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Diffusion induced recrystallization in alumina

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Abstract

When Fe_2O_3 was substantially dissolved into an (0001) alumina single crystal through a vapor phase at 1500 °C, recrystallization of the single crystal occurred. TEM observation showed that the nucleation of the recrystallized grains occurred through the formation of very small angle wall boundaries via a rearrangement of the misfit dislocations in the surface diffusion layer and their subsequent transformation into high angle grain boundaries. The dislocation wall mechanism appears, therefore, to be the nucleation mechanism of diffusion-induced recrystallization in single crystal alumina. However, an abrupt change in Fe_2O_3 concentration was observed across the boundary between the single crystal and the growing recrystallized grains, indicating that the growth of the recrystallized grains occurred by diffusion-induced grain-boundary migration. During extended annealing, the division of large recrystallized grains into small ones (repeated recrystallization) often occurred. The observed repeated recrystallization was attributed to the redistribution of dislocations formed in the grains where the solute concentration was non-uniform.

Keywords: Al_2O_3; Defects; Diffusion; Grain growth; Recrystallization

1. Introduction

When a crystalline solid comes in contact with a solute source, its equilibrium composition changes and thus alloying of solute atoms occurs. In many polycrystalline metals and ceramics,[1–3] equilibration has been observed to occur through the migration of grain boundaries, so-called *diffusion induced grain boundary migration* (DIGM) or *chemically induced grain boundary migration* (CIGM).[1–3] In the case of a single crystalline solid, which does not contain grain boundaries, recrystallization through the alloying of solute atoms has been reported to occur when there is a great supply of solute atoms.[4–6] Compared with conventional recrystallization induced by plastic deformation,[7] recrystallization by alloying has been called diffusion (or chemically) induced recrystallization (DIR or CIR), since it occurs under chemical inequilibrium.[1,2] When DIR occurs during heat-treatment, a drastic microstructural change results, as in conventional recrystallization. An understanding of DIR may therefore be important in controlling the microstructure and properties of materials in chemical inequilibrium.

Compared with the extensive study and knowledge of DIGM,[1–3] investigations on DIR have been very limited, especially in ceramics.[8–10] In previous studies of DIR, much attention was focused on the nature and origin of its driving force and several DIR mechanisms were proposed: volume-Kirkendall stress,[4] the tensile stress resulting from the difference in grain boundary diffusivity between solvent and solute atoms,[11] chemical-free energy arising from the chemical composition difference between parent and DIR grains,[12] and misfit dislocation.[5,6] Nevertheless, it appears that the experimental evidence for each mechanism is still insufficient and controversy over these mechanisms has continued among several study groups.

In this investigation, diffusion induced recrystallization has been studied in Al_2O_3, where DIR and DIGM have already been observed.[8,13,14] To carry out experiments under a well-defined condition, we used alumina single crystals with a known crystallographic orientation.

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Ferric oxide was selected as a solute to take advantage of its high solid solubility in Al_2O_3[15] and high vapor pressure[16] at the usual annealing temperatures of Al_2O_3. Elucidation of the mechanisms of nucleation and growth of recrystallized grains has been made through careful observation and characterization of the microstructural evolution during DIR.

2. Experimental procedure

Single crystal (0001) alumina disks (Meller Optics, Inc., Providence, RI 02904, USA) with a diameter of 10 mm and a thickness of 1 mm were used for the experiment. In order to relieve any residual stress and strain in the single crystals, they were annealed at 1600 °C for 10 h in air before the DIR treatment. After annealing, the alumina single crystals were placed on an Fe_2O_3 powder bed in a platinum crucible with a lid and heat-treated at 1500 °C for various periods of time, with a heating and cooling rate of 20 K/min. The microstructure of the heat-treated samples was observed using an optical microscope (OM), scanning electron microscope (SEM), and transmission electron microscope (TEM). For TEM observation, the samples were first ground to ~100 μm thickness from the opposite side of the DIR treated surfaces, dimpled, and finally ion-milled. For the OM and SEM observation, some samples were chemically etched in boiling H_3PO_4 for a few minutes. The Fe_2O_3 concentration in the alumina was measured by energy dispersive spectroscopy (EDS).

