particles in which the (forward) *t*  $\rightarrow$  *m* transformation had occurred during foil preparation, a common occurrence in ZTA. (A preliminary report showing micrographs of an *m*- $ZrO_2/Al_2O_3$  interface, in which such a *t*  $\rightarrow$  *m* transformation had occurred in an intragranular  $ZrO_2$  particle during thin-foil preparation, has been published elsewhere.<sup>4</sup>)

Before describing our results, we note that imaging conditions for HREM are very stringent. Firstly, the foil must be very thin,  $\leq 20$  to 30 nm. Secondly, both the  $ZrO_2$  particle and the  $Al_2O_3$  matrix have to be oriented such that a low index zone axis for both phases is exactly (or nearly) parallel to the electron beam. Because the  $ZrO_2$  particles in these dispersion-toughened ceramics are randomly oriented with respect to their  $Al_2O_3$  matrices, this requirement is very difficult to satisfy, particularly as the interface itself should also be parallel to the electron beam. Of the more than 100  $ZrO_2$  particles examined to date, only a handful satisfied these difficult constraints. In this paper, we report images of two intragranular  $ZrO_2/Al_2O_3$  interfaces from which useful structural information can be obtained.

Thirdly, it is customary to take a through-focus series of images at various amounts of defocus, as the optimum defocus to achieve maximum structural information in the final image (the so-called Scherzer defocus) is difficult to know *a priori*.<sup>5</sup> Finally, unambiguous image interpretation requires exact image matching between computed (simulated) and experimental images, starting with assumed structural models and known microscope parameters (amount of defocus, *C*<sub>s</sub>, etc.). While acceptable image matching for defect-free  $ZrO_2$  or  $Al_2O_3$  is straightforward (we have used both Skarnulis' CELLS program<sup>6</sup> and O'Keefe's SHRLI program<sup>7</sup> for this), modeling of the interface is much more difficult; this topic is currently a subject of much attention in our group. Because of the lack of computed interface images, our conclusions about interface structure must be considered tentative at this time.

## III. Results and Discussion

Two  $ZrO_2$  intragranular particles, one nearly spherical and one faceted, that satisfied the stringent HREM requirements are shown in Figs. 2(A) and (B), respectively. We discuss the spherical particle first.

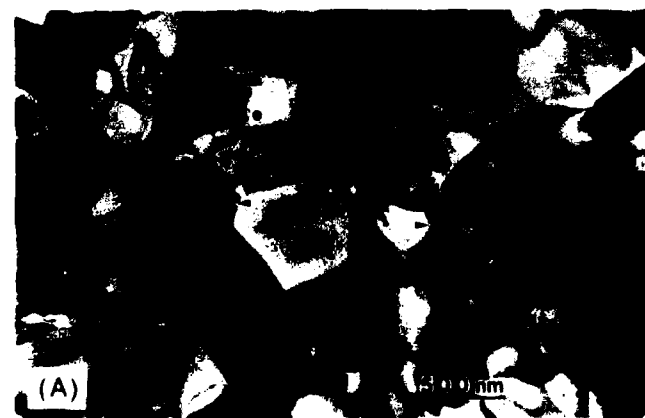


Fig. 1. Typical microstructure of  $ZrO_2$ -toughened  $Al_2O_3$  showing (A) intergranular and (B) intragranular  $ZrO_2$  particles; a few particles are arrowed.

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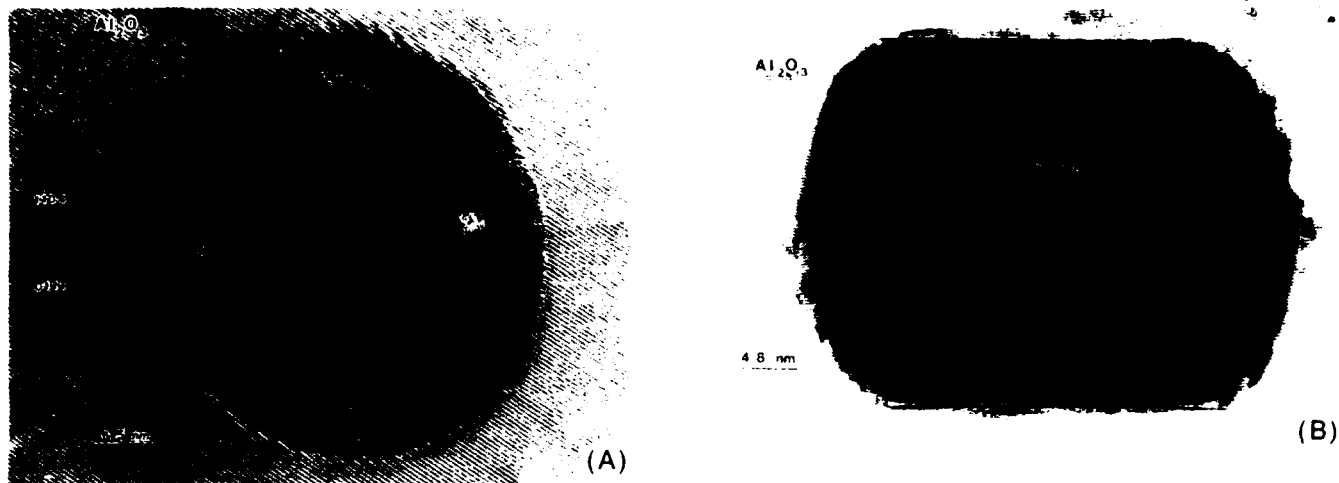


