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The Influence of Grain Boundary Misorientation on Ionic Conductivity in YSZ

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Abstract

Molecular dynamics (MD) was used to investigate the structure and ion transport properties of three interfaces in 8 mol% yttria-stabilized zirconia (YSZ); namely the Σ5 (310)/[001] and Σ13 (320)/[001] tilt grain boundaries and Σ5 (111) 60° twist grain boundary. Atomic interactions were described by a potential function of the Buckingham form. Diffusion rates of oxide ions in the grain boundary containing systems showed that the tilt grain boundaries reduce the overall ionic conductivity relative to a single crystal of 8 mol% YSZ, while the Σ5 twist boundary is able to support rapid diffusion and increases the total conductivity. The effect of segregation of dopant ions to the boundary regions was also investigated. © 1999 Elsevier Science Limited. All rights reserved

Keywords: grain boundaries, ionic conductivity, ZrO_2, fuel cells, molecular dynamics.

1 Introduction

Yttria-stabilized zirconia (YSZ) is the most important commercially available fast oxygen ion conducting ceramic, with applications in oxygen gas sensors, oxygen pumps and solid oxide fuel cells (SOFCs)[1,2]. It has been known for some time that the grain boundaries in stabilized zirconia contribute significantly to the overall electrical resistance, particularly at low to intermediate temperatures[3–5]. Even in nominally pure materials, the specific grain boundary conductivity is found to be on the order of 100 times less than that of the bulk[3,6]. This has been attributed to the presence of 'space-charge' regions and/or dopant segregation to the grain boundaries, resulting in 'trapping' of the otherwise mobile oxygen vacancies. Apart from an earlier molecular statics simulation,[7] no atomic level investigation of diffusion at interfaces in zirconia has been performed. We have therefore undertaken a study of grain boundaries in YSZ using the molecular dynamics (MD) method in an effort to understand the processes involved at a fundamental level, particularly the influence of grain boundary orientation on anion transport.

2 Methodology and Potentials

MD is essentially a technique for determining the thermodynamic and time-dependent properties of an ensemble of particles by integrating Newton's equations of motion over many discrete time steps, Δt. In this study, the MOLDY[8] code was used for the calculations, with a time step of 2 fs.

Interactions between rigid ions were divided into long-range Coulombic forces and short-range forces represented by a simple two-body potential of the Buckingham form:

$$\phi_{ij}(r) = A_{ij}\exp\left(\frac{-r}{\rho_{ij}}\right) - \frac{C_{ij}}{r^6} \quad (1)$$

where A_{ij}, r_{ij} and C_{ij} are potential parameters for the interaction between ions i and j, and r is the distance between the ions. We used the parameters of Lewis and Catlow[9] for systems of ZrO_2 and $(Y_2O_3)_{0\cdot08}(ZrO_2)_{0\cdot92}$, as these are able to reproduce the experimentally determined crystal properties.

Grain boundary systems were constructed according to Coincidence Site Lattice (CSL) theory[10] by joining two perfect single crystals with a given misorientation at the centre of the simulation box. When 3D periodic boundary conditions are applied to the simulation box, a second (inverted) grain boundary is generated at the box edges.

For each of the three interfaces considered—Σ5 (310)/[001] and Σ13 (320)/[001] tilt grain boundaries and a Σ5 (111) 60° twist grain boundary—the initial configuration was thermally equilibrated at 1273 K for at least 10^4 time steps at constant pressure. The simulation box was only permitted to expand perpendicular to the interfaces to reproduce the constraint exerted by the crystal bulk on

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*To whom correspondence should be addressed. Fax: + 81-52-871-8826; e-mail: fisher@mxj.mesh.ne.jp interfaces in real materials. After equilibration the average box dimensions were calculated and used to define the box sizes for subsequent MD runs. After a further equilibration at constant volume, simulation runs were performed for 6×10^4 time steps (120 ps) in the microcanonical ensemble. The atom positions were recorded every ten time steps during the course of a simulation run. These were used to calculate the mean square displacement, or *msd*, for each species, the time derivative of which is proportional to the diffusion coefficient.