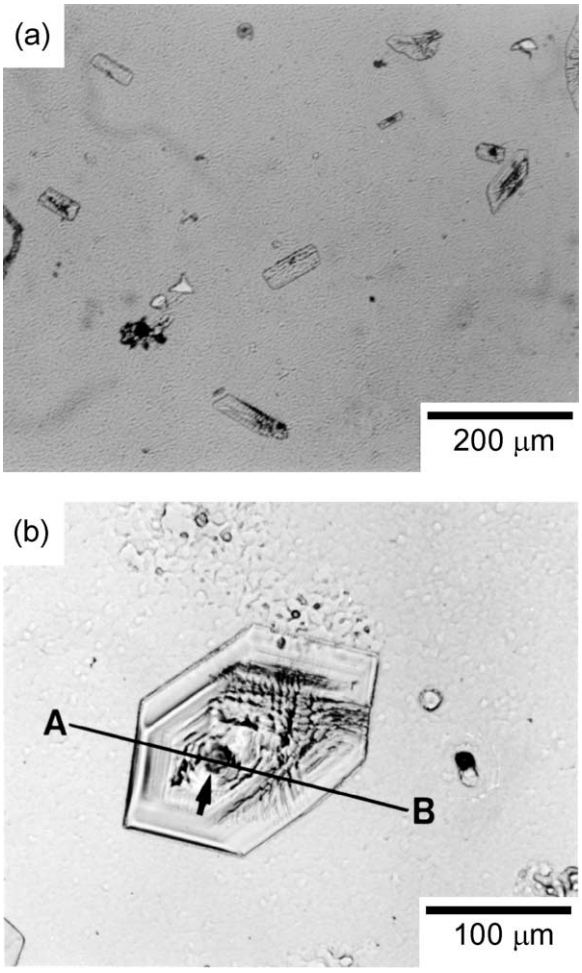


Fig. 1. Optical micrographs showing recrystallized grains on a (0001) alumina single crystal annealed at 1500 °C (a) for 1 h and (b) for 30 h on an Fe_2O_3 powder bed.

3. Results and discussion

During the annealing of (0001) alumina single crystals at 1500 °C in the presence of Fe_2O_3, randomly distributed and recrystallized grains of various shapes formed and grew on the (0001) surfaces of the alumina single crystals, as shown in Fig. 1. In some large recrystallized grains, nucleation sites and vestiges of moving boundaries were observed [Fig. 1(b)]. Fig. 2 shows the X-ray diffraction patterns of an (0001) alumina single crystal before (a) and after (b) the annealing for 30 h in the presence of Fe_2O_3 as well as a pattern from pure alumina powder (c). The (0001) single crystal pattern shows only an (0006) peak before the annealing [Fig. 2(a)]. But, after the annealing [Fig. 2(b)], the diffraction peaks became similar to those of alumina powder. It appears, however, that the peaks corresponding to $(11\bar{2}0)$ [indicated by ■ in Figs. 2(b) and 2(c)] and $(03\bar{3}0)$ (indicated by ●) planes, which are normal to an (0001) plane, are very low, compared with those of the powder sample [Fig. 2(c)]. Upon further recrystallization, the peak heights increased to some extent; nevertheless, they were much lower than those of the powder sample. The difficulty in the formation of $(11\bar{2}0)$ and $(03\bar{3}0)$ grains during recrystallization is somewhat surprising, but its reason is as yet unclear. It seems, however, that the strain energy induced by the nucleation of recrystallized grains is the major factor, because the surface energy difference between grains with different crystallographic orientations is not very high.[17]

