

Grain Boundary Mobility in Fe-Base Oxide Dispersion Strengthened PM2000 Alloy

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It has been possible to measure the average interfacial velocities of grain boundaries during the process of recrystallisation of an oxide dispersion-strengthened iron-base alloy manufactured using the mechanical alloying technique. The measurements could be made using optical microscopy because the recrystallised grains are orders of magnitude larger than the surrounding unrecrystallised material. Furthermore, the peculiar way in which the alloy recrystallises, made it possible to observe large, flat segments of boundaries as they advanced into the higher energy matrix. The data have been analysed bearing in mind the pinning effect of the non-random distribution of oxide particles. It is concluded that the boundaries have a high mobility. This conclusion adds to the growing evidence that the alloy has great difficulty in nucleating recrystallisation because of the ultrafine and uniform starting-microstructure in which the grain boundary junctions are so closely spaced that they prevent strain-induced grain boundary migration; in other words, the junctions themselves are powerful pinning points.

KEY WORDS: grain boundary; recrystallisation; mechanical alloying; iron alloys.

1. Introduction

An alloy can be created without melting, by violently deforming mixtures of different powders. As first discovered by Benjamin,^{1,2)} inert oxides can also be introduced into the microstructure using this technique. The resulting dispersion-strengthened alloyed powders are then consolidated using hot-isostatic pressing and extrusion, to produce a solid with a very fine grain structure on a sub-micrometer scale. Heat treatment then induces recrystallisation, either into a coarse columnar grain structure or into a fine, equiaxed set of grains.^{3,4)} Columnar grains occur for two reasons: the oxide particles tend to become aligned along the extrusion direction, making that a favoured growth direction. Alternatively, and in the absence of particle alignment, columnar growth can be stimulated by recrystallising in a temperature gradient; the latter may be a stationary gradient or one which moves along the sample, as in zone annealing.^{5–7)} The columnar microstructure is desirable in applications where the resistance to creep deformation is paramount.

Some of the most successful commercial oxide dispersion-strengthened (ODS) alloys are based on iron or nickel. The details of these alloys have been reviewed elsewhere,⁸⁾ but it is useful to discuss their strange isothermal recrystallisation behaviour, which was the motivation for the present work. Because of the mechanical alloying and consolidation process, the alloys have the highest stored energies

reported in the context of recrystallisation,⁹⁾ attributed to a large extent to the ultrafine grain structure prior to recrystallisation. And yet, they do not recrystallise unless the temperature is raised to a value close to the melting temperature. It could be argued that this is because of the presence of dispersoids which pin the grain boundaries.^{10–12)} However, when recrystallisation does occur, the limiting grain size is enormous (it can be as large as the sample itself), which means that the grain size at which the pinning force becomes comparable to the driving force for recrystallisation is far greater than that of the microstructure prior to recrystallisation. Furthermore, a small amount of non-uniform deformation, or the introduction of other non-uniformities, leads to a remarkable reduction in the recrystallisation temperature and a much finer recrystallised grain size.¹³⁾

These observations are consistent with a difficulty in nucleating recrystallisation; the cause of the difficulty is the fine and uniform grain size in the starting microstructure, so fine that the grain boundary junctions themselves are powerful pinning points which prevent the bowing of grain boundaries, a process important in the nucleation of recrystallisation.^{8,14)}

An alternative possibility is that the boundaries are made immobile by, for example, solute effects. The purpose of the present work was to see whether the mobility of moving grain boundaries in a commercial ODS mechanically alloyed ferritic steel (PM2000) could be measured directly.

2. Experimental Procedure

PM2000 is a yttria dispersion strengthened alloy (**Table 1**) containing aluminium and chromium for oxidation and corrosion resistance; it is produced using mechanical alloying in a high-energy ball mill, by Plansee GmbH.^{15,16} After alloying, the powder is consolidated by hot isostatic pressing and extrusion. The resulting material is sectioned in bars and gun-drilled to produce tube shells which are then formed into tubes by hot extrusion. In the case discussed here, the ingot material had an outer diameter of 173 mm and an inner diameter of 47 mm. The extruded tube had outer and inner diameters of 53.3 and 48.8 mm respectively. **Figure 1** shows the processing history used from ball milling to the final fine-grained extruded tube.