3 Results and Discussion

Before commencing simulations of $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$, systems of undoped ZrO_2 with the fluorite structure were modelled to assess the structure and diffusion properties of the interfaces. Although the cubic structure is not stable below ≈2600 K in real ZrO_2, these initial simulations were useful for separating the 'intrinsic' properties of the interface from those due to the presence of dopants and oxygen vacancies.

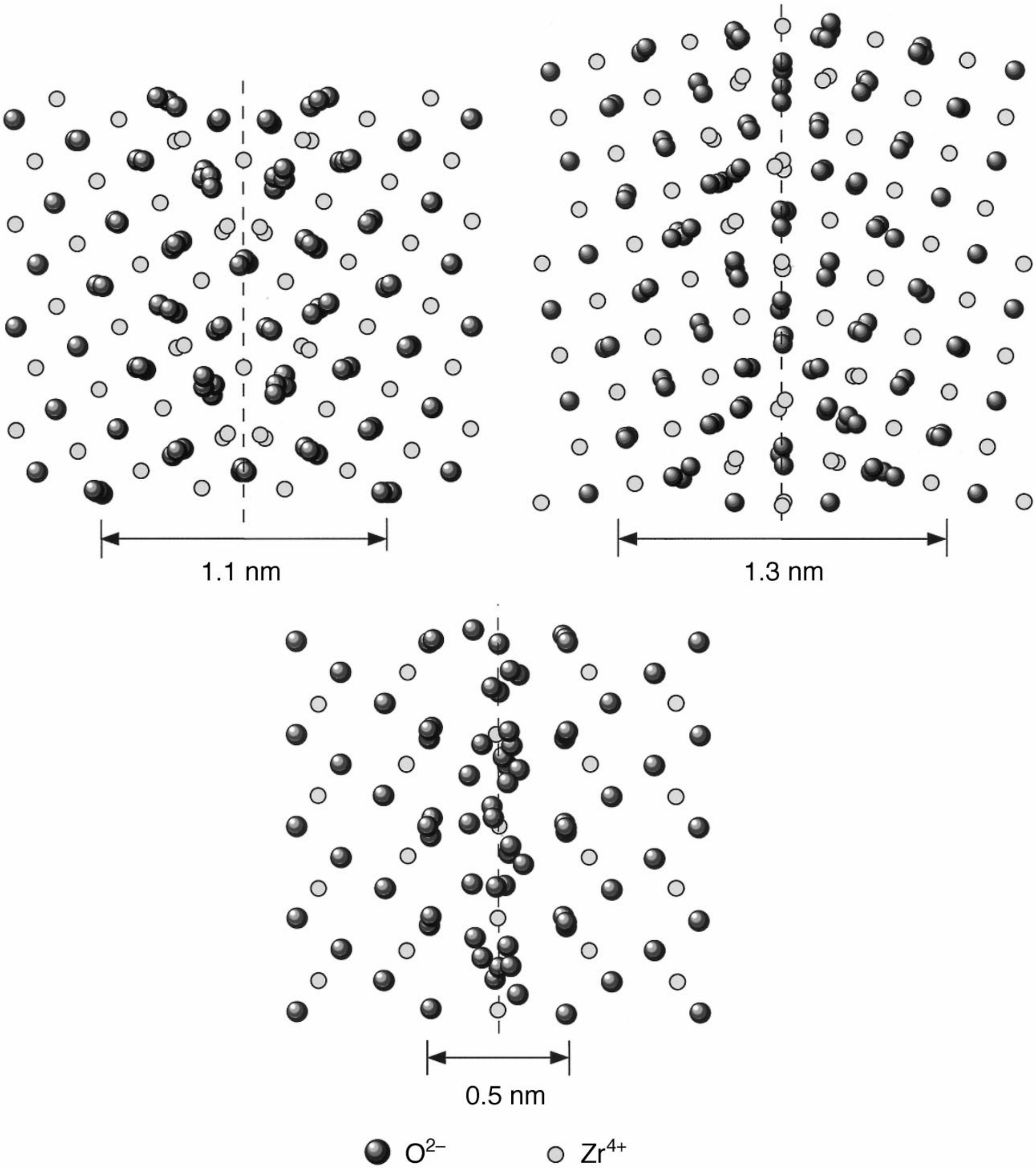

Fig. 1. Average positions of ions near grain boundaries at 1273 K; (a) Σ5 (310)/[001] tilt boundary; (b) Σ13 (320)/[001] tilt boundary; and (c) Σ5 (111) 60° twist boundary.

Table 1. Properties of grain boundaries in cubic ZrO_2

Grain boundary	*Excess volume (%)*	*Formation energy (Jm^{-2})*
$\Sigma 5$ tilt	1·1	2·7
$\Sigma 13$ tilt	0·9	3·1
$\Sigma 5$ twist	0·3	2·2

3.1 Grain boundary structure

The predicted structures of the two tilt grain boundaries and one twist boundary are shown in Fig. 1, with the corresponding formation energies and excess volumes listed in Table 1. The largest volume expansion on thermalizing the initial CSL configuration was shown by the $\Sigma 5$ symmetrical tilt boundary. Unlike the other two interfaces, the boundary plane in the $\Sigma 5$ tilt system shifted by one CSL lattice plane to reduce the repulsion between ions facing each other across the interface,[11] thereby increasing the excess volume of the boundary region. The twist boundary, in contrast, has only a small excess volume and low formation energy. It should be noted that the (111) plane has the lowest surface energy and forms the natural cleavage plane in fluorite-structured single crystals of zirconia.[7]