To understand the initial stage of alumina DIR, the nucleation process of recrystallized grains has been observed using a transmission electron microscope. Fig. 3 shows TEM micrographs of the surface diffusion layers of the (0001) single crystals annealed at 1500 °C for 1 h (a) and 30 h (b) in the presence of Fe_2O_3. A network of dislocations is observed in the layer of the sample annealed for 1 h. A two-beam diffraction analysis showed that the dislocations were of an edge type with Burgers vectors of $1/3[1\bar{2}10]$ or $1/3[01\bar{1}0]$. These two dislocation components are the Burgers vectors of the basal plane dislocations in Al_2O_3.[18] After DIGM treatment of Al_2O_3 with Cr_2O_3, Vaudin et al.[19] also observed the same types of misfit dislocations. These

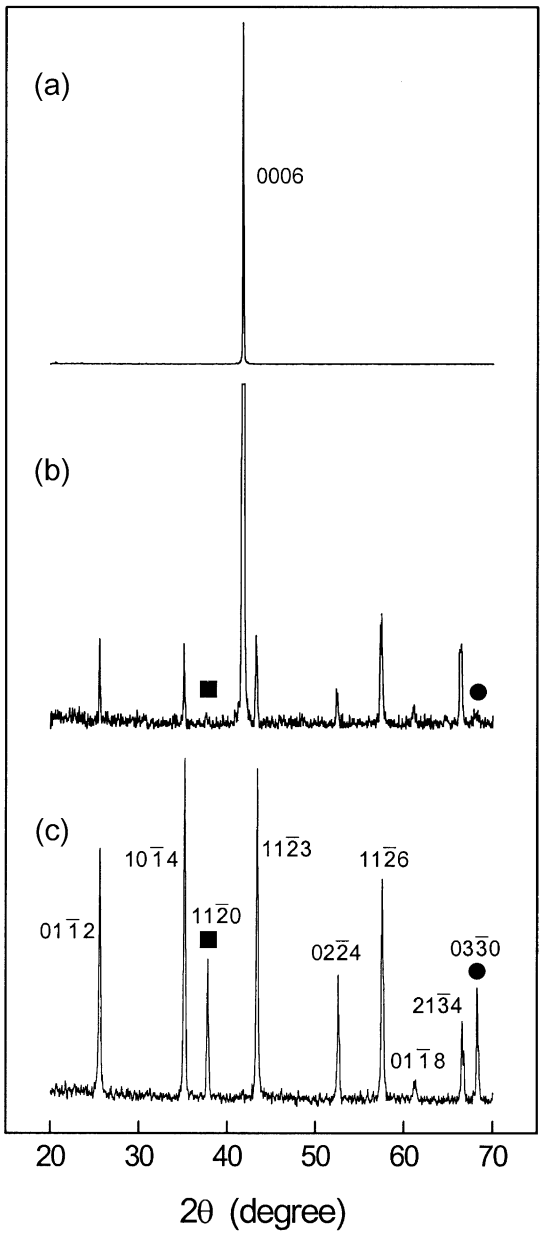


Fig. 2. X-ray diffraction spectra of (a) (0001) alumina single crystal, (b) recrystallized (0001) single crystal after annealing at 1500 °C for 30 h on an Fe_2O_3 powder bed and (c) alumina powder. The $(11\bar{2}0)$ and $(03\bar{3}0)$ planes, which are normal to an (0001) plane, are indicated by ■ and ●, respectively.

