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SYNTHESIS AND PROPERTIES OF ERBIUM OXIDE SINGLE CRYSTALS

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ABSTRACT

Erbium oxide (Er_2O_3, erbia) is a highly stable cubic rare earth oxide with a high melting point of 2430 °C. Because of this, it may have potential applications where high temperature stability and corrosion resistance are required. However, relatively little is known about the properties of this oxide ceramic. We have employed a xenon optical floating zone unit with a temperature capability of 3000 °C to grow high quality single crystals of erbia. The conditions for single crystal growth of erbia have been established. The mechanical properties of erbia single crystals have been initially examined using microhardness indentation as a function of temperature.

INTRODUCTION

The rare earth oxides Er_2O_3, Y_2O_3, and Sc_2O_3 have the lowest free energies of formation of any binary oxide ceramics (1,2). This means that they possess excellent high temperature stability and corrosion resistance, making them candidate materials for potential elevated temperature applications requiring these characteristics, such as fixturing which must be immersed in molten metals. These oxides have high melting points, possess a cubic crystal structure, and exhibit complete solid solubility with each other.

Over the past few years we have been focusing on the study of Er_2O_3 (3,4). The purpose of the present investigation was to grow high quality single crystals of erbium oxide and to initially investigate the mechanical properties of these erbia single crystals.

MATERIALS AND PROCEDURE

Single Crystal Growth

The high melting point of erbia, 2430 °C, makes the synthesis of single crystals relatively difficult. However, high quality erbia single crystals can be produced using a xenon optical floating zone apparatus (3,4). The xenon optical floating zone unit is shown schematically (5) in Figure 1. It consists of a high power xenon lamp which is situated within an ellipsoidal mirror cavity. This allows the xenon lamp's optical power to be focused at a spot for the heating and growth of single crystals. Seed and feed rods are positioned vertically within a sealed quartz tube along a line containing the focal point, and can be translated vertically with respect to the focal point. These rods are also counter-rotated in order to increase stirring action and convective heat transfer. In operation, the counter-rotating seed and feed rod tips are located at the xenon lamp focal point, then the lamp power is gradually increased until the rod tips become molten. At this point, the rod tips are brought together, and a stable molten zone between them is established. Once this molten zone is stable, the rods are then translated vertically in tandem, so that the molten zone propagates along the rod length, thus producing a single crystal. This approach has the major advantage of being containerless, which is important due to the high melting temperatures required for erbia. Melting can also occur in controlled atmospheres, established within the quartz tube that contains the seed and feed rods.

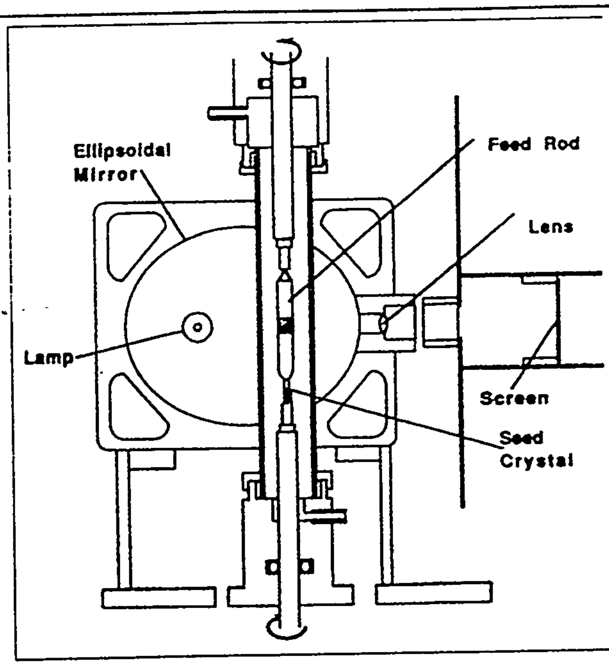

Figure 1: Schematic of xenon optical floating zone single crystal growth apparatus (5).

