

Molecular Dynamics Simulation of Cation Transport in Zirconia

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Diffusion and migration of ions in the yttria-stabilized zirconia were simulated by molecular dynamics method. Calculated Self-diffusion coefficients of oxide ions were consistent with experimental results. The migrations of cations were simulated using a point defect model. The intermittent chained migrations of cations were observed.

Key words: zirconia, ion transport, molecular dynamics simulation

1. INTRODUCTION

Yttria-stabilized zirconia (YSZ) is an interesting material for a heatproof use or a solid electrolyte. Effectiveness as such materials is influenced by the composition and the sintering process of YSZ. For elucidating microscopic mechanisms of the sintering process, it must be important to investigate the dynamics of atoms in the YSZ at high temperature. The diffusion of oxide ions has been investigated, because the property of the solid electrolyte makes use of the high diffusivity of oxide ions in YSZ [1-4]. On the other hand, the migration of cations is also indispensable to understand the total transport of atoms occurring in the sintering processes, but the microscopic features have not been investigated sufficiently. In this study, we investigated YSZ by means of the molecular dynamics (MD) simulation. The simulations were performed for single crystal models of YSZ as the basic study and the transport of constituent ions were analyzed.

2. CALCULATION

A pair wise interatomic potential model [5,6] was used with the potential parameters presented by Dwivedi and Cormack [7]. The parameters for yttrium were modified to reproduce experimental density of yttria at high temperature [8]. The shell term considered in the original works was neglected due to the limited computer resources.

The several compositions of YSZ were prepared by partial exchanging of atoms in the cubic ZrO_2 . Appropriate numbers of oxygen atoms were removed with mixing of yttria to keep the charge neutrality, and the composition was denoted as $yYO_{1.5} \cdot (1-y)ZrO_2$, ($0 \leq y \leq 1$).

The phase transition from tetragonal to cubic structure of YSZ was observed and the transition temperature decreased with y as known. The variation of the oxygen coordination numbers around zirconium and yttrium with y were also confirmed to be consistent with the EXAFS analyses [9, 10].

For the MD simulations for analysis of transport of ions, we used the MD cell that included about 1500 or 2500 atoms. The three-dimensional

periodic boundary conditions were used and pressure and temperature were controlled to keep 0.1 MPa and 1500 K to 2500 K, respectively. The simulations were calculated on CRAY C90 at RIPS AIST using MXDORTO code [11].

3. RESULTS and DISCUSSIONS

3.1 Diffusion of oxide ions

The high electric conductivity and the high diffusivity of oxide ions are most striking characteristics of YSZ. An example of the trajectories of oxide ions in the MD cell is shown in Fig. 1 as a two-dimensional projection. The

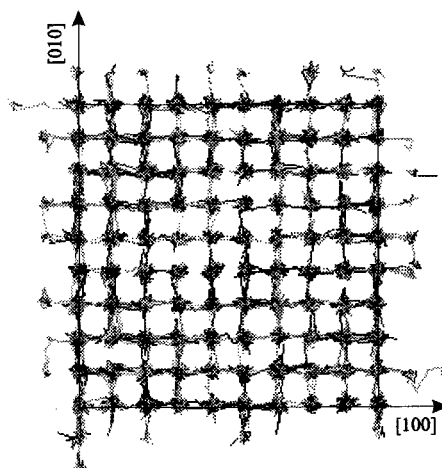


Fig. 1 Two-dimensional projection of trajectories of oxide ions in YSZ of $y = 0.15$, at 1800 K. Lines link positions at each 1 ps in 50 ps duration.

trajectories indicated that the basic motion of these migrations of oxide ions was a jump to $\langle 100 \rangle$ directions.

Temperature dependence of the self-diffusion coefficient, D of oxide ion was plotted in Fig. 2. Good linear relations were observed in this temperature range. Composition dependencies of D at each temperature were also investigated, and the existence of the maximum of D was observed. The composition was $y = 0.2$ at 2000 K. This is consistent with experimental results [2].

