Zr AND STABILIZER TRACER DIFFUSION IN CALCIA- AND YTTRIA-STABILIZED ZIRCONIA

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ABSTRACT

Tracer diffusion of yttrium and zirconium in single crystalline YSZ and CSZ (YSZ: yttria stabilized zirconia; containing 10 to 32 mol % Y₂O₃; CSZ: calcia stabilized zirconia; containing 11 to 17 mol % CaO) was measured at elevated temperatures. For zirconium and calcium diffusion, the stable isotopes ⁹⁶Zr and MCa were used and the samples were analysed using secondary ion mass spectrometry (SIMS). In the case of yttrium diffusion, the radioactive tracer ⁸⁸Y was used and a sectioning technique was applied.

The zirconium tracer diffusion is slower than the yttrium and the calcium tracer diffusion. The dependency of the diffusivity on the stabiliser concentration was evaluated with the following results: In YSZ, the zirconium tracer diffusivity decreases with increasing yttria content, but in CSZ it is independent of the calcium content. From the activation enthalpy (4.6 - 5.4 eV) and from the concentration dependence of the cation diffusion, it is concluded that the cation diffusion occurs either via free vacancies (V₂⁺ in YSZ) or via bound vacancies ([V₂⁺-2V⁰⁻] in CSZ).

Keywords: cation diffusion, CSZ, ⁸⁸Y, YSZ

INTRODUCTION

Stabilized zirconia exhibits a very high oxygen ion conductivity and is therefore used as electrolyte material in high temperature applications. While there is a considerable amount of data available on the oxygen transport (see e.g. (1), (2)), only little is known
about the cation transport in stabilized zirconia (3,4). Especially, nothing is known about
the self diffusion of Y. To our knowledge, only two sets of data have been obtained until
now, which result essentially from interdiffusion experiments: Oishi et al. (5) published
measurements on chemical diffusion in yttria stabilized zirconia (YSZ) containing differ­
ent yttria contents, and Solmon et al. investigated the cation transport using SIMS (3).
Both groups found that the yttrium transport should be faster than the transport of zirco­
nium. The very slow cation diffusion plays a crucial role in the understanding of funda­
mental processes such as ageing of the oxygen conductivity (1,2) and of some aspects of
mechanical behaviour (internal friction (6), creep (7)).

For calcia stabilized zirconia (CSZ), there are also only very few experimental results
concerning the tracer diffusion of the cations (8-10). The available data suggest similar
activation enthalpies but slightly faster diffusion coefficients in comparison to YSZ. The
data of Möbius et al. (8) suggest a fast diffusion process which might be attributed to
grain boundary diffusion. Rhodes and Carter (9) evaluated the bulk and the grain bound­
ary diffusion in CSZ and observed that for both cations the grain boundary diffusivities
are higher by a factor of less than 105 (between 1800 °C and 2150 °C) as compared to the
 corresponding bulk diffusion coefficients.

In an earlier publication we measured the bulk diffusion in CSZ but were not able to in­
vestigate the grain boundary diffusion in that material due to experimental limitations
(10): Usually, we perform stable isotope diffusion experiments and analyse the diffusion
profiles with SIMS. This method is fast and has a better local resolution than radiotracer
experiments, but in the case of self diffusion experiments, it is limited by the natural
abundance of the stable tracers used. Since the commonly used rare isotopes of both Zr
(96Zr: 2.78 %) and Ca (44Ca: 2.08 %) have a relatively high natural abundance, we are not
able to detect the grain boundary self diffusion of these elements in stabilised zirconia us­
ing SIMS. The radiotracer method has the unique advantage that the natural abundance
of radiotracers is principally zero, allowing investigations of the grain boundary self dif­
fusion.

In the present paper we present yttrium tracer diffusion experiments (in the temperature
range from 1400 °C to 1675 °C) yielding both bulk and grain boundary diffusion coeffi­
cients in YSZ. We compare these results to zirconium diffusion data in YSZ and also to
Zr and Ca diffusion data obtained in CSZ.

EXPERIMENTAL DETAILS

Sample preparation

YSZ single crystals (obtained from Zirmat Corp., Westford, USA, and Swarovski AG,
Austria) containing 10 to 32 mol % Y2O3 were cut into slabs of 5×5×1 mm3 and polished.
The rare stable isotope 96Zr (2.78 % natural abundance) was implanted with an energy of
150 keV and a dose of 6×1015 Zr+/cm2 from metallic zirconium. After implantation, the
samples were heated for appropriate times at temperatures between 1070 and 1700 °C.
Similarly, 44Ca (2.09% natural abundance) and 96Zr were implanted into CSZ containing
11.4 and 16.8 mol% CaO. In this system, the Ca tracer diffusion was investigated in the
temperature range from 960 to 1700 °C. The relative concentrations of the respective iso­
topes were monitored as a function of depth using SIMS. For further details on the ex­
perimental procedure, see refs. (4) and (10).
Radiotracer experiments