Erbia seed and feed rods were cold isostatically pressed from erbia powders (Rhone-Poulenc, 99.5% purity relative to rare earth elements). These rods were approximately 66 % dense. In previous work (4), it was determined that a reducing atmosphere of 94% Ar-6% H_2 at a slight overpressure of 76 KPa (11 psi) was effective in minimizing deleterious erbia "flaking" effects during melting in an air atmosphere, which complicated single crystal growth. This "flaking" may be due to vaporization and redeposition of erbium at the very high temperatures of erbia melting. A 94% Ar-6% H_2 atmosphere was employed for the present work.

Microhardness Testing

Erbia single crystals obtained using the xenon optical floating zone technique were studied using a Nikon QM-2 high temperature microhardness unit.

This unit has the capability to perform Vickers microhardness indentations from room temperature to 1500 °C, using diamond or sapphire indenters in a vacuum environment. Erbia single crystal specimens of suitable size (5 mm x 5 mm x 10 mm) were oriented crystallographically using Laue x-ray back reflection techniques, and then prepared using a slow speed diamond saw. The face of the specimen to be indented was polished down to a 0.25 μm diamond finish.

Using a 1000 gm load, Vickers indentations were made from room temperature to 1400 °C at 200 °C intervals, to characterize microhardness and indentation fracture toughness as a function of temperature. Indentation fracture toughness was calculated using the following relationship (6):

$$K_c = (0.016)\,(E/H)^{1/2}\,(P / c^{3/2}) \qquad (1)$$

where K_c = fracture toughness, E = elastic modulus, H = hardness, P = indentation load, and c = crack length. Polycrystalline values of the elastic modulus of erbia as a function of temperature were employed in the fracture toughness calculations (7).

RESULTS AND DISCUSSION

Er_2O_3 Single Crystals

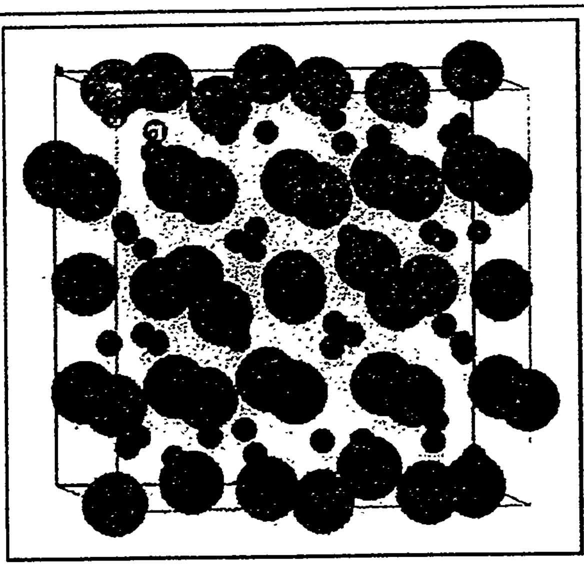

Figure 2: Unit cell of Er_2O_3. Large atoms are Er. Small atoms are O.

The crystal structure of erbium oxide (Er_2O_3) is body centered cubic (bcc), with a lattice parameter of 10.55 angstroms (8). The unit cell, shown in Figure 2, contains 80 atoms, 32 erbium atoms and 48 oxygen atoms. This crystal structure is essentially a modified fluorite structure, with one-fourth of the fluorite oxygen sites vacant.

Single Crystal Growth

The use of an Ar/H_2 atmosphere during crystal growth significantly reduced the deleterious "flaking" effects. However, it also caused the erbia melt to become more opaque to the xenon radiation. This in turn caused the melt to absorb more radiation at the surface and severely limit the amount of light radiation transmitted to the center, which caused both the molten and solidification interfaces to become more conical. During crystal growth, these cones would come into contact with each other and produce mechanical instabilities within the melt.