It is known that the diffusion of oxide ions in the stabilized zirconia originates in the vacancies

introduced with the mixing of the stabilizers. When the stabilizers are oxides of lower-valence cations compared with zirconium, the vacancies are introduced naturally to the oxygen sites with these stabilizers.

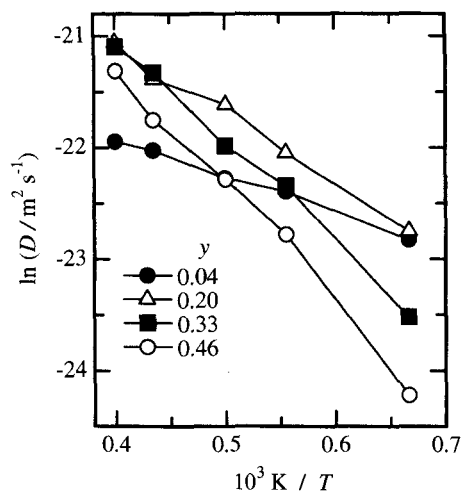


Fig. 2 Temperature dependence of D .

Increasing vacancy gives more chances of jumping for oxide ions. However, the decrease of D in $y > 0.2$ suggests that the excess addition of the stabilizer prevent the free migration of oxide ions. One reason of this is considered as the increase of backward jumping. The number of the oxide ions next to the vacant sites decreases with the increase of y . Therefore, there are few chances that the other oxide ions occupy the generated vacancy. On the other hand, the just moved oxide ion has more chances of return to the previous site.

3.2 Structure including defects

In the YSZ crystals, motions of cations were not active as oxide ions. It was confirmed by analysis of the trajectories that the cations stayed at the initial sites through the simulations. It was also observed as the smaller mean square displacement of the cations as shown in Fig. 3.

One of expected reason for the inertness of cations is the higher coordination number, i.e., the coordination number of cation sites is eight for the cubic zirconia structure. The activation energy of migration of these cations was expected to be higher than that of the ions in lower coordinated sites. In this situation, the existence of the defects must be important since if there were no defects like vacancy on the cation sites, any site change of cations might not occur. For confirming this speculation, we prepared new configurations that involved vacancies on cation sites, and observed the migration of the cations by MD simulation. The YSZ crystal models that including the Schöttky defect and the Frenkel

defect were prepared.

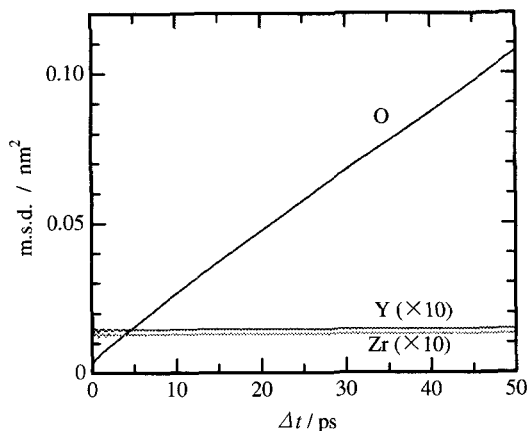


Fig. 3 Mean square displacements of ions in YSZ of $y = 0.2$ at 2000 K.

Schöttky defect: This model was presented by removing a zirconium ion and two oxide ions in the normal YSZ structure model. The cation defect site was monitored through the simulation and it was clarified that the vacancy on a cation site did not migrate. In other words, the nearest cations of the vacancy were not induced to occupy the vacant site.

Frenkel defect: The “Frenkel model” was prepared by moving of a zirconium ion or an yttrium ion from the original site to any interstitial site. The center of the unit cell of the cubic zirconia was selected as the interstitial site (Fig. 4). The interstitial ion moved actively to relax their configurations since the start of the simulation. The details were mentioned in the next section.

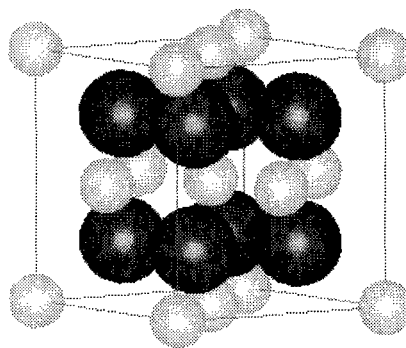


Fig. 4. A unit cell of cubic zirconia included an interstitial cation at the center of it. Large and small spheres indicate oxide ions and cations, respectively.

