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Grain boundary complexion and transparent polycrystalline alumina from an atomistic simulation perspective

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ABSTRACT

Transparent alumina is often processed with sintering additives such as, Y, La, and Mg, in order to limit its grain growth at high sintering temperatures. Usually, these additives segregate to the grain boundaries due to their larger cationic size than Al and low solubility in bulk α-alumina. The grain boundary excess of these additives plays a key role in determining stable grain boundary complexions and thereby, the grain growth characteristics of the polycrystalline alumina. In the current work, the grain boundary segregation of trivalent (Y, La) as well as bivalent (Mg) dopants on several alumina grain boundaries was simulated using the force field based energy minimization method. Calculated segregation energy plots and atomistic structure analysis, for the case of trivalent dopants, suggest that there is a critical concentration (3–4 atoms/nm^2) for achieving the lowest mobility monolayer grain boundary complexion. The bivalent dopant Mg plays a role in grain boundary complexion through creating ordered arrays of oxygen vacancies at the grain boundary and helps create the space for the easier occupation of the grain boundary cationic sites by the trivalent dopants in case of codoping. It was also observed that the twin grain boundaries are more preferable in comparison to general high angle grain boundaries to obtain monolayer complexions, which are necessary for limiting grain growth. The use of atomistic simulations can thus guide the experimentalist towards optimum dopant concentrations to better control ceramic microstructures. In a more general sense the possibility of second phase formation or an incipient second phase for high grain boundary concentrations >8 cations/nm^2 is briefly discussed.

1. Introduction

It is well established in the literature that nearly fully dense (>99.99%) alumina ceramics with submicron size grains (<500 nm) are required for obtaining high transparency [1] (i.e. with real in-line transmittance (RIT) >80%). Transition element oxides (Y_2O_3, La_2O_3) are often used as sintering additives for the processing of transparent polycrystalline alumina [2,3]. The bigger size cation additives segregate to the grain boundaries and limit the grain growth in the final stages of high temperature sintering due to the solute drag effect.

The aim of the processing experts is to increase the grain boundary excess of the dopants as much as possible in order to maximize the solute drag effect without causing a second phase precipitation, as a second phase will become another source of light scattering at the grain boundaries. The grain boundary excess of the dopants also plays a role in determining the stable grain boundary complexions, which determine the grain boundary mobility [4]. At the dopant levels below the solubility limit, microstructure evolution is strongly dominated by the grain boundary complexions, while it is controlled by second phase precipitation at higher concentrations [5]. According to the Dillon-Harmer complexion experiments [6], monolayer complexions are most effective in reducing the grain boundary mobility in alumina ceramics, and higher order grain boundary complexions (bilayer and above) lead to higher grain boundary mobility and thereby higher grain growth. Therefore, an optimum concentration is required in order to maximize the solute drag effect while maintaining the favorable monolayer complexion.

Lallemant et al. [7] reported an optimum Zr and La concentration for minimizing the grain growth and maximizing the real in-line transmittance in polycrystalline alumina. Stuer et al. [3] also showed that the highest transparency is obtained in transparent alumina at an optimum concentrations of Y and La dopants. The optimum concentration has been observed to be dependent on both the valence as well as the ionic size of the dopants [3,7–9].

One of the methods to characterize the grain boundary complexions is to measure the grain boundary segregation layer thickness, which is a characteristic property of grain boundary

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complexions [10]. Segregation layer thickness is generally of the order of couple of nanometers at the doping levels generally used for transparent polycrystalline alumina [10]. Atomic level resolution is required for the experimental characterization of the grain boundary complexions, which is not a trivial task even with the highly advanced microscopy techniques. Analytical models [11,12] based on the diffuse interface model and the lattice gas model have also been proposed to simulate the grain boundary phase diagrams.

With the rapid increase in computational power, the simulation of relatively large groups of atoms like grain boundaries has become possible using atomistic modeling methods. Frolov et al. [13,14] simulated the grain boundary complexion transitions as a function of temperature and defect concentration in the metallic systems using an improvised molecular dynamics method. Sun et al. [15] simulated grain boundary complexions in TiO_2 using first principle energy minimization of grain boundary structures. Although such atomistic simulation approach has not been applied yet in the ceramic systems to study the grain boundary complexions transitions, there are plenty of previous studies which have used atomistic modeling methods to study the grain boundary segregation in alumina systems using both ab initio methods [16–19] and force field based methods from our group [20–22].