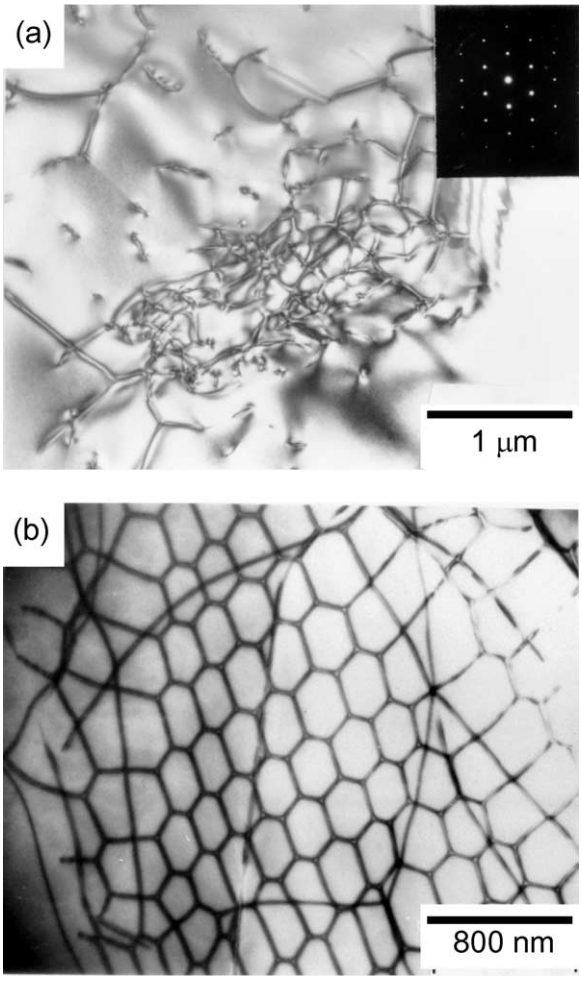


Fig. 3. Bright-field TEM micrographs showing (a) a bundle of misfit dislocations and (b) a hexagonal dislocation network formed at the surface region of (0001) alumina single crystals annealed at 1500 °C for 1 h (a) and 30 h (b), respectively, on an Fe_2O_3 powder bed. The beam direction of the electron diffraction in (a) is [0001].

two types of dislocations, therefore, seem to be common misfit dislocations in Al_2O_3. The electron diffraction pattern of the diffusion zone showed, however, that the crystallographic plane of the region was unchanged and, thus, that recrystallization had not yet occurred.

Upon further annealing of the single crystal with Fe_2O_3, the dislocations in the diffusion layer were rearranged and polygonized [Fig. 3(b)]. The polygonization of the dislocations in the diffusion layer indicates the formation of very small angle wall boundaries and thus subgrain boundaries. In some areas of the diffusion layer, new grains with orientations significantly different from that of the matrix appeared and thus high angle grain boundaries were observed, as shown in Fig. 4. In this figure, a large number of dislocations are present in the single crystal (B), but only a few dislocations are observed in the recrystallized grain (A). The observed nucleation behavior—generation of misfit dislocations, rearrangement and polygonization of dislocations to form low angle grain boundaries, and formation of high angle grain boundaries—was similar to that of conventional recrystallization in plastically deformed materials.

Once the recrystallized grains were nucleated, the recrystallized grains appeared to grow quite fast at the single crystal surface. Fig. 5 shows the Fe_2O_3 concentrations measured across the recrystallized hexagonal-shaped grain in Fig. 1(b). The recrystallized grain contains, at a maximum, 13 wt.% of Fe_2O_3, which is about the solubility limit at 1500 °C in the Al_2O_3–Fe_2O_3 system in air.[15] In the single crystal region, however, the