In Fig. 1 it can be seen that there are definite grain boundary regions within which cations and anions show a greater degree of disorder compared to ions in the bulk regions. The symmetrical tilt boundaries both have widths of ≈ 1 nm. This is in excellent agreement with recent HRTEM images of grain boundaries in thin films of YSZ,[12] as well as results from an earlier study by Badwal and Drennan.[5] The symmetrical twist boundary has a slightly smaller width of ≈ 0.5 nm. Unlike the symmetrical tilt boundaries, the disorder at the twist boundary is mostly confined to the oxygen sublattice. Indeed, within the first oxygen layer either side of the interface, the anions appear to be in a liquid-like state, with no fixed positions. This is a result of the close proximity of the oxygen ions across the interface in the initial CSL structure. The zirconium sublattice is very stable and restricts the expansion of the grain boundary that might be expected from anionic repulsion alone. The oxygen ions respond by scattering between the cation sites, but remain confined to the boundary region. This has implications for oxygen transport at twist boundaries in zirconia, as will be shown below.

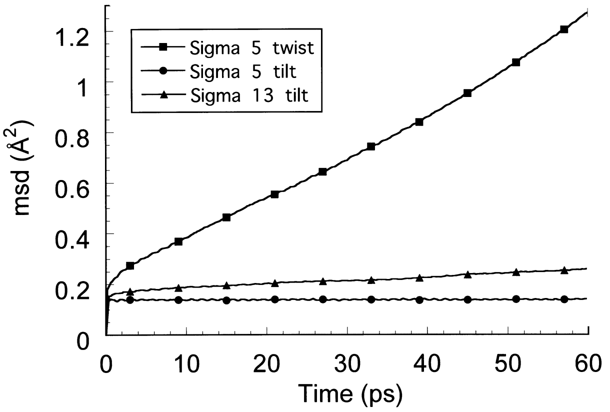

Fig. 2. Mean square displacement (*msd*) versus time for oxygen ions in grain boundary regions of cubic ZrO_2.■ $\Sigma 5$ twist, ● $\Sigma 5$ tilt, ▲$\Sigma 13$ tilt boundaries.