In the present work segregation of single dopants as well as codopants has been simulated using the force field based energy minimization method. The segregation energy plots in combination with the atomistic structure analysis showed the grain boundary complexion transitions as a function of grain boundary excess of dopants for trivalent dopants. Useful insights were also gained on the role of bivalent dopants in the codoped polycrystalline alumina complexions. The sometimes high grain boundary concentrations observed in the simulations are discussed with reference to possible second phase formation.

2. Computational method

Born model for solids was used to calculate the zero Kelvin energy of segregated grain boundaries. The inter-atomic potential between the atoms was represented by long range electrostatic potential and short range Buckingham potential. The polarizability of oxygen atoms was taken into account using the core-shell potential proposed by Dick and Overhauser [23]. The potential parameters developed by Lewis and Catlow [24] were used in the present work for energy calculations. The crystal structure of alumina was taken from the work of Liu et al. [25]. The current force field has been shown to reproduce atomic positions within 3% error for (01.2) and (00.1) grain boundaries calculated using ab initio methods [26]. One of the limitations of the energy minimization method is that it does not take into account the segregation entropy, which can play an important role at higher temperatures. But Harding et al. [27] showed that the contribution of vibrational entropy is negligible even at 1200 °C.

The computational method will be described only briefly here due to the space constraints. Readers are requested to refer to our previous papers for the computational details of the segregation energy calculation of single doping [26] and codoping [22] on twin grain boundaries and the general grain boundary [20]. Force field based energy minimization method was used to calculate the energy of the segregated grain boundaries. Segregation energies were calculated for single dopants and codopants on a total of 8 twin grain boundaries. One of the general grain boundary observed in our TEM studies [20] of the Y-La codoped transparent alumina samples was chosen for the simulation of the general grain boundary. General grain boundary cell was simulated using the near coincident site lattice approach [28]. Segregation energies were calculated for ~150 dopant configurations on twin grain boundaries and 30 configurations for general grain boundary. The minimum segregation energy of all the calculated dopant configurations was taken to plot the segregation energy as a function of dopant concentration. Galmarini et al. [22] also showed in their Monte Carlo based calculations that the average segregation energy at a given concentration lies very close to the minimum segregation energy given by the current energy minimization approach.

3. Results and discussion

3.1. Trivalent dopants

3.1.1. Segregation energy curves

Fig. 1 shows the La segregation energy plots for low energy and high energy grain boundaries separately, which show two different types of behavior. Segregation energy plots of Y as well as La-Y codoping show a similar behavior [22]. On one hand, the segregation energy reduces continuously at low concentrations for low energy grain boundaries and then slightly increases again before decreasing very slowly. It shows a minimum at a concentration of ~6–8 atoms/nm^2. On the other hand, segregation energy of high energy grain boundaries increases at low concentrations and then becomes more or less constant at higher dopant concentrations. We believe the behavior of low energy grain boundaries is due to the close packed nature of these grain boundaries. As the dopants segregate to the grain boundary, they create a disorder in the grain boundary structure and make it easier for the further segregation of dopant atoms, whereas the high energy grain boundaries already have enough disorder for the easier accommodation and thus segregation of larger sized dopants.

The common characteristic of the segregation energy plots of trivalent dopants (La, Y) for high energy grain boundaries, despite a certain amount of noise, is a possible discontinuity in the slope of the curve at an interface dopant concentration of ~3–4 atoms/nm^2 before becoming more or less constant at higher concentrations (~6–8 atoms/nm^2). As shown earlier in the literature [10], a discontinuity in the slope would suggest a grain boundary complexion transition. To confirm these observations the atomic structures of the minimum energy configurations of the single doped and codoped twin and general grain boundaries were analyzed in more detail and are discussed in the next section.

The possibility of the higher grain boundary concentrations and sometime ordered structures being layers with second phase-like properties has been previously discussed in some detail for both Y [26] and La [21]. For yttrium possible second phases, Y_2O_3, $AlYO_3$ and $Y_4Al_2O_9$, were analyzed with respect to their coordination numbers and mean atomic distances [26] but no close correspondence, in particular with the Y-Y distance were observed. For the La [21] no ordered structures are seen at the grain boundaries studied and segregation energies were grain boundary type dependent and minimum energies were found at quite high dopant concentrations up to 12 cations/nm^2. Again the coordination numbers and mean atom-atom distances were analyzed for probable second phases, namely La_2O_3, $LaAlO_3$ and $LaAl_{11}O_{18}$, but no clear trends were seen suggesting these layers were closely related to a particular crystal phase.

3.1.2. Complexion transitions

Figs. 2–4 show the atomistic structure evolution of grain boundaries with an increasing grain boundary excess of the singly doped Y, La and Y-La codoped, 11.1 twin grain boundaries, respectively. The observed grain boundary complexions are similar to