Fig. 2. (A) Intragranular  $ZrO_2$  particle; a single set of (111) planes is visible in  $ZrO_2$ , while  $Al_2O_3$  matrix is exactly oriented to  $[3\bar{1}2\bar{1}]$  zone. (B) Faceted  $ZrO_2$  particle in  $Al_2O_3$  matrix, which is oriented exactly to  $[10\bar{1}0]$  zone; note Moire fringes in  $ZrO_2$  particle.

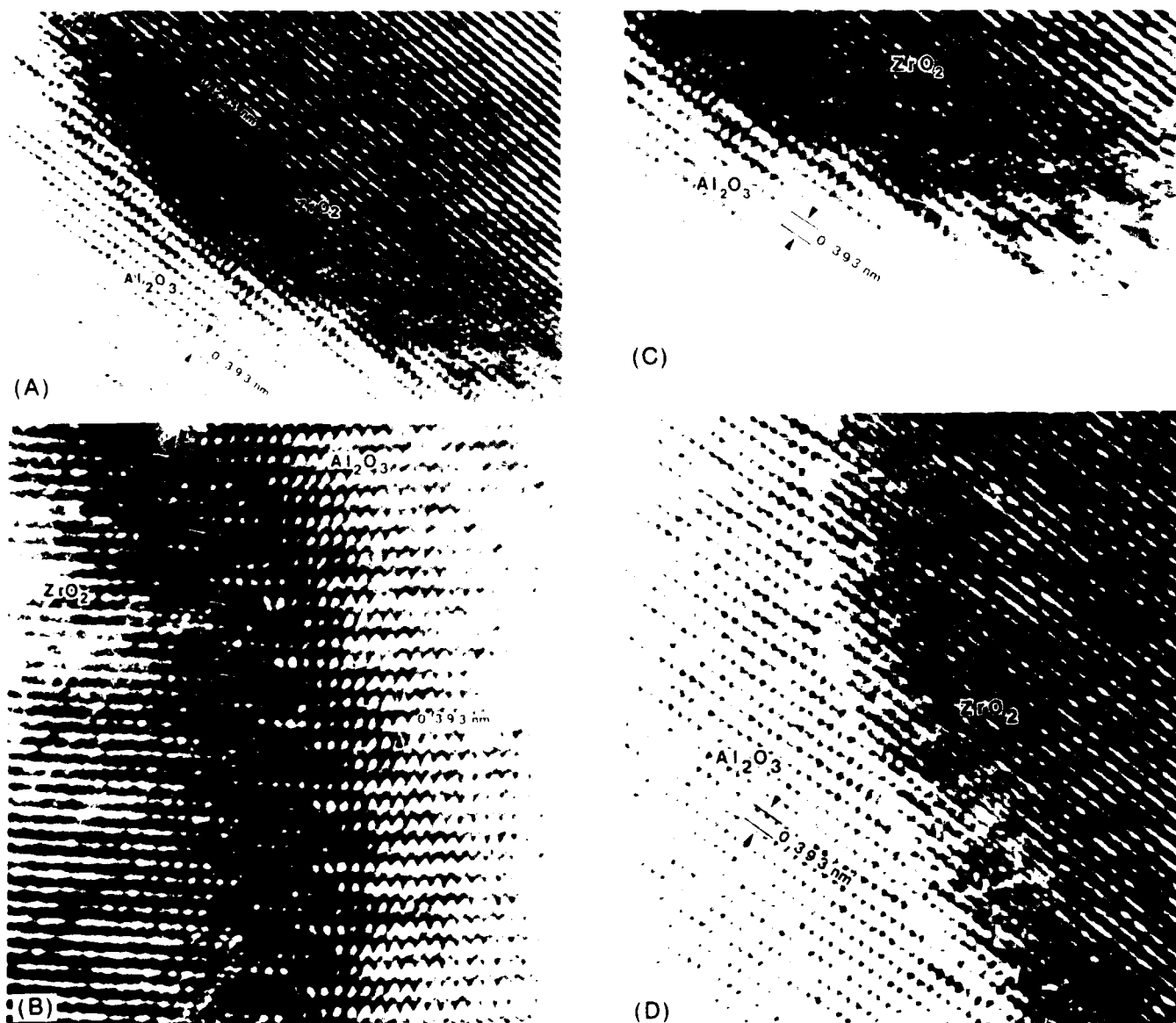


Fig. 3. Higher magnifications of various areas of Fig. 2(A). (A) Lattice mismatch accommodated by a series of ledges. (B) Periodicity changes along interface from every fourth  $Al_2O_3$  plane stopping short of interface (arrowed) to every third one. (C) Lattice mismatch accommodated by misfit dislocations. (D) Interface which appears smooth; sighting along atomic planes reveals misfit dislocations.

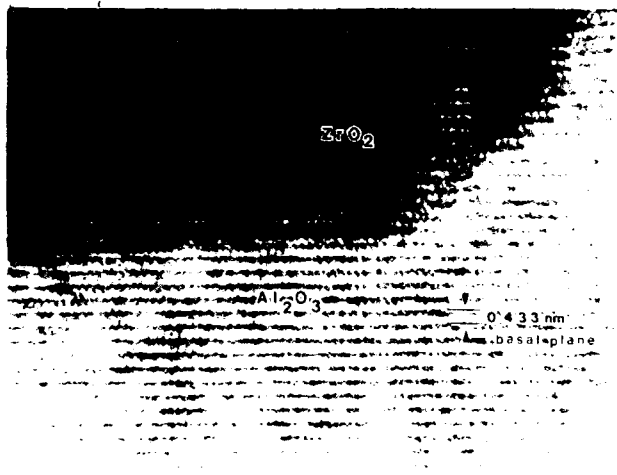


Fig. 4. Higher magnification of Fig. 2(B);  $\text{Al}_2\text{O}_3$  basal plane ( $d$  spacing of 0.433 nm) is parallel to  $\text{ZrO}_2$  facet.

As seen in the low-magnification micrograph of Fig. 2(A), the  $\text{Al}_2\text{O}_3$  matrix is oriented exactly to the  $[3\bar{1}21]$  zone axis and  $(0\bar{1}11)$  and  $(1\bar{1}0\bar{4})$  planes can be discerned. On the other hand, the  $\text{ZrO}_2$  particle, which has  $t$  symmetry, has only a single set of  $(111)$  planes visible, as the closest zone axis  $([110])$  is tilted by a few degrees to the electron beam. The  $(111)$   $\text{ZrO}_2$  planes are