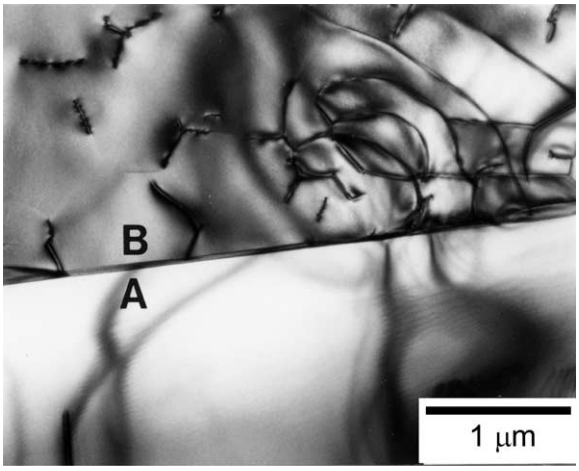


Fig. 4. Bright-field TEM micrograph showing a high angle grain-boundary between a recrystallized grain (A) and the original single crystal (B) after the annealing at 1500 °C for 30 h on Fe_2O_3 powder. The orientation relationship is $(10\bar{1}0)_B//(0\bar{1}11)_A$; $[0001]_B//[01\bar{1}2]_A$.

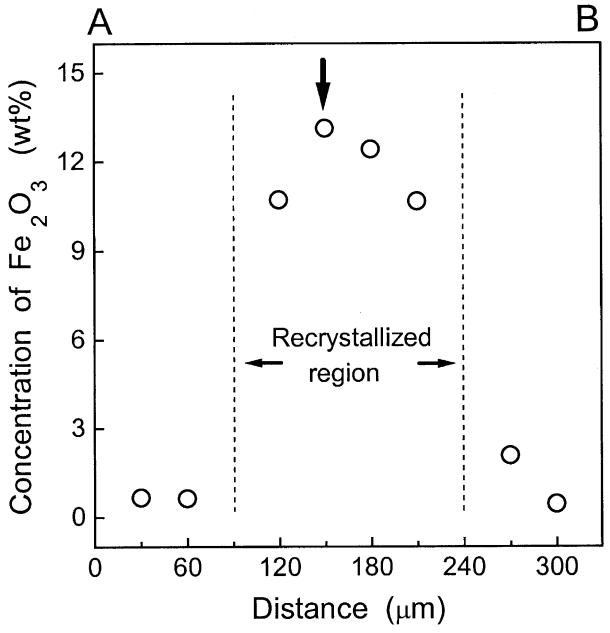
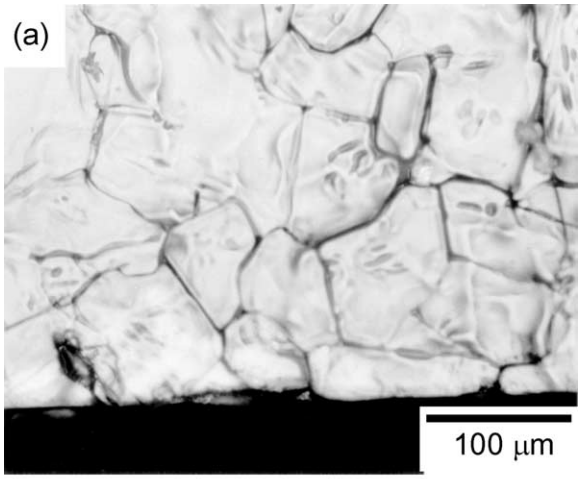


Fig. 5. Measured Fe_2O_3 concentration in the hexagonal grain in Fig. 1(b). Dotted lines indicate boundaries between the recrystallized grain and the single crystal.

measured Fe_2O_3 concentrations are below 2 wt.%. These values are similar to those measured in the previous DIR and DIGM experiments in Al_2O_3–Fe_2O_3.[8,13,14] The low concentration of Fe_2O_3 at the single crystal surface is due to the formation of a very thin diffusion layer of Fe_2O_3, resulting from the slow lattice diffusion of the Fe ions into alumina at 1500 °C.[20] The abrupt change in Fe_2O_3 concentration between the single crystal and the recrystallized grain indicates that the alloying of Fe_2O_3 into the single crystal during DIR occurred through the migration of a boundary between



