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Kinetics of grain growth in La-doped ultrapure Al_2O_3

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ABSTRACT

Kinetics of grain growth was measured in dense polycrystalline ultrapure alumina doped with 100 ppm of lanthanum. The evolution of grain size followed cubic kinetics, which can be attributed to the influence of solutes. Based on the increase of Gibbsian excess of segregating dopants with increase in the average grain size, it can be approximated that boundary velocity scales as inverse-square of grain size, leading to cubic grain growth kinetics. The activation energy of grain growth was found to be 418 ± 22 kJ mol^{-1} for La-doped alumina; comparable to that of undoped ultrapure alumina, and much lower than the activation energy of creep in La-doped alumina. The grain boundary mobility was found to be almost an order of magnitude lower than that of undoped ultrapure alumina, which can be attributed to the drag of oversized dopants segregated to the grain boundary core. These findings provide a basic understanding of the effects of segregating dopants on grain growth, and can be exploited in the production of coarsening resistant nanograined materials.

1. Introduction

A series of studies have established that trace amount of rare earth (RE) ions, including Y, La, and Nd, in polycrystalline alumina can reduce the creep strain rate by 2–3 orders of magnitude [1–3]. Metallic or oxide additions of Y, Zr, Hf, and La, in Al containing Ni, Fe, Pt based alloys have also shown improved oxidation resistance by suppressing growth of the thermally grown oxide (TGO) layer [4–6]. Due to the large ionic size of the dopant cations (La = 1.03 Å, Y = 0.89 Å) and the resulting strain energy, the solubility of the RE ions in alumina lattice is very limited [7,8]. It is well established by experimental and theoretical investigations that the rare earth dopants segregate to alumina grain boundaries [9–13]. Similar segregation of the RE ions have also been found in the thermally grown oxide layers in the Al containing alloys as well. These segregated boundaries profoundly affect high temperature properties. Several studies on the transport kinetics have indicated that creep and densification in rare earth doped alumina are boundary diffusion controlled processes [14,15]. However, there has been little or no study on the kinetics of grain growth in the RE-doped alumina system. Grain growth is an important aspect of materials engineering as it affects physical properties including toughness, strength, and creep. Understanding the effect of various reactive elements in alumina is key to the control of the TGO layer in turbine blades, and for the production of high strength alumina structural ceramics. Grain growth studies can also aid the mechanistic understanding of the various atomic processes involved.

To nullify the effect of densification, grain growth can be studied in theoretically dense compacts with the following empirical relation:

$$G_t^n - G_0^n = Kt \tag{1}$$

where G_t is the average grain size of the material at time t for a particular temperature, G_0 is the grain size at time $t = 0$ at that temperature, n is the grain growth exponent, and K is the temperature dependent rate constant. In classical grain growth, the boundary velocity can be defined as the product of curvature induced drag force and the boundary mobility [16]. The analysis results parabolic grain growth kinetics with a growth exponent of 2. However, an exponent of 3 (cubic growth kinetics) or higher has generally been observed for impure or doped ceramic microstructures [15,17], which is explained as grain growth influenced by a solute cloud [18]. The activation energy for grain growth can be calculated from the following Arrhenius equation

$$K = K_0^{\frac{-Q_{gb}}{RT}} \tag{2}$$

where R is the universal gas constant, K_0 is a temperature

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independent frequency factor, T is the absolute temperature, and Q_{gb} is the activation energy of grain growth.

In the current study kinetic measurements on grain growth in La-doped fully dense single phase polycrystalline alumina have been performed. The observation of cubic grain growth kinetics has been discussed. Additionally, the activation energy of grain growth, and boundary mobility of La-doped alumina have been compared with those of undoped ultrapure alumina.

2. Experimental

It is very critical to fabricate dense ultrahigh purity alumina samples with controlled dopant addition. Care must be taken at every processing step to avoid contamination. Therefore, all of the powder processing steps were carried out inside a Class 1000 clean room. Acid washed polytetrafluoroethelyne (PTFE) labwares were used for the wet processing steps. The process is briefly described as follows. Ultra high purity alumina (AKP 53, Sumitomo chemicals, Japan) was dispersed with methanol (ACS electronic grade) to prepare a slurry. Lanthanum nitrate ($La(NO_3)_3 \cdot 9H_2O$) (99.999%, Alfa Aesar) was mixed with methanol to prepare a stock solutions of La ions. Calculated amount of the aliquot was added to the alumina slurry to make 100 ppm cationic ratio (La/Al) doping. The doped slurry was jar milled with high purity alumina balls (99.99%, Union Process, Akron, OH, USA) in acid washed Nalgene bottles overnight for a uniform mixing. The slurry was then dried on a hot plate under a heat lamp while homogenizing the slurry with a magnetic spin bar. The dried powder was calcined at 600 °C for 6 h to remove residual organics. The calcined powders were packed in a graphite die (HPD-2, Poco Graphite, Decature, TX, USA) and hot-pressed (Astro, Thermal Technologies, Santa Clara, CA, USA) at 1250 °C for 6 h with 50 MPa pressure. The density obtained were very high, in excess of 99.8%. In such samples, further accurate measurement of density by Archimedes methods is not useful. In addition, the microstructure of the specimens did not show any porosity in general, except for occasional trapped pores. The dense compact was cleaned, sliced by a diamond saw, cube sized pieces roughly measuring 5 mm a side were cut from the core of the pellet, and annealed at different temperatures from 1350 °C to 1550 °C for various times ranging from 0 to 48 h in air in a box furnace (CM Furnaces, NJ, USA) with $MoSi_2$ heating elements. To reduce contamination from the furnace and heating elements the sample was placed inside a double crucible assembly of high purity alumina (Coors Tech, Golden, CO, USA). Annealed samples were mounted and polished (Abrapol) using diamond media. The final surface was prepared with vibratory milling for 12 h. In total, annealing experiments at 5 different temperatures were carried out, with 6–7 time scales for each temperature. About 35 samples were annealed separately. Scanning electron microscope with a FEG source was used (JEOL 6300f) for imaging the annealed microstructures. Linear intercept method was used for calculating the average grain size. At least 800 grains were counted, whereas on area basis at least 2500 grains were counted for each specimen. A geometrical correction factor of 1.56 was applied to calculate the final average grain size. To calculate G_0 (cf. Eq. (1)), the samples were ramped to T, and cooled instantly without further annealing.

