Letters

*Growth-Related Surface Features on BeO Crystals Revealed by Electron Microscopy**

Surface features on crystal faces are often key factors leading to a better understanding of the pertinent growth mechanisms [1]. Results reported in previous papers [2-4] on twinned BeO crystals indicated that prismatic and pyramidal crystals grow with an axial screw dislocation, surrounded by a core of one polarity, enclosed in a sheath of opposite polarity. A very small projecting cone on the (0 0.1) face of the inner twin surrounds the point of emergence of each screw dislocation in the core and is believed to be the source of layer generation on this surface. The emergence of the twin core creates a re-entrant edge which is also a site for easy nucleation of growth layers. The fact, that the core and the surrounding crystal continue to propagate in the same growth direction at the same rate, indicates that communication occurs between layers generated from nucleation events at the TBRE (twin boundary re-entrant edge) and at the screw dislocation source on the singular (0 0.1) surface.

Currently, the evidence supporting a layer mechanism of growth is somewhat indirect. Considerable understanding of the important details of this growth mechanism could be obtained by observing directly the topography of the layer sources and the structure of the active sites for BeO molecular attachment (kinks, ledges, or other surface features which contribute to roughness at layer edges). This note reports a study of these surface features with the high-resolution capabilities of the electron microscope.

The twinned beryllium oxide crystals used were grown from molten lithium molybdate by the temperature-gradient technique [5, 6]. The crystals were mounted in special holders to expose the active-growth end and were replicated by one- and two-stage techniques. Crystals to be examined by reflection electron microscopy [7] were prepared by slicing thin wafers perpendicular to the *c* axis including the growing end of the crystal.

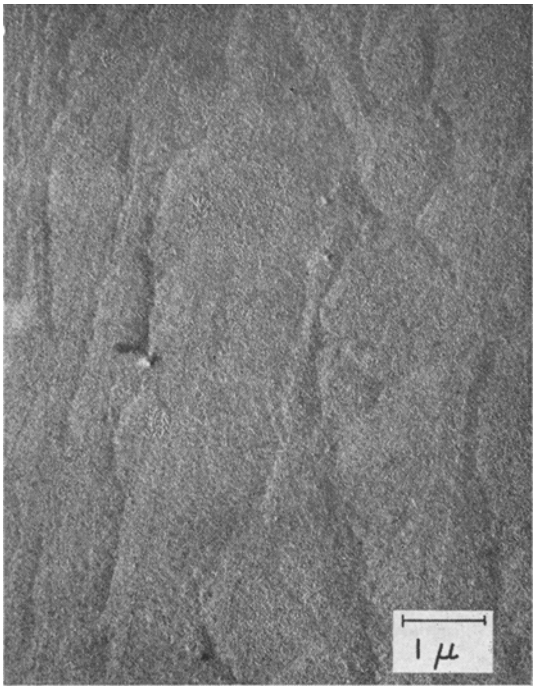

Figure 1 Electron micrograph of a portion of the replicated (0 0.1) surface.

Fig. 1 shows an electron micrograph of a typical (0 0.1) BeO crystal surface. Projecting cones do rise out of the surface but are very shallow. The slope angle is calculated to be as low as 2 min of arc. Growth steps, if they do emerge from a cone around the screw dislocation source, appear to be beyond the resolution of the replica technique, 250 Å. Fig. 2 is an electron micrograph showing selected portions of the replica near the twin boundary. This irregular, or serrated, twin boundary consists of a complexity of small, alternating, adjacent crystallographic facets of unknown orientation. Note the smoothness of the (0 0.1) face relative to the convoluted vicinal $(0\,0.\bar{1})$ surface. The vicinal surface appears to be highly convoluted near the twin boundary where the lateral motion and "traffic" of growth steps is greatest. Farther from the boundary, convolutions become more widely spaced as growth fronts annihilate and reinforce one another to produce a stable surface configuration.

Fig. 3 shows a reflection micrograph of a

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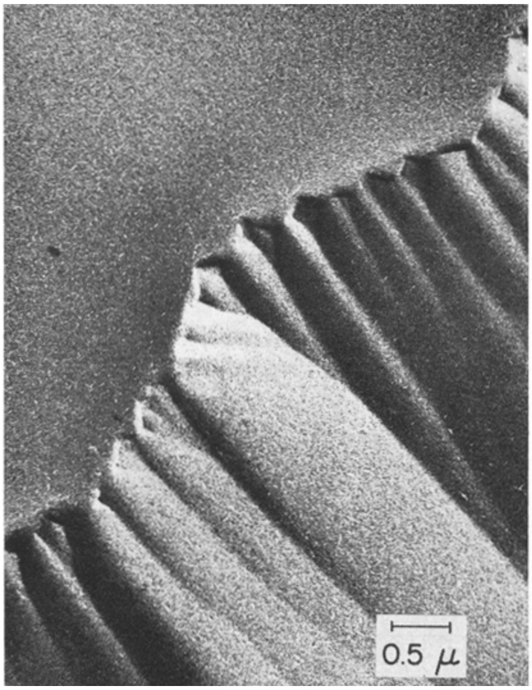

Figure 2 Electron micrograph of detailed multifaceted structure of the twin boundary on a replicated BeO crystal.

