Grain Size Refinement and Surface Modification of Bulk Polycrystalline Y_2O_3

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Abstract: Yttrium oxide (Y_2O_3) displays excellent optical transmittance in the mid-IR range [1]; hence it has become a potential replacement for sapphire in some applications. However, there is a need to increase the hardness of Y_2O_3 without comprising optical transmittance. This should be possible by reducing the grain size of the material to nanoscale dimensions, which may also enhance fracture toughness [2]. In this research, a reversible phase transformation (RPT) process is described to convert fully dense polycrystalline Y_2O_3 *directly* into the nanocrystalline state. It involves a forward transformation from cubic-to-monoclinic under a high pressure and a backward transformation from monoclinic-to-cubic under a lower pressure. In addition, a surface-localized columnar grain structure is observed when the material is subjected to high pressure for a relatively long time.

Disc-shaped samples (4 x 4 mm) of coarse-grained (~300 µm) polycrystalline Y_2O_3 prepared by sinter-HIP of powder compacts were obtained from Raytheon. The samples were subjected to various high pressure-high temperature (HPHT) treatments using a laboratory-scale high pressure cell of novel design **[3].** When processed at 1000ºC/8GPa/15 minutes, the initial coarse-grained polycrystalline Y_2O_3 invariably experienced a cubic-to-monoclinic phase transformation, accompanied by a significant reduction in grain size (300 to <100nm), **Fig. 1,** and ~6% decrease in volume. Moreover, when the pressure is relaxed to 1.0 GPa at the same temperature, a transformation back to cubic occurs, yielding a final grain size of <100 nm and accompanied with ~6% increase in volume. In addition, both transformations gave an increase in hardness relative to that of the un processed sample (35% forward and 15% backward). This is indicative of a trend perhaps obeying the familiar Hall-Petch relationship. TEM analysis, **Fig. 1 (b)**, confirms the presence of randomly oriented c-Y_2O_3 nanograins with grain size <100 nm.

A columnar-grained structure covering the entire sample surface to a depth of ~20 µm was observed when the sample was held for >240 min, **Fig. 2**. TEM observation combined with FFT analysis, **Fig. 2**, indicate that the columnar grains have cubic symmetry, as indicated by the (211) reflection planes, while the underlying material consists of fully-transformed m-Y_2O_3, with grain size <100 nm, as can be seen from dark field image.

EDS analysis of a fractured surface of the columnar grained structure shows that the Y/O intensity ratio for a smooth intergranular fracture is depleted in oxygen relative to that of a rough transgranular fracture. Hence, grain boundaries in c-Y_2O_3 appear to be susceptible to oxygen depletion relative to grain interiors, apparently due to reaction with the graphite heater. Hence, progressive reductive decomposition of the sample surface would account for the appearance of the oxygen-deficient columnar-grained structure, with relatively fast oxygen-ion diffusion occurring along the directionally-aligned grain boundaries. This probably also explains the significant difference in hardness between surface layer and sample interior (0.7±0.12 GPa vs 7.7±0.3 GP) due to a reduction in the number of strong Y-O bonds per unit volume.

Acknowledgements

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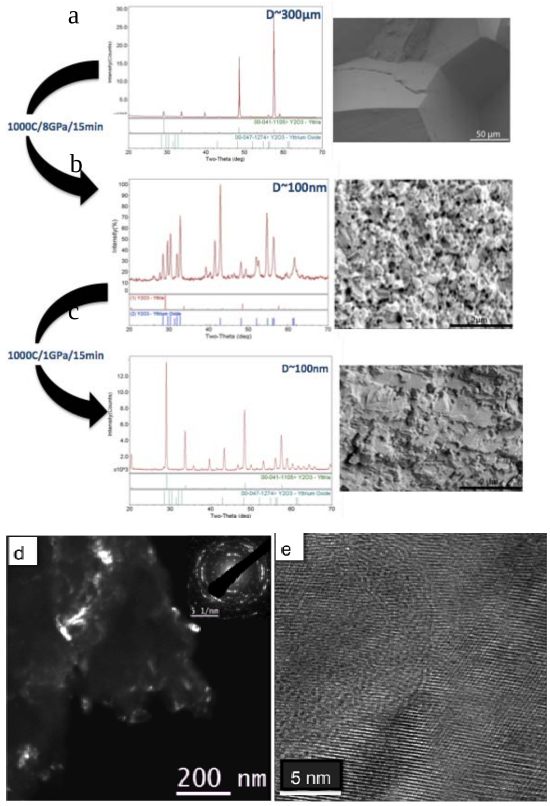

Fig.1(a-c) -XRD spectra along with their corresponding SEM micrographs showing a significant reduction in grain size (300 µm to 0.1 µm) for c-Y_2O_3. Fig.1(d-e) - Dark-field image (d) and high resolution lattice image (e) of nanograined c-Y_2O_3, after backward phase transformation at 1000°C/1GPa/15min. The inset in (d) is a diffraction pattern of the imaged region.

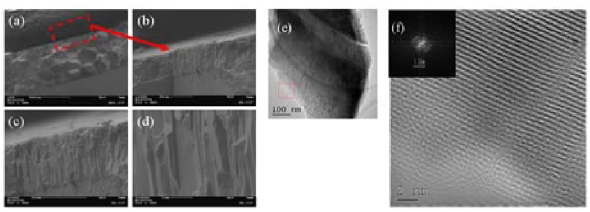

Fig. 2 - SEM (a-d) and TEM (e-f) micrographs of surface columnar grained structure. The inset in (f) is FFT of the HRTEM lattice image.