Available online at www.sciencedirect.com
ScienceDirect
Scripta Materialia 102 (2015) 15–18
Scripta MATERIALIA
www.elsevier.com/locate/scriptamat

A disconnection mechanism of enhanced grain boundary diffusion in Al_2O_3

A.H. Heuer* and M. Zahiri Azar

Dept. of Materials Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, United States

Received 8 December 2014; revised 22 January 2015; accepted 24 January 2015
Available online 12 February 2015

Enhanced diffusion in high angle grain boundaries in Al_2O_3 is usually attributed to relatively easy point defect jumping in the plane of the boundary, due to the more open and disordered geometry of random boundaries. However, the pre-exponentials revealed by recent diffusion experiments are incompatible with a point defect mechanism. Instead, such grain boundary diffusion is thought to occur by migration of disconnections, grain boundary ledge defects characterized by a step height h, and a Burgers vector, $\boldsymbol{b}$.

Keywords: Grain boundary diffusion; Ceramics; Disconnection; Oxygen permeability

---

Enhanced grain boundary diffusion in “dry” Al_2O_3 ceramics is of practical importance for fabrication of sintered components, and for high temperature properties of this widely studied and widely used material. In a recent paper [1] devoted to Al_2O_3 scale formation in Ni-base and Fe-base high temperature structural alloys, we suggested that grain boundary diffusion occurred by a ***collective*** mechanism involving migration of *disconnections*, grain boundary line defects characterized by a step height h and a Burgers vector $\boldsymbol{b}$. The purpose of this paper is to show that a disconnection mechanism of grain boundary diffusion is completely consistent with recent high temperature oxygen permeability experiments in dense Al_2O_3 ceramics.

Two arguments were put forward in Ref. [1] for the importance of disconnection-mediated grain boundary diffusion. Firstly, the ability of grain boundaries in polycrystalline Al_2O_3 to act as perfect sources or sinks for point defects (vacancies and/or interstitials) has been apparent since the earliest papers [2,3] on sintering Al_2O_3 to near-theoretical density. Considering vacancy annihilation (formation), the usual interpretation is that following a vacancy jump into (from) a grain boundary, the change in free volume of the boundary is accommodated by slight adjustments of the positions of grain boundary Al and oxygen ions; in other words, the vacancy has become *delocalized.* This renders problematical the very idea that enhanced grain boundary diffusion in Al_2O_3 (and possibly other high temperature ceramics) is due to easier jumps of point defects in the plane of the boundary.

Secondly, as first discussed by Harding et al. [4] and further emphasized by Heuer [5] in his review of diffusion in Al_2O_3, the literature data presented in Table 1 [1,6,9–11] show that the magnitudes of the pre-exponential factors for grain boundary diffusion in Al_2O_3 are inconsistent with a point defect hopping mechanism of grain boundary diffusion.

All measurements of grain boundary diffusivities yield values for δD_b (m^3/s), δ being the “width” of the region showing the enhanced diffusivity. Assuming δ has the conventional value of 1 nm, the pre-exponential D_{bo} values in Table 1 are orders of magnitude too large to be consistent with a point defect mechanism.

The simplest expression for D_{bo} for point defect diffusion is given by $1/6\ \alpha^2\ z\ v \exp -\Delta S_m/R$, where α is the jump distance, z the coordination number of the point defect, v the attempt frequency, ΔS_m the entropy term, and R the gas constant. No reasonable values for the terms that determine D_{bo} are consistent with the magnitudes of the experimental values shown in Table 1, and this is true for both tracer measurements [1,6–9,11] and indirect measurements, such as the oxygen permeability experiments to be discussed below [8,12–14].

While it is well established in fcc metals [15,16] that activation energies for grain boundary diffusion are ~0.4–0.6 those for bulk (lattice diffusion), Table 1 shows that this generalization does not apply for Al_2O_3. Further, the bi-crystal data and Fig. 9b of Ref. [1] show that all grain boundaries are not equal when it comes to diffusion. Assuming disconnection-mediated grain boundary diffusion, the various bi-crystal boundaries must have disconnections with different values of h and b, and thus different mobilities.

There is little doubt that disconnections are present in polycrystalline Al_2O_3. As discussed in Ref. [1], it is much easier to recognize disconnections in the TEM by the presence of ledges or steps, as the Burgers vectors are likely to

---

* Corresponding author; e-mail: ahh@case.edu

http://dx.doi.org/10.1016/j.scriptamat.2015.01.026
1359-6462/

Table 1. Diffusion data for Al_2O_3, assuming Arrhenius behavior.

Lattice diffusion	D_o (m^2/s)	Q_{lattice} (kJ/mol/RT)
Oxygen ($D^{\text{o}}_{\text{lattice}}$) [1]	$5.5 \cdot 10^{-3}$	600
Aluminum ($D^{\text{Al}}_{\text{lattice}}$) [1]	$6 \cdot 10^{-5}$	420
Polycrystalline diffusion	D_{bo} (m^2/s)[*]	Q_{boundary} (kJ/mol/RT)
Oxygen – ^{18}O/SIMS [6]	$1.6 \cdot 10^{10}$	921
Oxygen – ^{18}O/NRA [1]	55	825
Oxygen – permeability[a] [8]	0.4	395
Oxygen – permeability[b] [13]	150	506
Aluminum – permeability[c] [8]	$2.8 \cdot 10^{5}$	611
Aluminum ^{26}Al/ToF-SIMS [1,9]	1.1	400
Bi-crystal boundary diffusion		
$\sum 31$ $\{7\,\overline{11}\,4\,0\}$ ^{18}O/SIMS [10]	$8.4 \cdot 10^{3}$	627
$\sum 7$ $\{4\,\bar{5}\,1\,0\}$ ^{18}O/SIMS [11]	$4.0 \cdot 10^{7}$	820
$\sum 21$ $\{4\,\bar{5}\,1\,0\}$ ^{18}O/SIMS [11]	$4.7 \cdot 10^{4}$	720
$\sum 21$ $\{2\,\bar{3}\,1\,0\}$ ^{18}O/SIMS [11]	$9.2 \cdot 10^{4}$	710
$\sum 31$ $\{7\,\overline{11}\,4\,0\}$ ^{18}O/SIMS [11]	75	560
$\sum 7$ $\{2\,\bar{3}\,1\,0\}$ ^{18}O/SIMS [11]	14	540