Samples for metallographic examination were cut from the transverse and longitudinal orientations relative to the tube axis. They were etched using 2 g CuCl₂, 40 ml HCl, and 80 ml ethanol. Transmission electron microscopy was carried out on a JEOL 2000FX microscope operated at 200 kV. In order to minimise the defects introduced by sample preparation, foils were extracted by spark erosion. Samples were ground and polished to about 30–50 μm in thickness and were then thinned to perforation by ion milling. Microanalysis experiments were conducted on a scanning-transmission electron microscope (VG HB601 UX) with an energy dispersive X-ray microanalysis system and an operat-

ing voltage of 100 kV.

The dispersoids were analysed using energy-dispersive X-ray (EDX) analysis in a JEOL 2000 transmission electron microscope operated at 200 kV. As a statistical analysis of very small sized particles was required, it was decided to produce carbon extraction replicas of cross and longitudinal samples of the tube. This technique was used as it is possible to examine relatively large areas of a sample in the transmission electron microscope, compared to using thin foil method, which would have been extremely cumbersome and time-consuming in producing sufficient area of sample necessary to allow a statistical analysis of particle size.

The technique for the preparation of carbon extraction replicas is as follows: some of the oxide dispersion particles are presumed to be sitting on the surface of the polished sample. Carbon is then deposited on the surface of the specimen, from the vapour phase by striking an electrical arc between two carbon electrodes. The carbon film, with embedded oxide particles, is removed from the specimen by electrolysis in a solution of 5% HCl–95% methanol, it was then washed in methanol, floated off in distilled water, and collected on copper grids. The sizes of 700 particles were measured from photographic plates.

3. Results and Discussion

3.1. Initial Microstructure

There are two important points about the initial microstructure. Firstly, it consists of fine grains which are 0.2–0.8 μm in the transverse section and slightly longer, at 0.4–1.0 μm in the longitudinal section (**Fig. 2**). These are

Table 1. Chemical composition of PM2000 (wt%).

Cr	Ti	Y ₂ O ₃	Al	Fe
20	0.5	0.5	5.5	Bal.

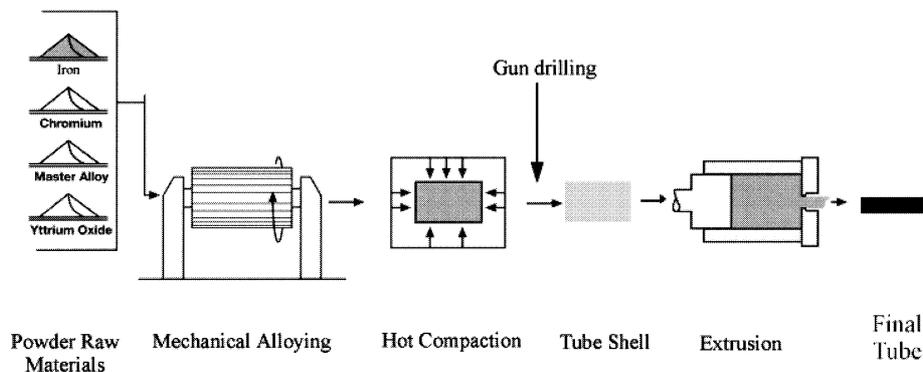


Fig. 1. Scheme of the Plansee alloy PM2000 tube processing.

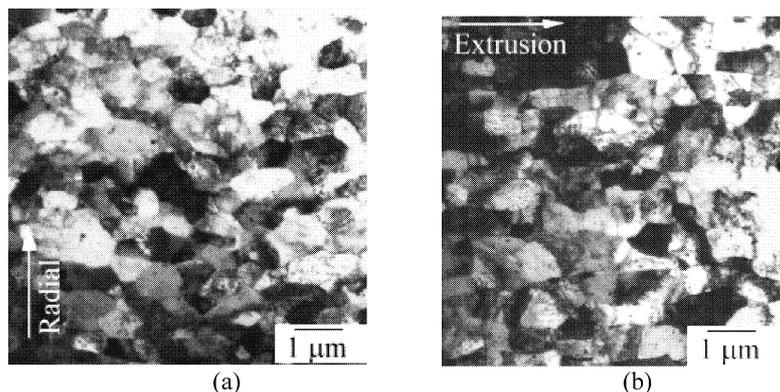


Fig. 2. TEM micrographs of as-extruded PM2000 tube. (a) Transverse section and (b) longitudinal section.