3.3 Effects of interstitial cations

The interstitial cation in the Frenkel model is considered unstable energetically. Monitoring the Coulomb and short-range repulsive energies of the system, they changed quickly with the progress of the initial relaxation. Then metastable condition was

achieved. However, it is conceivable that the system is metastable until the interstitial cation will be recombined with the vacant site. In this study, the initial position of the interstitial cation was artificially set far from the vacant site in order to observe the migration of the interstitial cation through the simulated duration.

The example of the migration of cations is shown in Fig. 5 as a two-dimensional projection of the trajectories to plane $(\bar{1}10)$. Here, the initial

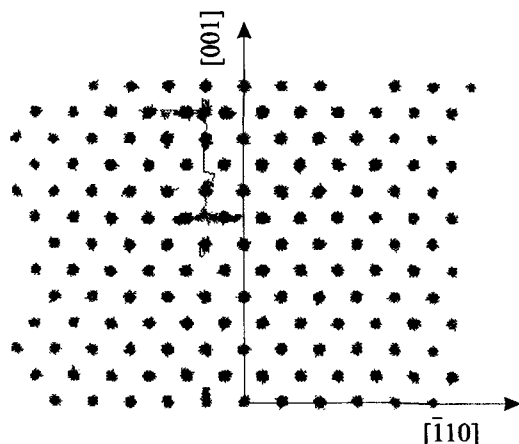


Fig. 5 Trajectories of cations in YSZ of $y = 0.2$ at 2000 K during 100 ps.

interstitial ion was zirconium. The initial position of it was shown just on the center of the z-axis drawn in Fig. 5. The trajectory for the first movement indicated an immediate migration of the initial interstitial ion to one of the adjacent cation site. It was revealed that this cation migration induced a simultaneous pushing of the adjacent cation. The pushed cation occupied another interstitial site as a new interstitial ion. The direction of the migrations was $\langle 100 \rangle$ but not $\langle 110 \rangle$ that is the direction link the nearest cation sites in the cubic zirconia. On the other hand, any migration was not observed in the neighborhood of the vacant site that was projected on the z-axis in Fig. 5. This was similar to the case of the Schottky defect model.

The cations around the interstitial cation were vibrated as shown in Fig. 5, and the one of them pop up as the next interstitial ion. This series of motion continued intermittently. There were two different types in the traveling trajectories in Fig. 5. First was the trajectory with vibration shown as tangled lines, and second was the rapid migration plotted as simple lines. The latter case is interesting because it suggests the possibility of coincident triple migration.

It was observed that the oxide ions surrounding the just moving cation also moved to the same direction, but any migration of the oxide ion to the adjacent site rarely occurred simultaneously. Most of them returned to the previous sites. It suggests that the site change of the

interstitial cation and the surrounding oxide ions are not always related directly, however, the opportunity of the site change must be affected by cooperative motion of them. The detail needs to be investigated further.

4. SUMMARY

Microscopic analyses of the migration of atoms by MD simulation were attempted for YSZ at high temperature. For oxide ions, the jump toward the nearest vacant site directed in $\langle 100 \rangle$ was confirmed as the dominant factor of the diffusion. The composition dependence of the self-diffusion coefficients of oxide ions was consistent with the experimental results. Its temperature dependence was also derived.

It seemed reasonable to consider that the existence of vacancy enhances the migration of cations. As for vacancy on the cation site, however, it was not occupied by the nearest cations through the simulated duration. On the other hand, the interstitial cation induced the intermittent chained migration of the cations. The reason of the difference in the two types of defects is understood by considering the stability of them. That is to say, the isolated vacancy on the cation site as a Schottky defect is relatively stable and does not affect the surrounding cations. While the interstitial cation like a Frenkel defect is unstable and it makes surrounding ions unstable. The latter condition will induce the migration of cations. Further study by the MD simulations for the defect structures must be stimulating to investigate the migration of cations.

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