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Grain Boundary Grooving Studies of Yttrium Aluminum Garnet (YAG) Bicrystals

M. I. Peters[†] and I. E. Reimanis*

Metallurgical and Materials Engineering Department, Colorado School of Mines, Golden, Colorado 80401

Grain boundary grooving experiments were conducted with $\Sigma 5$ (210) twist boundaries in $Y_3Al_5O_{12}$ (YAG) with the goal of extracting information on diffusion in YAG. Planar boundaries oriented 90° to the surface were annealed in air at various times and temperatures. Atomic force microscopy was used to characterize the subsequent grooves. The Mullins approach leads to the following expression for the diffusion coefficient: D (m^2/s) $= 3.9 \times 10^{-10} \exp[-330 \pm 75$ (kJ/mol)$/RT]$. The relatively low activation energy agrees well with earlier oxygen tracer diffusion measurements on YAG, suggesting that oxygen is the limiting diffusing species in boundary grooving of YAG.

I. Introduction

Yttrium aluminum garnet (YAG) has potential elevated temperature structural applications because of its high creep resistance and low susceptibility to degradation in oxidative environments.[1,2] As with most oxides, diffusional creep is expected to be an important deformation mechanism, particularly for polycrystalline YAG, since the large Burgers vector (10.4 Å, $\mathbf{b} = \frac{1}{2}[111]$) provides a considerable barrier for dislocation motion. There have been a limited number of creep studies on single-crystal YAG,[1–3] and only one on polycrystalline YAG.[4] A value of nearly unity for the stress exponent in the latter study suggests that polycrystalline YAG creeps principally by a diffusional mechanism, similar to other oxides. The reported activation energy for creep of polycrystalline YAG is 584 kJ/mol,[4] while those for single-crystal YAG tested at relatively low strain rates vary between 596 and 720 kJ/mol.[1–3] The fact that the activation energies for the single-crystal studies are similar to that for the polycrystalline study indicates that diffusion probably dominates mass transport during creep in single-crystal YAG. Further, as pointed out by Parthasarathy *et al.* ,[4] the fact that these activation energies are much higher than the activation energy (297–325 kJ/mol) for the volume diffusion of oxygen in YAG, as measured by tracer methods,[5] it seems likely that the cations rather than oxygen control diffusional creep in YAG. Indeed, a recent study concludes that the activation energy for lattice and grain boundary diffusion of the Yb cation YAG is approximately 550 kJ/mol.[6] The present study uses the indirect technique of grain boundary grooving to evaluate the diffusion coefficient of YAG. In this technique, the geometrical changes in YAG grain boundaries exposed to high temperature are measured. Subsequently, Mullins' theory of grain boundary grooving[7] is applied to describe the changes and back-calculate a diffusion coefficient. The activation energies calculated are compared with those reported in the literature.

II. Experimental Procedure

$\Sigma 5$ (210)/[001] twist boundaries in $Y_3Al_5O_{12}$ were formed by bonding two single crystals of YAG. The bonding procedure is briefly described here. Details may be found elsewhere.[7,8] High-purity (undoped) YAG single crystals grown along the [111] axis were sectioned to dimensions 25 mm in diameter and 25 mm in height, and polished on [210] faces to within 0.1° of the [210] plane. These crystal orientations were chosen as part of a study on the grain boundary structure in YAG.[9] The surfaces were sputter cleaned and bonded at 1550°C for 6 h under an applied stress of 5 MPa in an ultra-high-vacuum bonding machine (vacuum level $<7 \times 10^{-8}$ torr at maximum temperature) at Lawrence Livermore National Laboratory.[9] Grain boundary grooving specimens ~4 mm × 5 mm × 6 mm were subsequently sectioned from the bonded crystals using an Isomet slow speed diamond saw. The boundary plane intersected the surface at 90° as shown in Fig. 1. Crystals on both sides of the boundary had the same crystallographic orientation, and as a result, most of the observed groove profiles were symmetric, though some boundaries that were annealed for longer times exhibited groove asymmetry and even some grain boundary migration.[8] The surfaces on which grain boundary grooving measurements were made were polished with successively smaller diamond particle media, until the final polish with 0.1 μm diamond was completed. Samples were scanned with an atomic force microscope to quantify the surface roughness before heating.