true large-misorientation grains rather than the dislocation cell structures common in cold-deformed metals. It is not therefore surprising that the stored energy of the material is much higher than in conventionally deformed samples.^{17,18)}

The second feature is illustrated in Fig. 3, where it is seen that the yttria particles are not uniformly distributed; instead, they are aligned along the extrusion direction. The alignment observed is similar to that one reported by Jaeger and Jones in other alloys.^{19,20)} It is this which causes the development of columnar grain structures during isothermal recrystallisation.

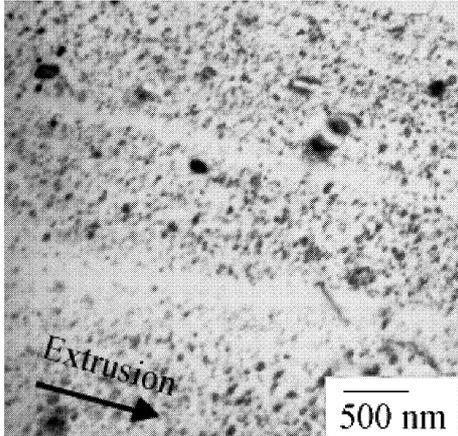


Fig. 3. Particles alignment along the extrusion direction.

The results show particles in the as-received transverse (Fig. 4(a)) and longitudinal (Fig. 4(b)) orientations relative to the tube axis. As expected, EDX microanalysis revealed that the particles are mainly aluminium- and yttrium-rich garnets (Fig. 5).

3.2. Observation of Grain Boundary Motion

Previous work²¹⁻²³⁾ has shown that because of slightly heterogeneous deformation during the tube-making process, heat treatment induces a few recrystallised grains to nucleate at the outer surface of the tube. These are able to develop by growth in the radial direction towards the tube centre and by longitudinal growth parallel to the extrusion direction (Fig. 6). The growth along the extrusion direction is much faster than in the radial direction, leading to columnar grains. It is the partially recrystallised samples illustrated in Fig. 6 that facilitate the measurement of average grain boundary velocities using samples quenched to ambient temperature after specified periods at the annealing temperature. For example, Figs. 6(a), 6(b) and 6(c) each show the thickness of a single recrystallised grain separated clearly from the unrecrystallised matrix at a well-defined recrystallisation front. The difference in thickness divided by the time interval between heat treatments gives the average boundary velocity in the radial direction. The results of a large number of such experiments are presented in Fig. 7 to be discussed later in the paper.

The growth of recrystallised grains is evidently anisotrop-

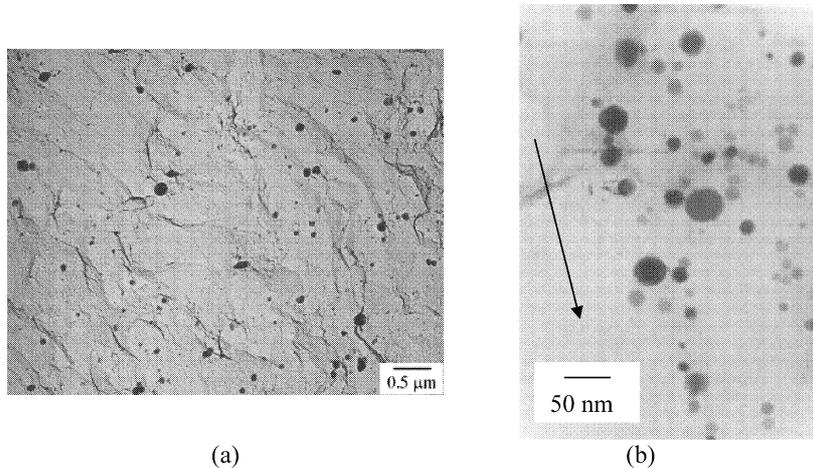


Fig. 4. Micrographs showing particles distribution in (a) transverse and (b) longitudinal orientations relative to the tube axis (arrow indicates extrusion direction).