3. Results

The microstructure of La-doped alumina samples was essentially unimodal and equiaxed at the hot pressed stage with grain size in the range of 1–1.2 μm. A grain size distribution of the as-hot-pressed samples could not be unequivocally calculated since annealing of the polished specimens introduced additional thermal history. The micrographs of samples annealed at 1350 °C for 8, 12, and 16 h are presented in Fig. 1. One can observe the grains to be equiaxed, and that the distribution is unimodal, in congruence with results from the literature [1–3,9,14,20,21]. Thermal annealing did not change the grain size distribution and morphology of the specimens, only subtle change in the average grain size was observed. High temperatures annealing also did not change the overall morphology of the samples (they remained equiaxed) or the grain size distribution (unimodal). Fig. 2 exhibits representative micrographs of La-doped alumina samples annealed at 1400 °C for 8 h, and at 1500 °C for 8 h. Grain size distribution statistics of the micrographs in Fig. 2 are presented in Fig 3a and b, respectively. The unimodal distribution of grains is evident from the statistics. Thus the development of self-similar microstructure as per classical normal grain growth was observed for all of the samples. No abnormal or anisotropic grain growth was observed in the temperature/grain size range studied.

The grain size evolution for the doped alumina samples exhibited some interesting trends. Based on the classical theory of parabolic kinetics the grain size data was treated with grain growth exponent of 2 (n = 2 in Eq. (1)). The regression coefficients (R^2 values) varied in the range of 0.915–0.958. The regression coefficients for $n = 3$ were in the range of 0.977–0.992 over the studied temperature range, thus indicating cubic kinetics (cf. Fig. 4). While the concept of parabolic growth kinetics is associated with curvature driven boundary migration, the agreement with cubic kinetics indicates that the boundary is dragged by the segregated dopants. The rate constant fits for cubic kinetics at various temperatures are presented in Fig. 4. The activation energy of grain

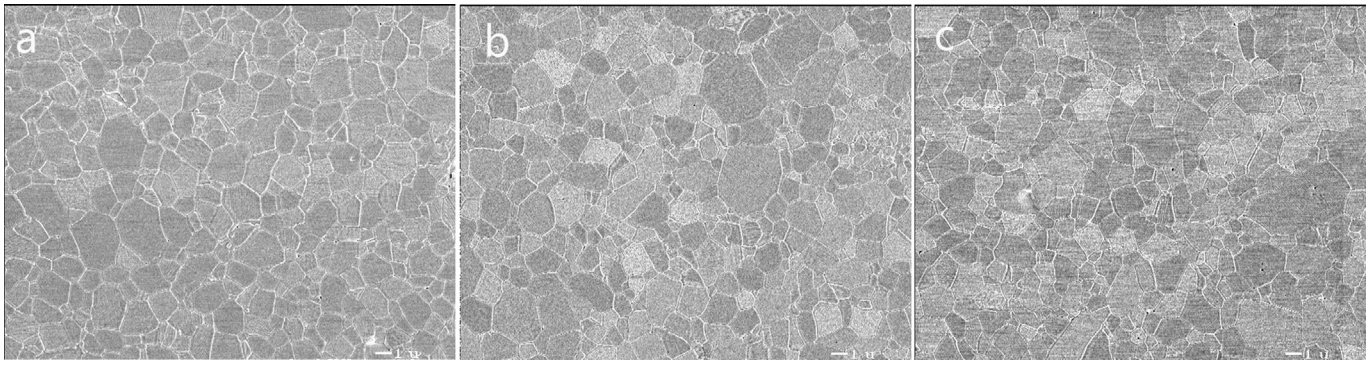

Fig. 1. Normal grain growth in La-doped alumina; Scanning electron micrographs of samples annealed at 1350 °C for (a) 8 h, (b) 12 h, and (c) 16 h.