misoriented by  $\approx 5^\circ$  from the  $(0\bar{1}11)$   $\text{Al}_2\text{O}_3$  planes; furthermore, the  $d$  spacings for these two sets of planes differ significantly, 0.295 nm for  $(111)$   $\text{ZrO}_2$  and 0.393 nm for  $(0\bar{1}11)$   $\text{Al}_2\text{O}_3$ . In spite of this marked lattice mismatch, no microcracks or other gross distortions appear in the HREM image of the interface.

Various regions of the  $\text{ZrO}_2/\text{Al}_2\text{O}_3$  interface are shown at higher magnification in Fig. 3. In the region shown in Fig. 3(A), the lattice mismatch between the two phases appears to be accommodated by a series of ledges, each one atomic plane high; such ledges are commonplace in semicoherent interfaces, as can occur between a precipitate and its matrix, but it is somewhat surprising to see them in the incoherent interface in Fig. 3(A).

$\text{Al}_2\text{O}_3$  and  $t\text{-ZrO}_2$  have significantly different thermal expansion coefficients ( $7 \times 10^{-6}$  to  $8 \times 10^{-6}$  and  $9 \times 10^{-6}$  to  $11 \times 10^{-6}$   $^\circ\text{C}^{-1}$ , respectively, depending on orientation), and thermoelastic strains between 0.2% and 0.4% are expected, assuming the system was stress free during sintering and stress relief mechanisms are inoperable below  $\approx 1000^\circ\text{C}$ . (Thermal strains of this order have been detected by Rühle and Kriven<sup>5</sup> using HVEM techniques.)