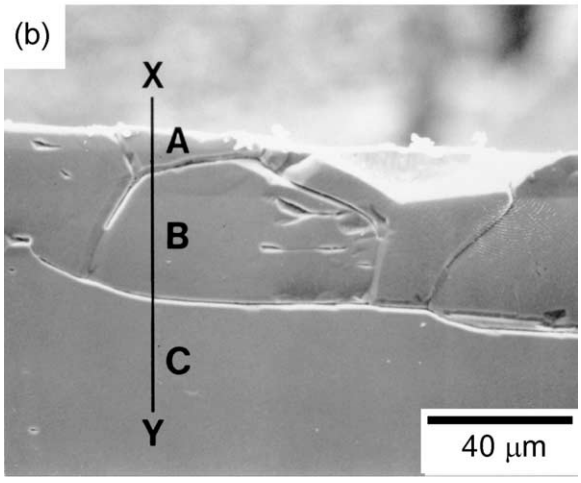


Fig. 6. Microstructures showing recrystallized grains of (a) the surface and (b) the cross section of a (0001) alumina single crystal chemically etched in boiling phosphoric acid after annealing at 1500 °C for 60 h on an Fe_2O_3 powder bed.

the recrystallized grain and the single crystal, i.e. the growth of recrystallized grains. It appears, therefore, that the recrystallized grains grow by DIGM.

One of the typical features in Fig. 5 is that the measured Fe_2O_3 concentration in the migrated region is not uniform. The measured concentration is at a maximum of 13 wt.% Fe_2O_3 in the nucleated region of the hexagonal grain in Fig. 1(b) and decreases as the recrystallized grain grows. In DIR, the nucleation of a recrystallized grain occurs only when the solute dissolution exceeds a certain critical value: in our case, ~13 wt.% Fe_2O_3. On the other hand, the solute concentration in the recrystallized grains during their grain growth through DIGM is determined by the solute concentration in a thin diffusional layer formed at the interface of the receding grains (single crystal). Therefore, the solute concentration in the growing region is expected to be lower than that in the nucleation region, as can be seen in Fig. 5. The solute concentration in the thin diffusional layer may also be variable possibly

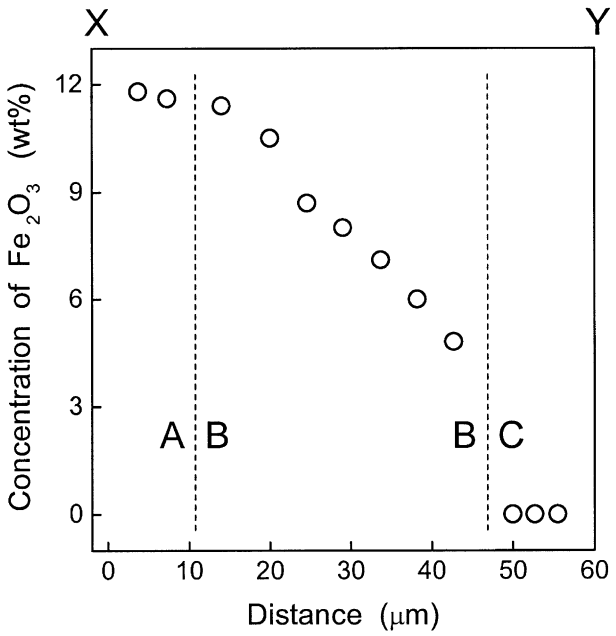


Fig. 7. Measured Fe_2O_3 concentrations along the line from *X* to *Y* in Fig. 6(b). The Dotted lines AB and BC, respectively, indicate the grain boundaries between the recrystallized grains A and B, and the recrystallized grain B and the single crystal C.

because of the uneven movement of the interface [Fig. 1(b)], and the non-uniform distribution of crystal imperfections.