Five different bicrystal specimens were heated at ~10°C/min to 1550°, 1587°, 1623°, 1663°, and 1700°C for 30 to 150 min in an air furnace with $MoSi_2$ heating elements. The cooling rate was ~10°C/min from elevated temperatures to about 1000°C, at which temperature the rate became slower. The soak time for the two specimens heat-treated at the highest temperatures was shorter because at longer times, the geometry of the boundary became asymmetrical, invalidating the Mullins approach. A sixth specimen was heated at 1600°C for 2.5 h, cooled, then subsequently heated for an additional 5 and 10 h. The purpose of this sixth specimen was to use the relationship between the groove growth and the time to establish the mechanism of diffusion. As discussed below, Mullins' analysis predicts different relationships for volume diffusion, surface diffusion, and evaporation–condensation mechanisms.[7] After heating, there was no visible contamination (e.g., with silica from $MoSi_2$ elements) on the YAG surfaces, but a detailed inspection was made. On each specimen, eight atomic force microscopy area scans were performed along the length of the boundary using a multimode atomic force microscopy scanner (Digital Instruments, Santa Barbara, CA). Each area scan was sectioned 10 times at different locations along the boundary to produce an average of 80 scans for each temperature. From each of these scans, an average peak-to-peak distance of the grain boundary groove was recorded.

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*Member, American Ceramic Society.

[†]Present address: Los Alamos National Laboratory, Los Alamos, NM 87545.

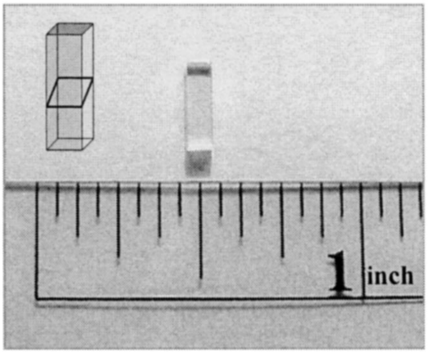

Fig. 1. YAG bicrystal specimen (boundary not visible) with schematic showing the boundary orientation relative to the surface.

III. Results

Figure 2 illustrates a typical groove geometry formed after a heat treatment of 1600°C for 2 h. As may be seen, the groove shape is symmetrical. The groove peak-to-peak distance, *W*, is plotted as a function of time on a logarithmic scale for the sample exposed three times at 1600°C in Fig. 3. These data reveal a power exponent equal to 0.346 ± 0.045, very close to 1/3 that is predicted when a volume diffusion mechanism dominates the groove evolution. In comparison, the predicted power exponent for surface diffusion is 1/4. Based on this, it was assumed that volume diffusion controls most of the mass transport at the grain boundary groove.

Diffusion coefficients were calculated using[10]

$$W = (A't)^{1/3} \tag{1}$$

where *W* is the peak-to-peak distance on the groove, *t* is time, and A' is given by

$$A' = 125n\Omega^2 D\gamma_v/kT \tag{2}$$

n is the number of atoms per unit volume ($n = 9.23 \times 10^{22}$ atoms/cm^3), Ω is the atomic volume ($\Omega = 1.73 \times 10^{-21}$ cm^3),[11] D is the volume diffusion coefficient, γ_v is the surface energy of YAG, k is Boltzmann's constant, and T is the temperature. Because the value for the surface energy of YAG is not known, the calculated value for Al_2O_3 at 1650°C ($\gamma_v = 2500$ erg/cm^2)[11] was used. This approximation influences the accuracy of the calculated diffusion coefficient, but not the activation energies. Table I summarizes the results and Fig. 4 plots the diffusion coefficient as a function of inverse temperature.