For $^{88}$Y diffusion, the isotope $^{88}$Y ($t_{1/2} = 106.6$ d; EC > 99 % / $\beta^+ 0.21$ %; E = 1.84 MeV) was applied from aqueous solution onto samples of YSZ containing 10.2, 11.1, 18.6, and 24.0 mol% $\text{Y}_2\text{O}_3$, dried and heated at 1400 to 1676 °C in air. After cooling, two procedures have been applied to get the depth profile: In the first case, the sample height was detected using a profiler, its radioactivity was measured (Ge:Li detector / multichannel analyzer), and a small amount of the sample was removed (polishing with SiC paper of 4000 to 800 inch$^2$ grit). Alternatively, the sample was weighed (Sartorius SC2), its radioactivity was measured (NaI detector/multichannel INEL analyzer), and a small amount of the sample was removed (diamond polishing, 0.1 to 3 μm particle size). The weight loss was converted into depth using the density of YSZ (6.0 g/cm$^3$). These procedures were repeated and finally penetration profiles like that given in Fig. 1 were obtained. For more details on the radiotracer sectioning technique, see refs. (11) and (12).

In Fig. 1 two regions can be distinguished: Very close to the surface, the activity decreases rapidly which indicates a bulk diffusion process. At a penetration depth beyond 10 μm, the decrease is less fast, suggesting dislocation or grain boundary diffusion. In order to calculate the diffusion coefficients, appropriate solutions of Fick's equation were applied for the bulk diffusion coefficient $D_{\text{bulk}}$ (Eq. [1], (13)) and for the grain boundary diffusion coefficient $D_{\text{gb}}$ (Eq. [2], (14)). Here $\Delta C(x,t) = C(x,t) - C_0$ where $C_0$ is the natural abundance of the tracer ($C_0 = 0$ in the case of $^{88}$Y), $x$ is the penetration depth, $t$ the diffusion time, and the grain boundary width $\delta$ was assumed to be 3 Å:

$$\frac{C(x,t) - C_0}{C(0,t)} = \exp\left(\frac{-x^2}{4D_{\text{bulk}}t}\right)$$  \hspace{1cm} [1]$$

$$\delta D_{\text{gb}} = 1.322 \left(\frac{D}{t}\right)^{1/2} \lambda^{-5/3}$$

$$\text{with } \lambda = -\frac{\partial\ln(c - c_{\infty})}{\partial x^{1/5}}$$

[2]

Figure 1: Penetration profile (plotted according to Eq. [2]) for $^{88}$Y in YSZ containing 11.1 mol% $\text{Y}_2\text{O}_3$ after heating for 72 hours at 1598 °C. Also shown are the results of fits according to Eqs. [1] and [2] in the near-surface region and at high penetration depths.
RESULTS

Yttrium tracer diffusion in YSZ

Yttrium bulk and grain boundary diffusivities are given in Fig. 2. It can be seen that the grain boundary diffusion is much faster and that it has a lower activation enthalpy than the bulk diffusion (3.5 eV instead of 4.2 eV). It should be noted that the grain boundary diffusion of yttrium is faster than the bulk diffusion by a factor of $10^6$. Extrapolating this to the higher temperatures as applied by Rhodes and Carter in their investigation of CSZ (14), the difference should be less distinct, since the activation enthalpies of both processes are different. Unfortunately, at the moment no data concerning the Zr grain boundary diffusion in YSZ is available, which would be interesting to compare to our results. In contrast to our finding that the grain boundary diffusion has a lower activation enthalpy than the bulk diffusion are the results of Waller et al., who looked at the diffusion of Mn in YSZ and found a higher activation enthalpy for the grain boundary diffusion of this element than for bulk diffusion (15). The authors explained this effect by a change of the oxidation state of manganese during the annealing, and the diffusivities should be a function of the oxidation state. Since the oxidation state of yttrium ($Y^{3+}$) is stable, there should be no such influence in our experiments.

![Figure 2](image-url)

Figure 2: Temperature dependency of the Y tracer diffusion for YSZ containing 11, 18 and 24 mol% $Y_2O_3$. Also shown are the grain boundary diffusivities.
**Bulk diffusion in YSZ**

The temperature dependency of the bulk diffusion coefficients of Zr, Y and Sc in yttria-stabilized zirconia are shown in Figure 3. It can be seen that the Zr diffusion is faster for YSZ containing 10 mol % than for YSZ containing 32 mol % yttria which indicates a diffusion mechanism via free vacancies V\text{Zr}_{4-}(\text{see} \ (4)).

Furthermore, the diffusion of the lower charged cations Sc\textsuperscript{3+} and Y\textsuperscript{3+} is also faster than the Zr diffusion in YSZ: The diffusion coefficient of Y is about 3 times higher than the corresponding value for Zr. The Sc diffusivity is twice that of Zr. Solmon et al. (3) observed that in YSZ the stabiliser ions moved faster than the host cations by a factor of 2.5 which is similar to the value observed here.

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Figure 4: Ca and Zr diffusion in CSZ containing 11.4 and 16.8 mol % CaO. Results of two joint fits of Ca and Zr diffusivities for both samples are also shown.