The instabilities resulting from feed rod/seed rod conical contacts were minimized using a combination of high counter-rotation rate, lamp power setting, and crystal growth rate. Conditions for the synthesis of erbia single crystals using 6.2 mm diameter seed and feed rods were established at a 55 rpm counter-rotation speed, power setting of 2.86 kW which produced a ratio of molten zone neck diameter to zone length of 0.4-0.8, and a growth rate of at least 20 mm/hour. Surface cracks which penetrated approximately 0.5-1.0 mm from the rod surface towards the center were observed. However, below this surface crack level, the erbia single crystal was sound and of high quality. An example of the best erbia single crystal produced to date is shown in Figure 3. The diameter is approximately 5 mm, while the length is 70 mm. Pronounced growth striations can be seen on the crystal surface. The preferred growth direction using polycrystalline erbia powder seed and feed rods was <111>.

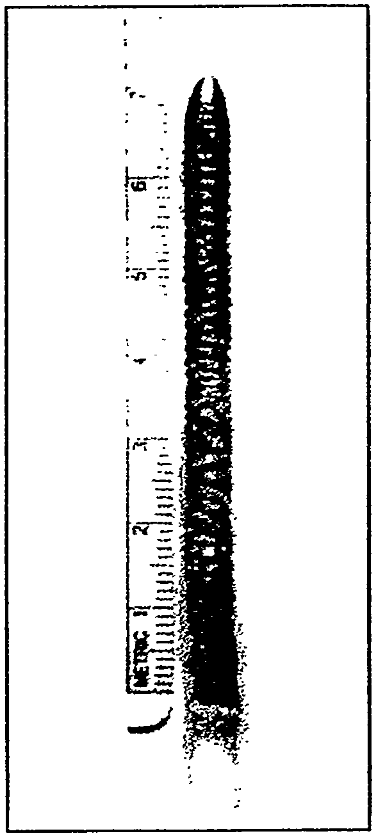

Figure 3: Er_2O_3 single crystal.

During crystal growth experiments, it was observed that the erbia turned from pink to black in color when melted in the reducing Ar/H_2 environment. The material had remained pink when melted in an air environment. This suggests that Er_2O_3 is susceptible to substoichiometry effects when heated at elevated temperatures. Limited work in the literature confirms that erbia becomes substoichiometric to a level of $Er_2O_{2.978}$ when melted in a vacuum or reducing environment (9). It was observed that the heating of black erbia in air at 1600 °C for a few hours caused the erbia to return to its original pink color. This strongly indicates that the substoichiometry effects are due to the loss of oxygen (9).

Indentation versus Temperature

Two erbia single crystal specimens were tested as a function of temperature using the Nikon QM-2 high temperature microhardness tester. These two specimens were synthesized according to the erbia single crystal growth conditions described in this paper, and were from the same single crystal growth run. Specimen ET-98-11-2 was in the as-synthesized condition, and was black in color, indicating that it was substoichiometric. Specimen ET-98-11-1 was heat treated at 1600 °C for 4.5 hours in air following single crystal synthesis, and was pink in color, indicating that it was more stoichiometric. The indentation plane of these specimens was {110}, with the perpendicular side faces oriented on {111} and {112} faces.

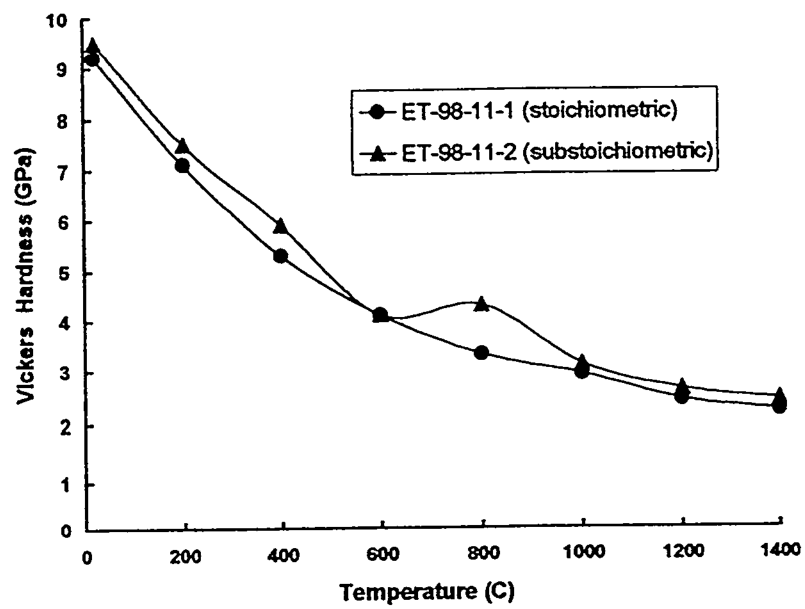

Figure 4: Er_2O_3 single crystal microhardness versus temperature. Average standard deviation is 0.35 GPa.