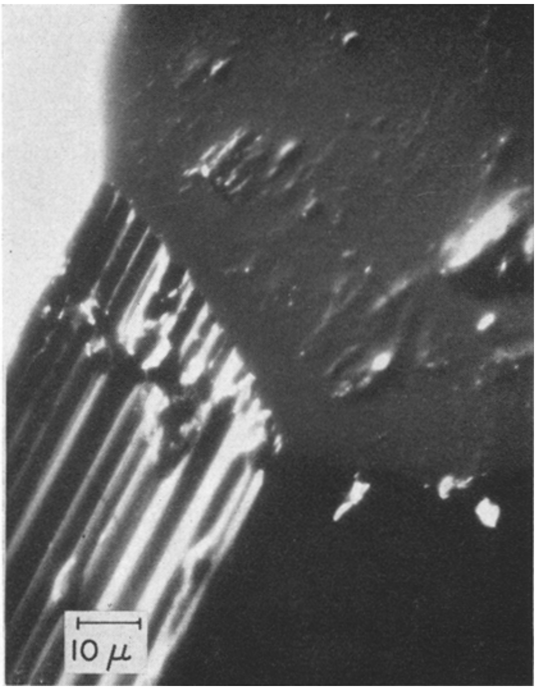

Figure 3 Reflection electron micrograph of surface features present at the twin boundary of a BeO crystal.

portion of this same crystal, also near the twin boundary. The serrated boundary is evident and the convoluted structure of the vicinal $(0\,0.\bar{1})$ surface is clear. The faceting at the twin-boundary interface is apparent but not as obvious as in the replicas. Other details are below the limit of resolution of the technique, 250 Å. (The diffuse circle in the centre of each micrograph is attributed to a diffraction phenomenon.) The other features visible in micrographs are dust particles on the surface, which were very difficult to prevent.

Thus, the micrographs yield little new information regarding the possible existence of growth steps on the imperfect singular (0 0.1) face. Either the shallow, projecting cones are not the sources of growth layers or the steps are in small multiples of the unit cell height, 4.3772 Å, and thus are below the limit of resolution of the techniques employed. The latter possibility is considered the more likely.

Perhaps the most positive result obtained and the most unusual feature observed is the multifaceted structure of the twin boundary. This non-equilibrium structure suggests three implications which may be important to mechanisms of growth. One, the twin boundary has a much lower boundary energy and a much larger number of re-entrant sites available for BeO molecular attachment than heretofore realised. Two, the growth kinetics at this site are highly anisotropic and consistent with the basic requirements for extended TBRE growth as given by John and Faust [8]. Three, the departure of the interface from its equilibrium morphology may be the macroscopic consequence of a large driving force perpendicular to the facets. Tarshis and O'Hara [9] have shown that such driving forces are orders-of-magnitude larger than that required for layer edge passage and are necessary to drive the layer generation process efficiently. This is further evidence for believing that growth is controlled by the kinetics of interface attachment.

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Discussion on the Letter "Grain Boundary 'Pest' in the Intermetallic Compound NiAl" by P. A. Turner, R. T. Pascoe, and C. W. A. Newey (J. Matls. Sci. 1 *(1966) 113)*

The present authors published the results of an investigation [1] on oxygen-induced grain-boundary hardening in NiAl in 1965. It was shown in this work, as in the case of NiGa [2] quoted by Turner *et al*, that grain-boundary hardening occurred both at a free surface and at grain boundaries. The hardening observed by Turner *et al* in the 54 at. % alloy, and attributed by them to the result of stresses caused by the oxidation of Al_2O to Al_2O_3, apparently was observed only at grain boundaries and not at the surface of the sample. While we do not claim that the mechanism suggested by Turner *et al* cannot occur, in our studies [1] of alloys containing up to 51.3 at. % Al we have seen no convincing evidence of the type shown in their micrographs. On the contrary, we have looked very carefully for evidence of grain-boundary precipitates, and have never observed any phase which could be related to the occurrence of grain-boundary hardening or embrittlement. Our experiments included electron microscopy by replica and by transmission. The hypothesis of grain-boundary splitting or opening followed by a progressive oxygen penetration would require microscopic evidence of such grain-boundary parting, along with the continual presence of the oxidised particles; this simply was not observed in our work. It may be that the difference in composition, 51.3 versus 54 at. % Al, is responsible.

In any case, the equivalence of bulk hardening at a free surface and grain-boundary hardening in the precipitate-free, less aluminium-rich alloys forces one to look elsewhere for an explanation for the oxygen embrittlement in our alloys. The mechanism of oxygen-atom-vacancy interaction, which deposits vacancies either at a free surface or at a grain boundary but then leaves the oxygen atom stranded nearby, appears to explain all of the observed phenomena as outlined by Seybolt, Westbrook, and Turnbull [3]. Finally, it might be pointed out that, if the authors' proposed Al_2O to Al_2O_3 transformation does occur under some circumstances, it would bring about a local impoverishment in dissolved oxygen near the precipitation site, e.g. the grain boundary, and hence soften that region via the Seybolt, Westbrook, and Turnbull mechanism. This would seem to be a more tenable explanation for the softening observed by Turner *et al* concomitant with transformation of their precipitate than an implied difference in the hardening between Al_2O and Al_2O_3 dispersions.