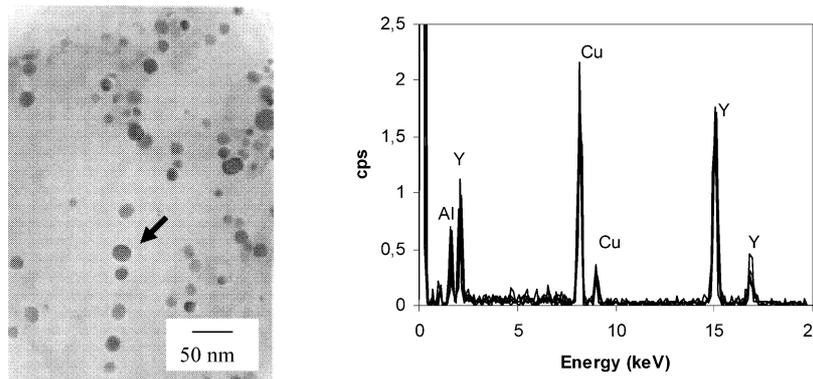


Fig. 5. EDX microanalysis of the particle indicated with an arrow.

ic because of the strong alignment of the yttria particles along the extrusion direction.²⁴⁻²⁶⁾ The particles hinder boundary motion more effectively in the transverse direction. Figure 7 shows the large difference, about four orders of magnitude, in the measured interfacial velocities as a function of orientation relative to the extrusion direction. The boundary propagates by the motion of ledges in the radial direction. The ledges develop not because of an orientation-dependent interfacial energy but because of the anisotropic distribution of yttria particles. A similar mechanism was proposed by Ricks and Howell²⁷⁾ in the context of the growth of transformation of austenite into ferrite. Ledge

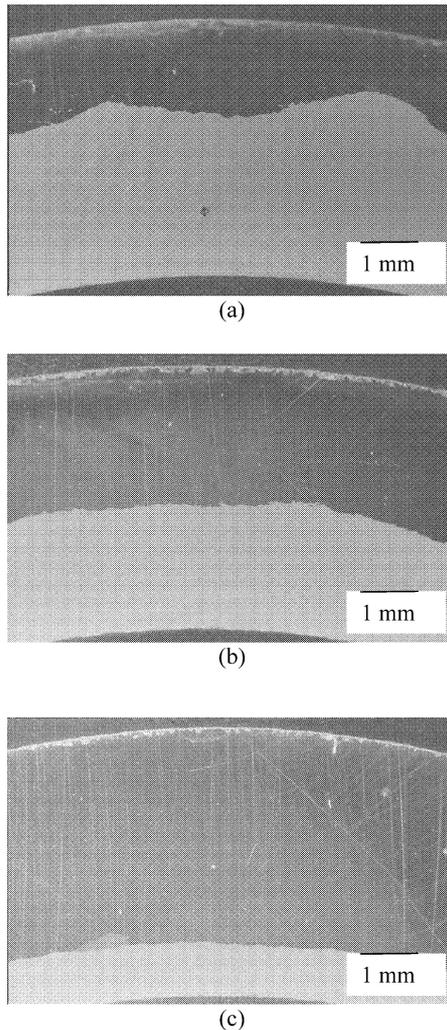


Fig. 6. Transverse sections of the tube after annealing at 1573 K for (a) 1 h, (b) 2 h and (c) 3 h.