[*] Assuming $\delta = 1$ nm.

[a] $P_{O_2}(\text{II})P_{O_2}(\text{I}) = 1\ \text{Pa}/10^{-8}\ \text{Pa}$.

[b] $P_{O_2}(\text{II})P_{O_2}(\text{I}) = 1\ \text{Pa}/10^{-4}\ \text{Pa}$.

[c] $P_{O_2}(\text{II})P_{O_2}(\text{I}) = 10^{5}\ \text{Pa}/1\ \text{Pa}$.

be quite small. Figure 1 shows a very good example of disconnections in nominally un-doped polycrystalline Al_2O_3; a similar image of disconnections in HfO_2-doped Al_2O_3 (but not so identified) has recently been published [17].

Consistent with the lattice diffusion data shown in Table 1, recent oxygen permeability experiments in thin (0.25 mm) wafers of dense polycrystalline Al_2O_3 [8,12–14] demonstrated (not surprisingly) that oxygen permeation occurs solely by grain boundary diffusion. In addition to allowing the grain boundary diffusivities of both oxygen and Al (δD_{gb}^{Oxy} and δD_{gb}^{Al}, respectively) to be determined, these beautiful but difficult experiments also suggested that the band structure of polycrystalline Al_2O_3 plays an important role in vacancy creation/annihilation, as has been discussed elsewhere in the context of Al_2O_3-scale formation in NiCrAl and FeCrAl alloys [1,18].

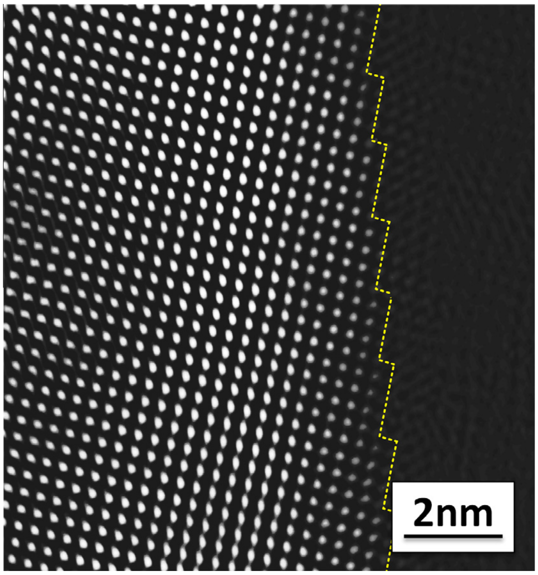

Figure 1. Fourier-filtered HR TEM image of disconnections in a high angle grain boundary in polycrystalline Al_2O_3 (Tecnai F30, 300 keV). The left hand grain is oriented to a $[2\ \bar{2}\ 0\ 1]$ zone axis, whereas the right hand grain is 4 degrees from a $[4\ 1\ \bar{5}\ 0]$ zone axis. High purity α-Al_2O_3 powder (TM-DAR, Taimei Chemicals Co., Ltd., Nagano, Japan) was sintered to full density at 2073 K for 10 h, and had a ~10 μm grain size. The ~30 nm thick TEM foil was made using conventional ion thinning.

While the ***mechanism*** of grain boundary diffusion did not occupy a prominent place in the interpretation of the permeability work, the (near-universal) assumption was made that easier point defect jumping in the plane of the boundary, compared to point defect jumping in the lattice, was the origin of the enhanced diffusivity. A contrary point of view is presented here.

In analyzing these oxygen permeation experiments in terms of disconnection-mediated grain boundary diffusion, we refer to *high pressure* experiments as those in which the high and low oxygen pressures that established the $p(O_2)$ gradients were 10^5 Pa and 1 Pa, respectively, and *low pressure* experiments as those in which the high and low oxygen pressures were 1 Pa and either 10^{-8} or 10^{-4} Pa respectively. (see footnotes a, b and c in Table 1[8,12–14]).

Regardless of the actual $p(O_2)$ gradient, O_2 molecules dissolved in the ceramic at the high oxygen pressure interface, and were released into the local ambient at the low oxygen pressure interface. Analysis of the permeation data, and post-mortem microstructural observations of the high $p(O_2)$ and low (pO_2) interfaces, provided important insights into grain boundary diffusion.

Thermal grooving was invariably observed at both interfaces in the low pressure experiments, and at the low $p(O_2)$ interface in the high pressure experiments. Significantly, however, grain-boundary ridges rather than grooves were observed at the high $p(O_2)$ interfaces in the high $p(O_2)$ experiments.

These data were interpreted as indicating oxygen permeation by oxygen grain boundary diffusion at low oxygen pressures, but a more complex process involving Al grain boundary diffusion at high oxygen pressures. In particular, dissociative adsorption of O_2 molecules occurred in the