Lanthanide diffusion in calcia stabilized zirconia: experimental and theoretical study

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Multiple diffusion experiment of all stable lanthanides was performed simultaneously in calcia-stabilized zirconia (CSZ). The bulk diffusion coefficient obtained increases with increasing ionic radius. The experimental activation enthalpy is near 6 eV and is not very much affected by the type of lanthanide. These results can be correlated with calculations of the cation diffusion using the Mott-Littleton-Approach.

INTRODUCTION

The degradation process in ZrO_2-based ceramics is believed to be governed by the slow diffusion of cations and in particular related with the size mismatch between the stabilizer and host cations as was proposed for yttria stabilized zirconia (YSZ), (1). A systematic study on bulk diffusion in calcia-stabilized zirconia was performed using lanthanides as probe elements.

EXPERIMENTAL

A 16.8 mol % CSZ single crystal was cut into slabs, polished and heated at 1400°C for 1 week before doping. A lanthanide solution was dropped onto the surface of the crystals. For diffusion anneals, the dried samples were heated in air at 1286 °C, 1376 °C and 1463 °C for 10 days, 3 days and 1 day respectively.

The depth distribution of the cations was analyzed using a SIMS (VG SIMS lab). Ar^+ ions (7 kV, 320 nA) were scanned over a range area of $250 \times 250 \mu m^2$. The sputter profiles were converted into depth using a surface profiler. The results were analyzed according to standard mathematical procedures.

Figure 1 represents the bulk diffusion coefficients dependence as a function of lanthanide ionic radii. An 8-fold coordination was assumed (according to the expected fluorite structure), (2).

It can be seen that the diffusion coefficient is constant for ionic radius below 1.0 Å and then increasing by a factor of 3-5 to remain constant above 1.1 Å. The lower value is similar to the value of the zirconium self-diffusion, the higher values are close to the values of calcium self-diffusion. The activation enthalpy is near 6 eV, not showing a significant effect in relation with the lanthanide type.

COMPUTER SIMULATION

To clear up the effect of the lanthanides on the cation diffusion, computer simulations using the Mott-Littleton-Approach were performed. With this method, the migration energy for ionic migration can be modeled within perfect cubic ZrO_2. For comparison, two different potential models were used and the resulting migration energy is shown in Fig. 2.

As can be seen from Fig. 2, the migration enthalpy is around 4 and 5 eV. Results obtained with Grimes' model (5), developed for CeO_2, shown a small ionic radius dependency; the migration energy is decreasing slightly from 4.7 to 4.3 eV when increasing the ionic radius. With Jackson's potential set (6), the energy is more strongly dependent and increases from 3.5 to 5.2 eV.

On comparison the experimental and the calculated values a change in the ionic radius-dependency of the evaluated parameters around 1.0 Å was observed. A previous study on the lanthanide diffusion in YSZ gave the same result (1), indicating that there is a similar diffusion mechanism in both systems.

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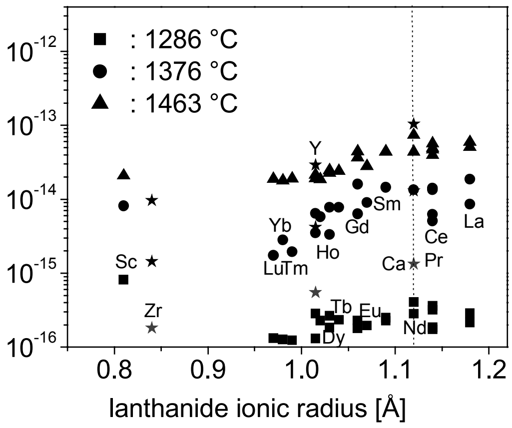

Figure 1. Cation diffusion coefficients for the different lanthanides plotted as a function of their ionic radius. The line indicates the stabilizer ionic radius. Stars are taken from references (3), (4).

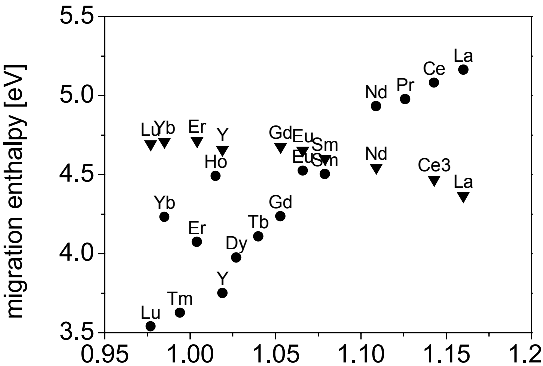

Figure 2. Computer simulation of cation migration in cubic zirconia using parameter sets of Jackson (6) (circles) and Grimes (5) (triangles).

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