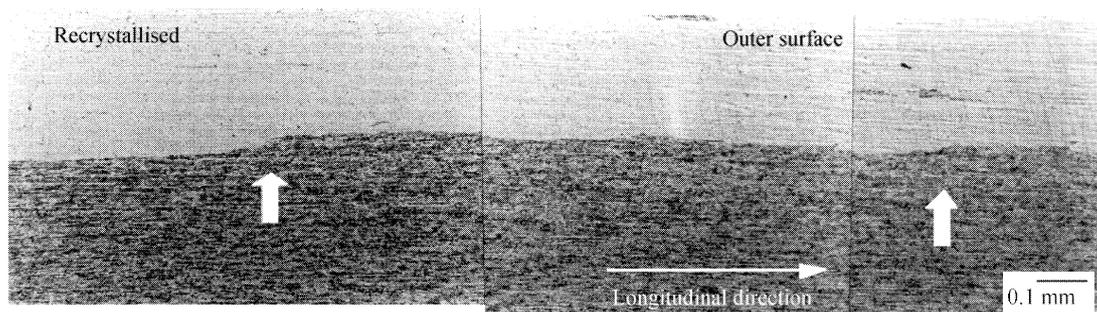


Fig. 8. Optical micrograph shown ledges (arrows) during the recrystallised grain growth in longitudinal direction during annealing at 1598 K for 37 min.

growth is readily detected metallographically by observing partially transformed samples, as shown in Fig. 8.

3.3. Solute Segregation at Grain Boundaries

The alloy used here is of commercial purity so it is possible that solute may segregate within the moving grain boundaries. The purpose of the work reported here was to check the recrystallisation front for evidence of yttrium in the boundary. There is a remote possibility that a fine particle of yttria located at a boundary may partially or wholly dissolve. This could lead to an increase in the activation energy for grain boundary motion.^{28,29)}

Several randomly chosen boundaries were selected and orientated parallel to the incident electron beam; microanalysis scans were then conducted across the boundary plane covering a distance of about $0.16 \mu\text{m}$ on either side of the boundary, avoiding any particles. This involved point analysis at intervals of just 2.5 nm. The data illustrated in Fig. 9(a) show a concentration scan through a precipitate-free segment of the grain boundary. There is no evidence of any obvious segregation at the grain boundary. By contrast Fig. 9(b) shows the linescan across a segment of grain boundary with an aluminium–yttrium oxide particle; the result demonstrates the ability of the technique to detect chemical compositions of interest.

3.4. Kinetics of Boundary Motion

It is clear from Fig. 3 that the fine aluminium–yttrium garnets in PM2000 are not randomly distributed, and therefore, the Zener pressure on a moving grain boundary will vary with the position of the boundary and from place to place on the boundary.

The PM2000 microstructure is modelled as shown in Fig. 10(a). Oxide particles are aligned to the extrusion di-

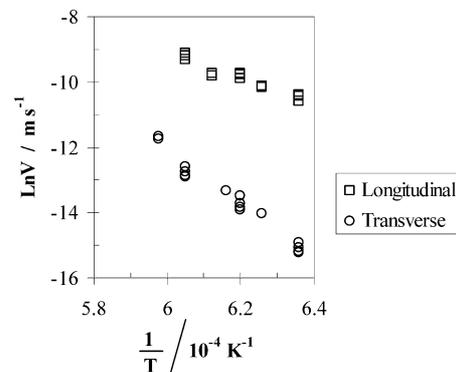


Fig. 7. Experimental grain boundary velocity measured in transverse and longitudinal direction of PM2000 tube.