Fig. 6 shows optical micrographs of the surface (a) and the cross section (b) of an (0001) alumina single crystal completely recrystallized at its surface. Even after annealing for 60 h, only one or two grains appeared on the cross section of the recrystallized regions, as shown in Fig. 6(b). Since the thickness of the recrystallized layer on the single crystal surface is about 40 μm after 60 h annealing, the growth rate into the single crystal is estimated to be less than 1 μm/h on average, a very slow rate. In contrast, the lateral growth rate on the surface was much faster, at least a few tens of microns per hour at the beginning [Fig. 1(a)].

Fig. 7 shows the measured Fe_2O_3 concentrations on the cross section along the line from *X* (surface) to *Y* in Fig. 6(b). The Fe_2O_3 concentration in the recrystallized grain A of the surface is about 12 wt% while that in the recrystallized grain B shows a gradual decrease from 12 to 5 wt.% along the line. On the other hand, the Fe_2O_3 concentration in the single crystal C is zero. The abrupt change in Fe_2O_3 concentration at the boundary between the recrystallized grain and the single crystal indicates again that the growth of the recrystallized grains occurrs by DIGM. The gradual decrease in Fe_2O_3 concentration within grain B and the slower growth of recrystallized grains into the single crystal than on the surface must result from the longer distance for grain-boundary diffusion with the growth of recrystallized grains into the single crystal and, thus, a lower supply of Fe_2O_3 with increasing distance from the surface.

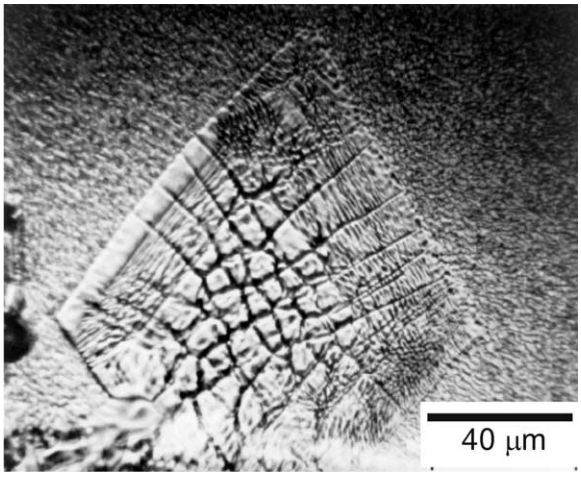


Fig. 8. Optical micrograph showing repeated recrystallization inside a recrystallized grain on a (0001) alumina single crystal annealed at 1500 °C for 30 h on an Fe_2O_3 powder bed.

During the growth of recrystallized grains, however, the large ones were often divided into several small grains, as shown in Fig. 8. Comparing the size and shape of the grains in Fig. 1(a) and Fig. 6(a), the grains in Fig. 6(a) appears to result not only from the recrystallization but also from the division of large recrystallized grains (a repeated recrystallization). Such a repeated recrystallization is rarely observed in the DIR of other materials. Since a concentration variation resulted in the recrystallized grains during their growth (Fig. 5), lattice misfit dislocations must be introduced during the growth because of the lattice parameter variation. We think that the cause of the repeated recrystallization is related to the redistribution of dislocations formed during the growth of the recrystallized grains through DIGM.

4. Conclusions

When an alumina single crystal disk with a (0001) surface was heat-treated in the presence of Fe_2O_3, diffusion induced recrystallization (DIR) occurred. The recrystallized grains nucleated at the surface and then grew into the crystal as well as along the surface. After annealing for 60 h, the whole crystal surface was covered with recrystallized grains. TEM observation showed that the nucleation of the recrystallized grains in a single crystal of alumina occurred through the generation of misfit dislocations and their rearrangement, forming dislocation walls and high angle grain boundaries, i.e. through the misfit dislocation wall mechanism. The measured abrupt change in Fe_2O_3 concentration at the boundary between a recrystallized grain and the single crystal indicated that, after nucleation, the

growth of recrystallized grains occurred by diffusion induced grain-boundary migration (DIGM), which enhanced the alloying of the Fe_2O_3 into the alumina single crystal.

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