3.2 Oxygen ion transport

Rapid oxygen ion diffusion in YSZ is made possible by the high concentration of oxygen vacancies introduced by acceptor doping. *Msd* calculations for the systems of undoped zirconia, however, reveal that grain boundaries are able to support limited oxygen diffusion, even in the absence of extrinsically introduced vacancies. Ions within the grain boundary regions were labelled separately to those in the bulk and their *msds* plotted against time (Fig. 2). At the $\Sigma 5$ tilt boundary, only a few oxygen jumps were observed at 1273 K, so the diffusion rate was very small, but this has been shown to increase with temperature.[11] The lower misorientation angle and smaller excess volume of the $\Sigma 13$ tilt boundary resulted in more rapid diffusion, although still less than that observed in single crystals of 8 mol% YSZ. In contrast, the $\Sigma 5$ twist boundary, in which the oxygen ions immediately adjacent to the interface have no fixed positions, was able to support an oxygen flux in excess of that of 8 mol% YSZ. While some oxygen ions from the bulk were exchanged with those in the boundary, most of the diffusion took place parallel to the boundary plane, that is, in two dimensions.

In the case of grain boundary systems containing 8 mol% Y_2O_3, *msds* were calculated by averaging over all oxygen ions in the system and compared with that of a single crystal of YSZ (Fig. 3). Both

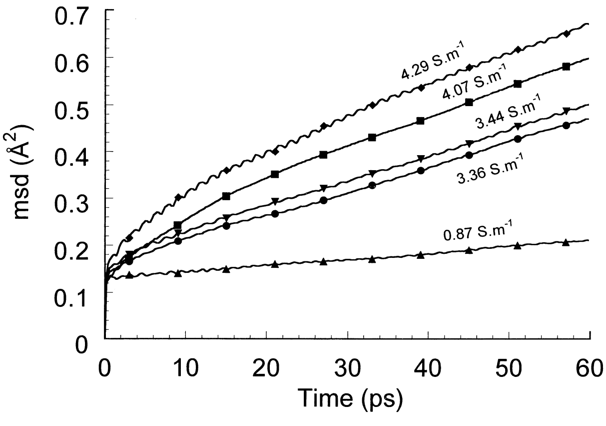

Fig. 3. Mean square displacement (*msd*) versus time for oxygen ions in systems of 8 mol% YSZ: ■single crystal; ●$\Sigma 5$ tilt; ▲$\Sigma 5$ tilt with Y^{3+} segregated to grain boundary; ▼$\Sigma 13$ tilt; ◆$\Sigma 5$ twist. The numbers indicate the calculated conductivities for each curve.

dopant ions and oxygen vacancies were initially placed at random in each system. The results reveal that while the two symmetrical tilt boundaries decrease the overall conductivity, the twist boundary leads to a noticeable increase. Analysis of the directional components of the *msd* indicated that there was only small anisotropy favouring diffusion parallel to the interface.

The rapid diffusion along the Σ5 twist boundary suggests that improvements in YSZ's ionic conductivity may be possible if materials containing pure twist grain boundaries only can be synthesized. However, the Σ5 twist boundary is a special case in which the particular geometry and fortuitous matching of the cation sublattices between the two grains do not allow significant expansion at the interface, thereby forcing the oxygen ions at the grain boundary to form a liquid-like layer. Further simulations are therefore required to determine whether this is the case for other twist boundaries. In the polycrystalline materials used in practice, the majority of grain boundaries are a complex mixture of tilt and twist components. As has been shown experimentally, the overall effect of the grain boundaries is to impede the flow of oxygen ions, which suggests that the entrapment of vacancies at the boundaries, as observed in the Σ5 and Σ13 tilt boundaries studied here, predominates.