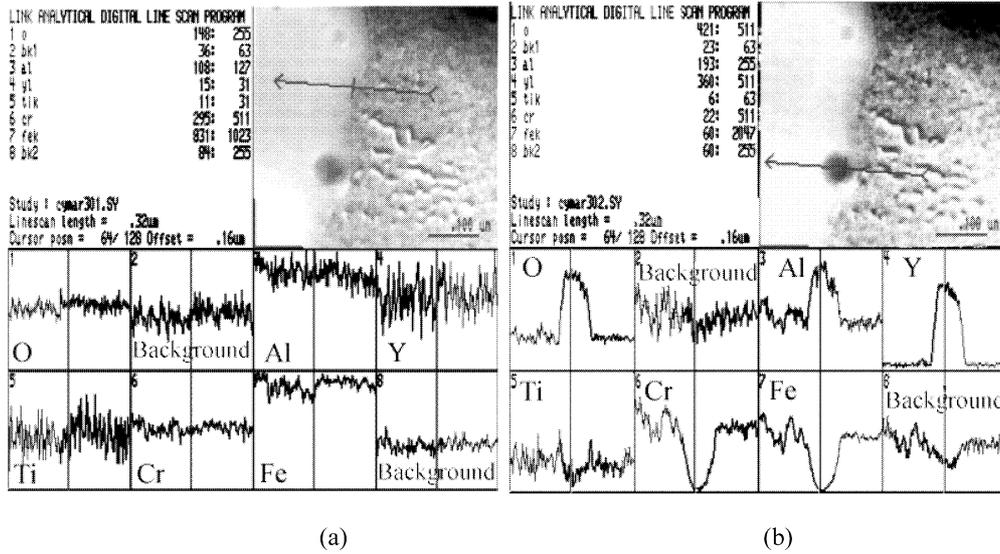


Fig. 9. STEM-EDX microanalysis. (a) Precipitate-free segment of the grain boundary. The arrow shows the location of the scan and the mark on the arrow the position of the cursor. (b) A dispersoid particle.



Fig. 11. Evolution of shear modulus (G) with temperature in PM2000.

shown that the boundary is expected to propagate in a staggered manner as shown in Fig. 10(c). In this sense, the Zener drag pressure of a planar boundary which is normal to the ED-direction, and which moves in this direction, is expressed by³¹⁾:

$$P_Z^{ED} = \frac{3f\gamma}{4R} \epsilon^{0.47} \dots\dots\dots(1)$$

where f is the volume fraction of particles, which in the alloy studied has a value of $f=0.018$; the boundary energy is taken as $\gamma=0.5 \text{ J m}^{-2}$ ³²⁾; and R is the distance between particles and the boundary (a value R of about the particle size °been considered). A planar boundary moving in the normal direction will of course experience no Zener drag in between the bands of particles but when the boundary passes through the particles the Zener pressure will be given by:

$$P_Z^N = \frac{3f\gamma}{2R\epsilon^{1/3}(1+\epsilon)} \dots\dots\dots(2)$$

where $\delta=l/d$. The driving pressure, P^* , during primary recrystallisation is derived from the stored dislocation density, ρ , and can be expressed as³³⁾:

$$P^* = \frac{\rho G b^2}{2} \dots\dots\dots(3)$$

where G is the shear modulus and b the Burger's vector, of magnitude $2.48 \times 10^{-10} \text{ m}$. Figure 11 shows the evolution

rection (ED) and distributed in layers of thickness d and spaced a distance l apart. Each particle has an ellipsoidal shape characterised by 2 diameters (a and b with $b>a$, and therefore an eccentricity $\epsilon=a/b$) with the b -diameter aligned to the extrusion direction. Average values of $a=36 \pm 2 \text{ nm}$, $b=45 \pm 3 \text{ nm}$, and $\epsilon=0.8$ have been measured.

Assume that a constant pressure P^* acts on a planar boundary lying perpendicular to the bands as shown in Fig. 10(b). The pinning force is greater normal to the bands and this anisotropy will be reflected in the shape of the grains. Nes *et al.*³⁰⁾ have modelled the case of drag on a moving interface from non-random particle distribution. They have

of G with temperature for PM2000.³⁴⁾ Spooner and Lempenauer¹¹⁾ reported a value of $\rho=1.0 \times 10^{15} \text{ m}^{-2}$ for PM2000 alloy after consolidation and extrusion. Assuming a situation as schematically shown in Fig. 10, and considering that the length of the recrystallised grains are substantially bigger than the recrystallisation nucleus, the migration speeds of the boundary in the directions of the ED- and N-axes can be written as³⁰⁾:

$$V_{ED} = M(P^* - P_Z^{ED})$$

$$V_N = M \left(\frac{l(P^* - P_Z^N)P^*}{(l-d)(P^* - P_Z^N) + lP^*} \right) \dots\dots\dots(4)$$

where M is the mobility of the grain boundary. The mobility is temperature dependent and is often found to obey an Arrhenius type relationship of the form:

$$M = M_0 \exp\left(-\frac{Q}{RT}\right) \dots\dots\dots(5)$$

The slope of the plot of $\ln M$ against $1/RT$ therefore yields a value of Q , the apparent activation energy which is related to the atom-scale thermally activated process which controls boundary migration.