Evidence for such strain is also available in the image of Fig. 3(A). As noted above, the  $t\text{-ZrO}_2$  is tilted  $\approx 2^\circ$  off its  $[110]$  zone axis such that only one set of  $(111)$  planes is being imaged. Near the interface, however, one set of  $(222)$  planes, with half the spacing of the  $(111)$  set, is visible, as well as an apparent structure image. We believe that the lattice bending due to these thermal expansion mismatch strains has tilted the lattice toward the  $[110]$  zone axis so that the  $(222)$  planes are apparent, but computer simulation is necessary to confirm this interpretation.

Figure 3(B) shows another region of the  $\text{ZrO}_2/\text{Al}_2\text{O}_3$  interface, which accommodates the lattice mismatch without any apparent use of ledges. This region of the interface exhibits a type of periodic quasi-fringe contrast in the low-magnification image of Fig. 2(A). At higher magnification this periodic contrast (at the top of Fig. 3(B)) is seen to be due to every fourth  $\text{Al}_2\text{O}_3$  plane (arrowed) extending less far into the interface than its neighboring planes. As

the interface orientation changes, so does the period of the interface structure, so that near the center of Fig. 3(B), it is every third  $\text{Al}_2\text{O}_3$  plane which stops short of the interface.

This periodic contrast has some similarities to misfit dislocations which can also exist in semicoherent interfaces to accommodate lattice mismatch; this type of mismatch accommodation is certainly in evidence in the region of interface shown in Fig. 3(C), although there are also ledge-like regions in conjunction with the dislocation-like regions in this micrograph. Finally, Fig. 3(D) shows a region of the interface which is apparently smooth and free of ledges; however, viewing along the planes of the images reveals the presence of periodic misfit dislocations. It appears that for this incoherent  $\text{ZrO}_2/\text{Al}_2\text{O}_3$  interface, the lattice mismatch is accommodated by a combination of ledges and misfit dislocations, depending on interface orientation.

A higher-magnification image of the faceted interface of Fig. 2(B) is shown in Fig. 4. As noted in this figure, the facet plane is parallel to the basal plane of  $\text{Al}_2\text{O}_3$  and this orientation of  $\text{ZrO}_2/\text{Al}_2\text{O}_3$  interface must have a lower interfacial energy than any of the interface orientations of Fig. 3. Unfortunately, as will now be discussed, we have been unable so far to specify the  $\text{ZrO}_2$  orientation that leads to this low-energy interface.

It is common in HREM to determine the crystal orientation of the material under study by taking an optical diffraction pattern of the image, using a laser diffractometer; and the crystal orientations shown in Fig. 3 were determined in this way. The Moiré fringes visible in Fig. 4 indicate that this is not possible with this image; in spite of the fact that this region of foil appeared to be quite thin ( $\approx 20$  nm), the  $\text{ZrO}_2$  particle apparently does not go through the foil and must be overlaid with some of the  $\text{Al}_2\text{O}_3$  matrix. In fact, this suggests the existence of still another low-energy faceted  $\text{ZrO}_2/\text{Al}_2\text{O}_3$  interface, in this case parallel to the  $(10\bar{1}0)$  foil plane of Fig. 4. We are presently seeking other examples of faceted  $\text{ZrO}_2/\text{Al}_2\text{O}_3$  interfaces in which the  $\text{ZrO}_2$  extends through both the top and bottom of the foil so that the interface orientation can be specified exactly.

#### IV. Conclusion

HREM can be used to image incoherent  $\text{ZrO}_2/\text{Al}_2\text{O}_3$  interfaces in ZTA. Both spherical and faceted  $\text{ZrO}_2$  particles occur in ZTA; in the spherical particles, the mechanism of lattice accommodation of the two phases is a combination of ledges and misfit dislocations which depends on interface orientation.

The occurrence of faceted particles implies the existence of low-energy  $\text{ZrO}_2/\text{Al}_2\text{O}_3$  interfaces. Although we are not yet able to specify the  $\text{ZrO}_2$  orientation that leads to the low-energy interfaces, both basal  $(0001)$  and prism plane  $\{11\bar{2}0\}$   $\text{Al}_2\text{O}_3$  orientations appear to be present.

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