Atomic diffusion mechanism in α-Al$_2$O$_3$ by fist principles calculation and SIMS

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α-Al$_2$O$_3$ is well known to maintain high mechanical strength, toughness, and corrosion resistance up to high temperature, which are advantages for the applications as high temperature structural materials. An understanding of diffusion process in alumina is crucial for controlling these high temperature properties, such as creep deformation, densification in sintering, grain growth, etc. Although investigations of the diffusion behavior in alumina have been extensively studied, many questions are substantially remained in unresolved. For instance, major migration mechanism (via vacancy or interstitial) and rate-determining species (Al or oxygen) are still under debate. In this paper, the atomic-scale diffusion mechanism in alumina was investigated by combining theoretical and experimental approaches.

By using first-principles calculation with nudged elastic band method, the cost in "one" jump of the atom can be determined. In nudged elastic band method, a series of images corresponding to a trajectory of an atom migrating between initial and final position is made, and each image is constrainedly relaxed only in the plane perpendicular to the hypertangent between the two neighbor images. Structural optimizations are performed using the projector augmented wave (PAW) method as implemented in the VASP code and Perdew-Burke-Ernzerhof GGA (generalized gradient approximation) to density functional theory (DFT) was employed. The plane-wave cutoff energies were 500eV and sampled k-point mesh is the Γ point. It is assumed that an atom jump occurs by vacancy, interstitial, or interstitialcy mechanism, and Al and Cr atoms are considered as the migrating atoms. In this study, the calculations for all paths were done using 120 atoms supercell w by 2× 2× 1 expansion of unit cell and then about predicted effective paths recalculations were carried on by 270 atoms supercell, 3× 3× 3 expansion of primitive cell. The atomic positions of the first and second nearest neighbors (1NN, 2NN, respectively) of introduced vacancies or interstitial atoms are optimized.

In the experiments, four kinds of high-purity sapphire substrates, which are oriented to parallel to (0001), {11$\bar{2}$0}, {1$\bar{1}$02}, and {10$\bar{1}$0} planes respectively, were prepared. Metallic Cr was evaporated on the mirror surfaces and these substrates were annealed. Using SIMS, diffusion profiles can be obtained in the near surface region of specimens. We estimated volume diffusion coefficients along each direction in alumina lattice from these depth profiles. Cr was selected as the tracer instead of Al because no suitable radioactive Al can be used, and Cr$_2$O$_3$ is known to make an intimate solid solution with Al$_2$O$_3$.

Table.1 shows calculated migration energies for each path obtained. "Out-of plane" and "in-plane" represent perpendicular and parallel to c-plane, respectively. It is found from the table that atom migrations via vacancy is energetically preferable than other mechanism. In addition, the atomic migrations to 1NN, 2NN, and 3NN sites by vacancy mechanism (As shown in Fig.1) are also found to be quite favorable. In order to confirm the validity of the calculations, those three migration paths were recalculated by using 270 atoms cells. It can be concluded that the diffusion to the 3NN site, which is in-plane direction, is the most preferable path for Cr.

In addition, the present calculations reveal that the diffusion behavior of Cr is different from that of Al, such as Cr has stronger tendency to migrate in in-plain direction than Al.

Table.1 Calculated Al and Cr migration energies for each path

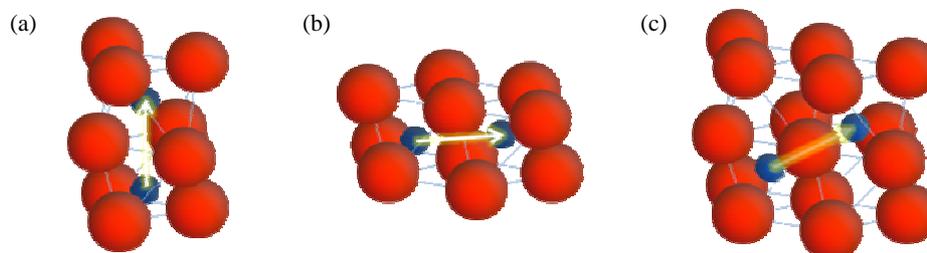| Migration path	Migration energy (eV)			
Vacancy	Al(120atoms)	Al (270atoms)	Cr(120atoms)	Cr (270atoms)
1st NN (out-of-plane)	1.72	1.76	2.94	2.98
2nd NN (in-plane)	2.03	1.8	2.40	2.19
3rd NN (in-plane)	1.67	1.4	2.11	2.04
4th NN (out-of-plane+in-plane)	4.08			
Interstitlal				
1NN (out-of-plane+in-plane)	4.39		4.5	
2NN (in-plane)	*		*	
Interstitialcy				
1NN (out-of-plane+in-plane)	3.36		3.72	
2NN (in-plane)	4.08		*	* Not converged

(a)   (b)   (c)

Fig.1 Cation migration path to (a) 1NN site (b) 2NN site (c) 3NN site of migrating atom

Cr diffusion profile obtained by SIMS as a function of the sputtered depth are plotted in Fig.3. Cr intensity was normalized by AlO. Figure.2 indicates in-plane diffusion, namely along m-axis and a-xis, occurs faster than out-of-plane diffusion, along c-axis and r-axis. Volume diffusion coefficient to each direction was estimated by Fick's law corresponding to the 'instantaneous source condition', and summarized in table.2. It is found that the in-plain diffusion is, totally, faster than out-of-plain diffusion. These experimental results are consistent with predicted diffusion orientation dependency by the calculation.
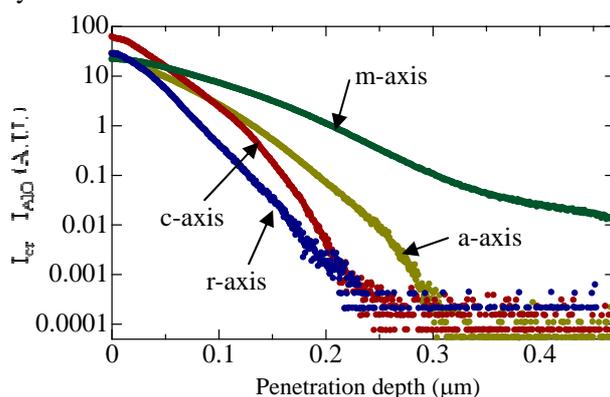
Table.2 Cr diffusion coefficients in each direction

Direction	Diffusion coefficient m^2/s
c-axis (0001) in-plane	6.86×10^{-21}
a-axis$\{11\bar{2}0\}$ out-of-plane	1.26×10^{-20}
r-axis$\{1\bar{1}02\}$ out-of-plane+in-plane	7.82×10^{-21}
m-axis $\{10\bar{1}0\}$ out-of-plane	2.56×10^{-20}

Fig.2 Depth profiles of Cr concentrations of specimens annealed at 1350