Comparison of data

In order to understand the order of the diffusivities of the cations, some potentially interesting properties of the cations are summarised in Table 1:

Table 1: Ionic radii of cations in YSZ (a) and CSZ (b) in octahedral co-ordination (from (16)), relative cation diffusion coefficients, normalised to the corresponding Zr diffusion coefficients, ionic 'field strength', and their atomic mass.

| Ion   | Octahedral ion radius \( r_i \) / pm | Relative cation diffusion coefficient | \( z/r_i^2 \) / pm\(^2\) | Atomic mass / amu |
|-------|-------------------------------------|--------------------------------------|-------------------|------------------|
| Zr\(^{4+}\) (a) | 98                                  | 1                                    | 4.1-10\(^4\)       | 91.2             |
| Sc\(^{3+}\) (a)    | 101                                 | 2                                    | 2.9-10\(^4\)       | 45.0             |
| Y\(^{3+}\) (a)     | 116                                 | 3                                    | 2.25-10\(^4\)      | 88.9             |
| Ca\(^{2+}\) (b)    | 126                                 | 7                                    | 1.26-10\(^4\)      | 40.1             |

Assuming that, in stabilised zirconia, cations and oxygen vacancies are ideally distributed within the cubic lattice, one might expect that the difference in cation diffusivities is only affected by the mass difference of the ions (13). In stabilised zirconia the 'light' elements Ca and Sc show a different behaviour as well as the 'heavy' elements Y and Zr. Thus, the masses of the cations are not responsible for the difference in the diffusion coefficients. An influence of the cation charge can be ruled out, too, since the fastest ion, calcium, has the highest negative excess charge on a zirconium site. Therefore, this negative electrical field around Ca\(_{Zr}\)\(^{2+}\) would repel the negatively charged cation vacancy V\(_{Zr}\)\(^{4-}\).

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The size mismatch between $\text{Zr}^{4+}$ and the stabiliser ions decreases in the order $\text{Ca}^{2+} > \text{Y}^{3+} > \text{Sc}^{3+}$. The difference between the diffusion coefficients of zirconium and of the other cations decreases in the same direction. This suggests that the substitution of one ion by another of different size might cause a mechanical stress in the material enhancing the cation diffusion. Kirkaldy et al. (17) have observed this effect when they investigated the interdiffusion in binary alloys. They claimed that large ions enhanced the diffusion by producing and 'collecting' vacancies in their neighbourhood. This should lead to a significant enhancement of the attempt frequency of diffusive jumps and consequently of the diffusion coefficient. Whether or not this explanation holds true for ionic materials is at the moment unclear. Also, there seems to be an inverse correlation of the ionic field strength and the relative cation diffusion coefficients: The higher the charge density (the 'harder' the cation), the lower the cation diffusion coefficients. Which of the discussed effects are really responsible for the difference in cation diffusion coefficients and which not, is not yet clear.

Another aspect is how the different cation diffusion coefficients may influence kinetic demixing phenomena: This effect occurs when a system containing of at least two different oxides is exposed to any kind of external force, either an electrical field (18), an oxygen partial pressure gradient (19), or a mechanical stress gradient (20). Then, demixing occurs according to the relative mobilities of the cations. In ref. (19) it has been shown that under the working conditions of a YSZ-based SOFC significant demixing should occur due to the different oxygen partial pressures for the case that the two cation diffusion coefficients differ by a factor of $>4/3$: If the oxygen partial pressures vary by a factor of 10 and the diffusivities differ by a factor of 2, the equilibrium concentration of the fastest cation is three times higher at the high-pO$_2$ side than at the low-pO$_2$ side of the YSZ electrolyte! Similarly, it is found that demixing occurs in YSZ if the sample is exposed to an external electrical field (20), but here the effect is only very small (less than 500 ppm variation). According to our experimental work, we would expect the demixing to occur in the SOFC, since we have found that yttrium moves three times faster than zirconium.

In order to answer these questions, more work is in progress. In particular, self diffusivities in scandia-stabilised zirconia (ScSZ) will be measured, and it will be tried to explain the cation tracer diffusion in different stabilized zirconia by performing model calculations.

**CONCLUSIONS**

For the first time, yttrium tracer diffusion in YSZ was measured by using the radiotracer $^{88}\text{Y}$, and both bulk and grain boundary diffusivities were obtained from the resulting profiles. The following results are deduced:

1. Yttrium self diffusion is three times slower than Zr diffusion. The activation enthalpy (4.2 eV for YSZ containing 11 mol % Y$_2$O$_3$) is slightly lower than the respective value of the zirconium self diffusion.

2. In the investigated temperature range (1400-1675 °C) the grain-boundary diffusion of yttrium in YSZ is about 6 orders of magnitude faster than the bulk diffusivity and has a lower activation enthalpy (3.5 eV for YSZ containing 11 mol % Y$_2$O$_3$). Extrapolating this behaviour, the grain boundary diffusion will become even more dominant at low temperatures.
3. The yttrium bulk diffusion coefficient seems to decrease with increasing yttrium content, similar to the observation made for zirconium self diffusion indicating that the cation transport occurs via vacancies.

4. Both for YSZ and CSZ, the diffusion of zirconium is the slowest one in the system, being therefore responsible for effects such as mechanical creep.

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