A Theoretical Study of Temperature Dependence of Vacancy Formation at Grain Boundaries in Non-doped α-Alumina

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Alumina scale is formed on Al-containing alloys of thermal barrier coatings and control of the scale growth is necessary in order to enhance durability. Recently, the mechanism of mass transfer in α-alumina scale at high temperatures has been investigated by oxygen permeation experiments [1], indicating a switching behavior of the predominant defect species (i.e. $V_O^{\bullet\bullet}$ or V_{Al}''') at grain boundaries (GBs) depending on oxygen partial pressure, P_{O2}. We have developed a theoretical model to understand this behavior using density functional theory (DFT) [2]. These calculations reveal that the bandgap of a GB can decrease by ~40% compared to that of a single crystal depending on the amount of interface disorder. By including this bandgap narrowing effect, the switching behavior of the formation energies of $V_O^{\bullet\bullet}$ or V_{Al}''' is demonstrated for T = 1900K (1627℃). This is consistent with the experimental findings, which were performed at various temperatures above 1400℃ (1673 K). In this study, we investigate the temperature dependence of the formation energies and its effect on the switching behavior.

Following Zhang and Northrup's formalism, the formation energies of vacancies are defined as depending on P_{O2} and T of the surrounding O_2 gas and Fermi level of the electrons. The Fermi level determining the energies of charged vacancies was calculated by imposing a charge neutrality condition between $V_O^{\bullet\bullet}$, V_{Al}''' , and electronic carriers, given by $2[V_O^{\bullet\bullet}]-3[V_{Al}'''] + [h^{\bullet}] - [e'] = 0$, where $h^{\bullet}$ and e' are hole and conduction electrons, respectively. Details of the calculation method are given elsewhere [2]. A GB bandgap of 60% of that of the bulk was used.

Vacancy formation energies, E_f, as a function of P_{O2} (Fig. 1) show that, as temperature decrease, the formation energy of oxygen vacancies increases while those of aluminum vacancies decrease and the crossover point shifts to the lower P_{O2} region. This suggests that the switching behavior may be observed only at high temperatures. The concentrations of the charged species under the same conditions as the results in Fig. 1 are plotted in Fig. 2. While in the high P_{O2} region, around 10^4 Pa, dominance of holes and aluminum vacancies is unchanged even at low temperatures, in the lower P_{O2} region, around 10^{-8} Pa, concentrations of electrons and oxygen vacancies apparently decrease with decreasing temperature. The reason for this is considered to be the decrease in the rate of thermal excitation of electrons at lower temperatures. The narrow bandgap of GBs, therefore, appears to have a strong influence on whether switching behavior occurs or not.

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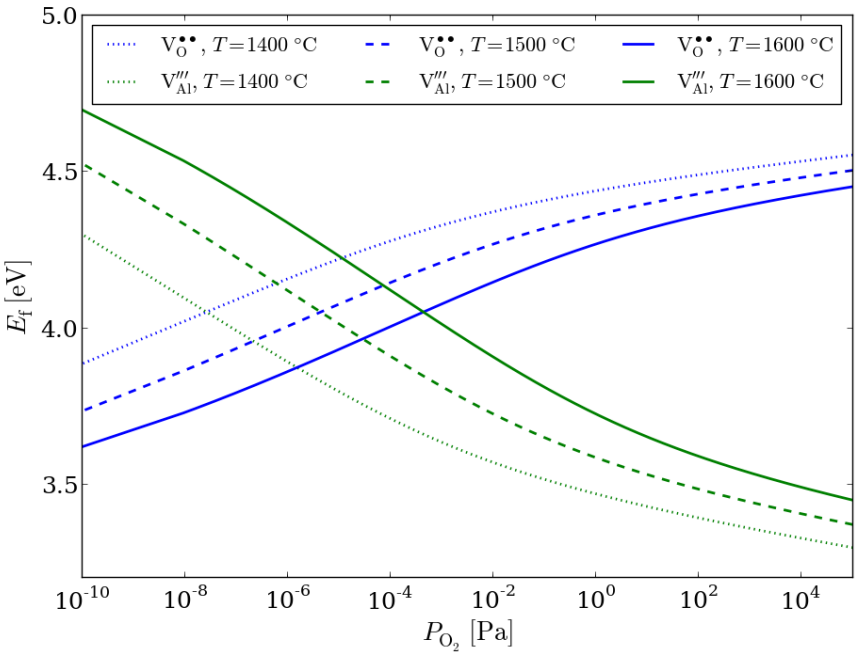

FIG. 1. Formation energies, E_f, of O and Al vacancies as a function of oxygen partial pressure for T = 1400, 1500, and 1600℃.

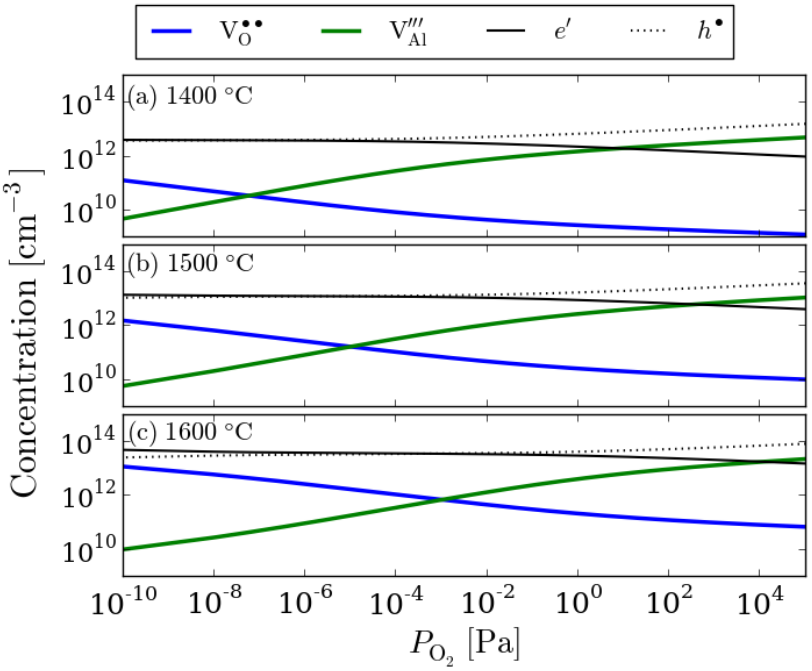

FIG. 2. Concentration of vacancies and electronic carriers as a function of oxygen partial pressure for (a) T = 1400℃, (b) 1500℃, and (c) 1600℃.

References

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