Vickers microhardness (1000 gm load) data as a function of temperature are shown in Figure 4. Microhardness generally decreased with increasing temperature, by roughly a factor of three between room temperature and 1400 °C. Stoichiometry appeared to have little effect on hardness.

Figure 5 shows indentation fracture toughness as a function of temperature. Room temperature fracture toughness levels were in the range of 1.8-2.5 MPa $m^{1/2}$. Fracture toughness values of stoichiometric and substoichiometric Er_2O_3 were similar as a function of temperature. Toughness

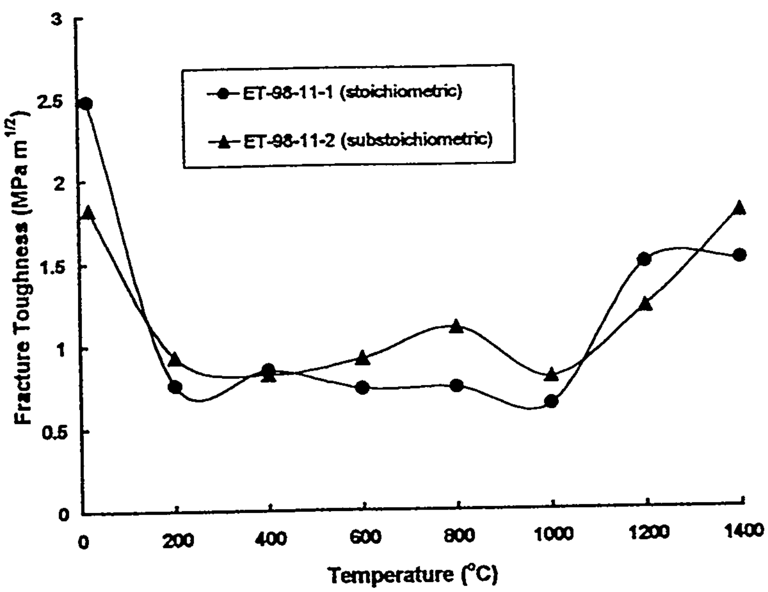

Figure 5: Er_2O_3 single crystal indentation fracture toughness versus temperature. Average standard deviation is 0.23 MPa $m^{1/2}$.

values decreased to less than 1 MPa $m^{1/2}$ in the temperature range of 200-1000 °C, then increased above 1000 °C. The increase in fracture toughness above 1000 °C is likely due to the onset of plastic deformation processes. However, the reasons for the reduction in toughness between room temperature and 200 °C are unclear at the present time.

CONCLUSIONS

High quality Er_2O_3 single crystals were grown using a xenon optical floating zone single crystal growth apparatus. Erbia single crystal growth occurred in an Ar/H_2 atmosphere, at growth rates of 20 mm/hour or greater, and at power levels that maintain a molten zone neck diameter/neck length ratio of 0.4-0.8. As-synthesized erbia single crystals were black in color, as a result of substoichiometry produced by melting in a reducing atmosphere, due to loss of oxygen. Annealing the black crystals at 1600 °C in air returned them to a stoichiometric state and pink color.

The hardness of erbia single crystals decreased by approximately a factor of three from room temperature to 1400 °C. Room temperature hardness was in the range of 9 Gpa. Stoichiometry level had little effect on hardness. Room temperature fracture toughness values were in the range of 1.8-2.5 MPa $m^{1/2}$. Toughness values decreased to less than 1 MPa $m^{1/2}$ in the temperature range of 200-1000 °C, then increased above 1000 °C.

ACKNOWLEDGEMENTS

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