Repeated measurements at fixed temperatures of grain boundary grooves revealed no more than a 15% error in the diffusion coefficient values. The error bars in Fig. 4 represent this error. A best linear fit is shown in Fig. 4. The slope of this linear fit reveals an activation energy of 330 kJ/mol (±75 kJ/mol). Accordingly, the diffusion can be expressed as

$$D_{(Y_3Al_5O_{12})} = 3.9 \times 10^{-10} \exp[-330 \pm 75\ (\text{kJ/mol})/RT] \tag{3}$$

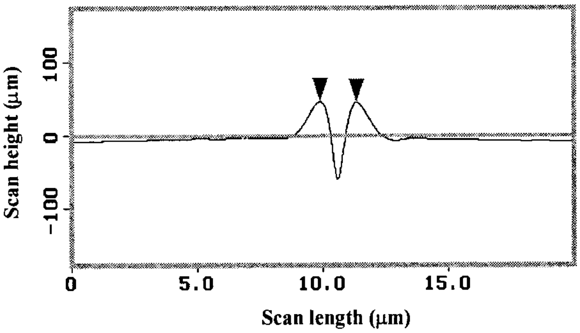

Fig. 2. Typical grain boundary groove, measured by atomic force microscopy. Note the symmetrical shape of the boundary.

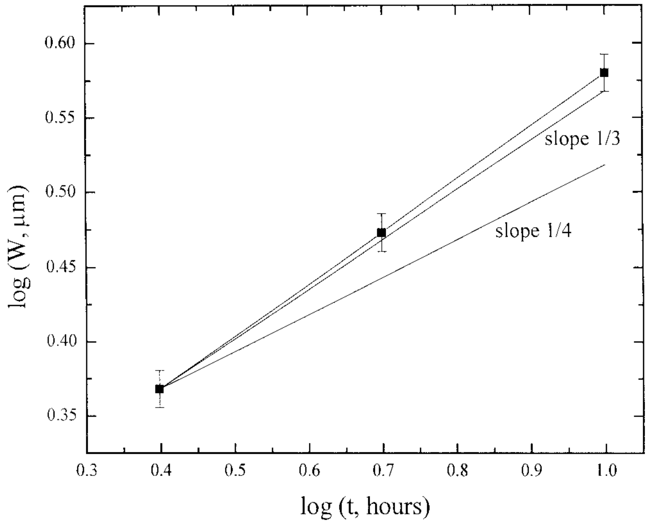

Fig. 3. Groove peak-to-peak distance, *W*, plotted as a function of time, *t*, for YAG heat-treated at 1600°C.

IV. Discussion

The relatively small diffusion coefficients and high activation energy measured here are commensurate with the observation that polycrystalline YAG is extremely creep resistant compared with other oxides. There exists very limited information concerning mass transport in YAG. Besides the oxygen tracer diffusion measurements of Haneda *et al.*,[5] and the direct measurements of Yb diffusion by Jiménez-Melando *et al.*,[6] the only other measurements of mass transport in YAG are from creep experiments.[1–4] If one assumes that diffusion controls creep in these latter studies, then the measured activation energies should be the same as those for diffusion. These creep activation energies for the creep of single-crystal and polycrystalline YAG vary between 550 and 720 kJ/mol.[1–4] In comparison, that measured here for grain boundary grooving is much lower: 330 ± 75 kJ/mol. The difference suggests that the diffusional process that controls grain boundary grooving is different from that controlling creep in YAG. Because the activation energy measured here is nearly equivalent to that measured for oxygen diffusion in YAG (297–325 kJ/mol),[5] it is inferred that oxygen diffusion limits atomic transport in grain boundary grooving. In contrast, as suggested by Parthasarathy *et al.*,[4] it must be that cation diffusion limits atomic transport in creep. If it is assumed that volume diffusion operates in both bulk creep and grain boundary grooving, then it must be that the presence of the free surface alters the diffusion process. Specifically, if cations diffuse rapidly along the free surface, then oxygen diffusion through the bulk would be rate limiting.

Table I. Diffusion Coefficients at Various Temperatures

Temperature (°C)	Heat treatment time (min)	*W* (±5%) (nm)†	Diffusion coefficient (±15%) (cm^2/s)
1550	150	1040	9.1×10^{-15}
1587	150	835	4.7×10^{-15}
1625	150	957	74×10^{-15}
1663	60	1020	2.3×10^{-14}
1700	30	957	3.8×10^{-14}

†Average "peak-to-peak" distance.