Figure 12 shows the calculated values of grain boundary mobility for PM2000 in axial and cross orientation relative to the tube axis. These M values are derived from Eq. (4) for ED- and N-directions, and considering the parameters listed in Table 2 and the experimentally measured grain boundary velocities presented in Fig. 7. Combining these results with Eq. (5), an empirical value of $Q=353 \text{ kJ mol}^{-1}$ is obtained.

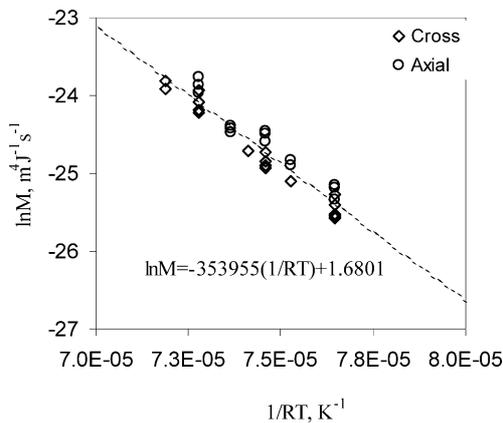


Fig. 12. Activation energy for boundary migration (M) for PM2000.

Table 2. Parameters used in grain boundary mobility calculations.

Parameter	Value
l (μm)	1
d (μm)	0.5
ε	0.8
f	0.018
γ (J m^{-2})	0.5
R (m)	36×10^{-9}
G (Gpa)	$-0.0307T + 90.879$
ρ (m^{-2})	10^{15}
b (m)	2.48×10^{-10}

Humphreys and Hatherly³²⁾ reported typical experimental data for the mobility of high angle boundaries, obtained by several techniques in a variety of high purity metals. From a comparison between the activation energy for boundary migration and the activation energy for boundary diffusion, it is concluded that the activation energy for boundary migration in high purity metals is often close to that for grain boundary diffusion, *i.e.* about a half that for bulk diffusion.

However, in the present case the recrystallisation front has a coarse scale (several hundred micrometers) and advances into a myriad of much finer grains (typically half a micrometer in size). Given that adjacent fine grains in the unrecrystallised microstructure are known to have large relative misorientations,³⁵⁾ it follows that on average, the recrystallisation front can be considered as a high energy boundary with a low degree of coherency. It is known that the activation energy for the motion of an incoherent boundary in an impure material approximates that of a volume diffusion coefficient,³⁶⁾ it is expected that the measured activation enthalpy should be much larger than for grain boundary diffusion.

The activation energy Q presented in this work is higher than that for self-diffusion in α -iron with $Q=250 \text{ kJ mol}^{-1}$.³⁷⁾ However, it is well-established that because of increasing contributions from divacancies the activation enthalpy of self-diffusion in δ -ferrite is much higher at about 296 kJ mol^{-1} . This latter value comes from precise measurements by Ijima *et al.*^{38,39)} in δ -ferrite in pure iron in the temperature range 1665 to 1811 K. Of course, there is no fundamental difference between δ -ferrite and α -ferrite, except that the former is associated with very high temperatures. It happens that the recrystallisation in PM2000 occurs at a temperature which is consistent with δ -ferrite so the higher value of activation enthalpy (296 kJ mol^{-1}) is appropriate. The measured value of the activation energy for grain boundary mobility is somewhat higher, at 354 kJ mol^{-1} . It is possible that the remaining discrepancy could be attributed to solutes, although there are no data available for the diffusion of yttrium in ferrite; other solutes have activation enthalpies which are similar to that for the self-diffusion of iron in ferrite.⁴⁰⁾

4. Conclusions

The mechanism of grain boundary mobility during recrystallisation in Fe-base oxide dispersion strengthened PM2000 alloy has been clarified. The recrystallisation front propagates by a ledge mechanism which is a consequence of the anisotropic distribution of yttria particles in the microstructure. The particles tend to be aligned along the extrusion direction; the boundary velocity along that direction is much faster than in an orientation normal to the arrays of particles. The theory of boundary migration due to Nes *et al.*³⁰⁾ has been used to represent grain boundary mobility in PM2000 alloy. This gives an energy of activation for grain boundary migration which is similar to the activation enthalpy for self-diffusion of iron in δ -ferrite.

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