3.3 Yttrium dopant segregation

Several studies have reported segregation of dopants to interfaces in YSZ.[2,3,12] The main driving force is the reduction in lattice strain when the Y^{3+} ions, which are larger than the matrix Zr^{4+} ions, migrate to the relatively open grain boundary or surface regions. Although cationic diffusion is slow in zirconia, the high temperatures experienced by the electrolyte in applications such as SOFCs can be expected to lead to significant segregation over time.

To investigate the interaction between dopant segregation and grain boundary structure, we performed calculations on a Σ5 tilt boundary system in which the entire yttrium content was placed within the grain boundary regions. This effectively gave the grain boundaries a composition of ≈32 mol% Y_2O_3. Although such extreme segregation will not occur in practice, the simulation serves to highlight the considerable influence segregation can have on ionic conductivity in zirconia.

The total oxygen ion *msd* calculated for the grain boundary segregated dopant, shown in Fig. 3, is substantially lower than that of a system in which the Y^{3+} ions are randomly distributed. By following the motion of oxygen vacancies in the segregated system, it was observed that during the equilibration stage, the initially randomly distributed vacancies quickly move towards the dopant ions, and remain trapped within the grain boundary region for the duration of the simulation. The formation of a 'space charge layer' was not observed, however, as the vacancies were distributed between and closely associated with the dopant ions.

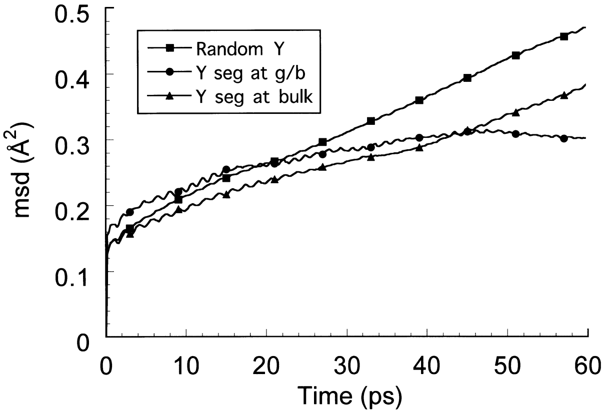

Fig. 4. Mean square displacement (*msd*) versus time for oxygen ions in systems of 8 mol% YSZ with and without dopant segregation: ■ Σ5 tilt with randomly distributed Y^{3+}; ● Σ5 tilt with Y segregated to grain boundary; ▲ Σ5 tilt with Y^{3+} segregated to bulk.

To determine whether the conductivity decrease was due simply to the increased dopant concentration, we also performed a simulation in which all the dopant ions were concentrated in the *bulk* of the grains. *Msds* of anions within the concentrated dopant regions shown in Fig. 4 reveal that the bulk segregated region permits faster diffusion than a Σ5 boundary with segregated dopant ions. In the boundary segregated system, the *msd* reaches a plateau after a short period of time, indicating that the oxygen vacancies have become trapped and do not contribute to long-term diffusion. This suggests that tilt boundaries have a binding energy comparable or greater than that of dopant rich regions. It appears, therefore, that the decrease in conductivity due to dopant segregation is a result of two factors: (1) association between dopants and vacancies that increases ion transport activation energies in crystals with high dopant concentration, and (2) entrapment of vacancies in low conductivity grain boundary regions. Future work will determine whether segregation has the same influence on conductivity in twist boundary systems.

4 Conclusions

Symmetrical tilt grain boundaries, although able to support intrinsic oxygen diffusion, impede the overall conductivity in systems of 8 mol% YSZ. Segregation of dopant ions to the Σ5 symmetrical tilt grain boundary further decreases the overall conductivity by trapping vacancies in the grain boundary regions. The Σ5 (111) twist boundary, in contrast, enables rapid diffusion in two dimensions and may provide a means of enhancing the ionic conductivity of YSZ ceramics.

Acknowledgements

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