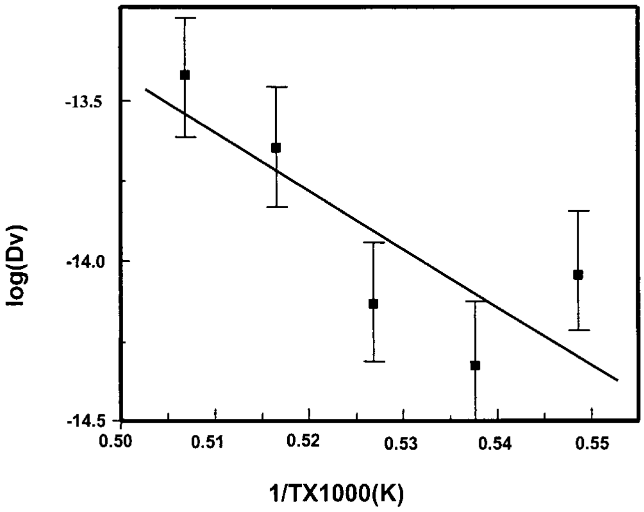

Fig. 4. Diffusion coefficients of YAG as a function of temperature calculated from grain boundary groove measurements.

Another explanation for the difference between reported activation energies for creep and grain boundary grooving in YAG concerns the applicability of the Mullins analysis to the experimental conditions used here. In particular, it is possible that an evaporation/condensation or a surface diffusion mechanism operates during grain boundary grooving. Two comments in this regard are made. First, it is unlikely that an evaporation/condensation mechanism dominates the grooving, since the resulting boundaries would have very different profiles from those observed here. In evaporation/condensation the grain boundary region forms a groove, but there are no protrusions formed higher than the original surface, as is the case for surface and volume controlled diffusion. Second, if it is assumed that surface diffusion dominates grain boundary grooving, an application of Mullins' analysis leads to an activation energy on the order of 300 kJ/mol, on the same order as that found for volume diffusion. Thus, in the case where surface diffusion dominates, it would also be concluded that oxygen diffusion is rate limiting during grain boundary grooving.

It is finally pointed out that the conclusions reported here depend on the 1/3 width versus time exponent reported in Fig. 3. If this value is in error, and if surface diffusion dominates the grooving process (see the slope ¼ line in Fig. 3), then the conclusions reported here would be different. Specifically, the implication would be that surface diffusion is controlled by cation transport which coincidentally has about the same activation energy as oxygen diffusion in the lattice, namely ~300 kJ/mol. It is also noted that the data were obtained at one temperature, and it is possible that the rate-controlling mechanism is a function of temperature. Future work should determine this. In summary, based on the data in Fig. 3, the conclusions drawn in this paper are sound.

Only a direct technique of measuring diffusion, such as a tracer method will establish whether oxygen or cations control diffusion for the different geometrical situations discussed above. Until those measurements are performed, indirect methods such as grain boundary grooving provide insights into possible diffusional mechanisms. In the present case, the experimental observations, when considered in conjunction with the earlier deduction that cations control diffusional creep in YAG[4] lead to the conclusion that cations diffuse more rapidly on the surface than in the bulk. It seems difficult to ignore this deduction since the cations in YAG are large ions and since it is fairly well established that cations control diffusion in other oxides. It is not immediately obvious why cation diffusion might be more rapid on the surface. Nor is it clear why oxygen diffusion would not also be correspondingly more rapid. Further studies on diffusion in YAG should be directed at establishing diffusional mechanisms for bulk, grain boundaries and surfaces.

V. Conclusions

Grain boundary grooving studies have been used to extract information on diffusion in YAG. An application of Mullins' theory of grooving shows that volume diffusion controls mass transport during grain boundary grooving. The diffusion coefficients at various times and temperatures were calculated, based on the geometric changes in the groove. The surface energy of Al_2O_3 was used in the calculation, introducing an error in the diffusion coefficients. However, the activation energy calculated is not affected. The activation energy determined was comparable to that measured for oxygen diffusion in YAG, implying that diffusion during grain boundary grooving is limited by oxygen diffusion.

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