HIGH-TEMPERATURE DIFFUSION-INDUCED GRAIN BOUNDARY MIGRATION IN AN Fe-5 AT.% Al BICRYSTAL DURING ZINC DIFFUSION

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ABSTRACT

In recent studies [1,2] of the penetration of Sn and Zn along $43°<001>\{001\}$ tilt grain boundaries (GBs) in Fe-Si alloys and the associated premelting phase transition no migration of the GBs was observed. In the present study the diffusion of Zn in an Fe-5 at.% Al alloy at 850°C was examined. The GB penetration of Zn in the Al containing alloy, unlike that into Si containing alloys, results in the extensive (about 100 μm) migration of both the GB and the thin liquid film of the wetted part of the GB near the surface by diffusion induced grain boundary migration (DIGM) [3] and liquid film migration (LFM) [4], respectively. Also a layer of recrystallized subgrains, presumably formed by diffusion induced recrystallization (DIR) [3], is observed to form on the surface. Extensive volume diffusion is observed ahead of the migrating boundaries and liquid films. The morphology of the above reactions was characterized and volume and GB diffusivities of Zn were determined.

EXPERIMENTAL

The $43°<001>\{001\}$ tilt boundary bicrystal of Fe-5 at.% Al alloy used in the present study was grown at a rate of 1 mm/min by electron beam zone melting from an alloy prepared from 99.99% Fe and 99.99% Al. After spark erosion cutting and mechanically grinding the surfaces of the specimens and chemically polishing them in an 80% H_2O_2, 14% H_2O and 6% HF solution, a 100 - 150 μm Zn layer (99.998% Zn) was applied to the two opposite surfaces perpendicular to the tilt axis. These specimens were then encapsulated in evacuated ($<4 \cdot 10^{-4}$ Pa) quartz glass tubes and annealed at 850°C for 23 h in a tube furnace maintained within ±2°C. Electron probe microanalysis (EPMA) measurements were carried out by wavelength dispersive analysis on a JEOL 6400 electron probe microanalyser operated at 15 kV. For the determination of the concentration profiles the beam was stepped at 1 to 5 μm intervals. Electron back scattering (EBS) measurements were carried out in a scanning regime on a JEOL 100CX electron microscope operated at 100 kV.

RESULTS AND DISCUSSION

Figure 1(a) shows a cross section of a bicrystal perpendicular to its tilt axis. It can be seen that the GB and what at the annealing temperature had been a thin liquid film, which wet the GB up to point B, migrated about 100 μm to the right during annealing. The migration of both GB and liquid film were greatest at a depth of about 100 μm below the Zn coated surface with little migration of the liquid film being observed near the surface and the migration of the GB tapering off with increasing depth below the surface until essentially no migration was observed at depths greater than 200 μm. The liquid film segment near the surface up to the depth of 50 μm essentially did not migrate. As can also be seen in Fig.1(a) a surface layer about 50 μm thick of what looks like a layer of new recrystallized grains has formed. However, the misorientations between these

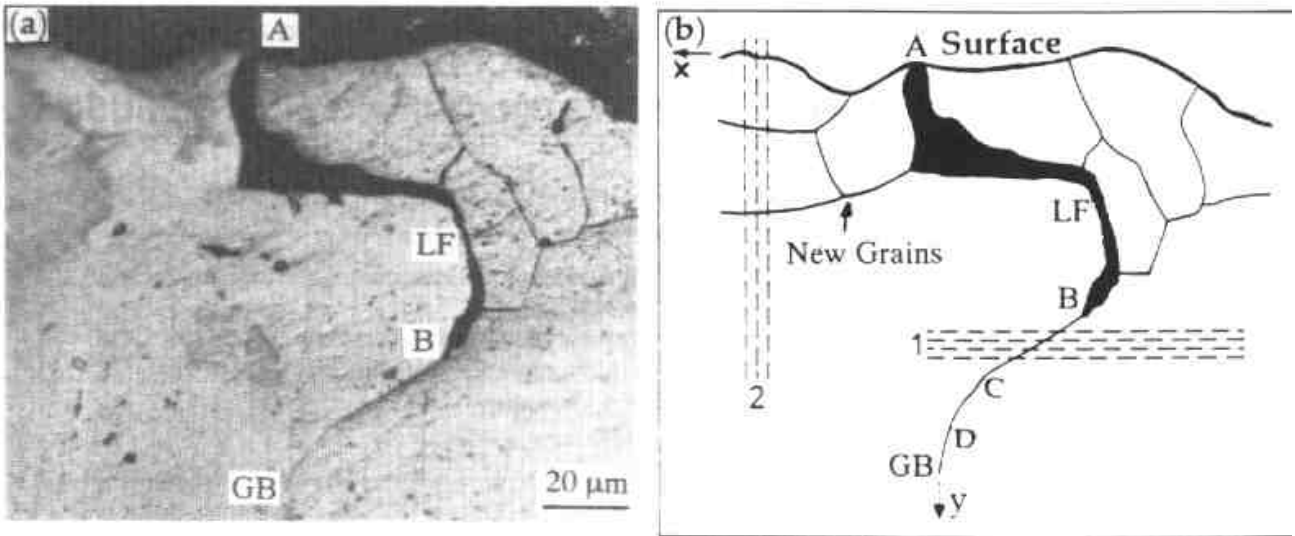FIG.1.(a) Photomicrograph of a specimen cross section perpendicular to the tilt axis of the 43°<001>[001] tilt GB showing wetting of the boundary from point A at the zinc coated surface to point B and migration of the liquid film (LF) and the grain boundary immediately below it. A layer of new grains presumably formed by diffusion induced recrystallization (DIR) is observed near the Zn coated surface. EBS measurements show that the mutual misorientations of these little grains do not exceed 6-7°. 850°C for 23 h. (b) Schematic diagram of (a) showing the locations of concentration profile measurements.
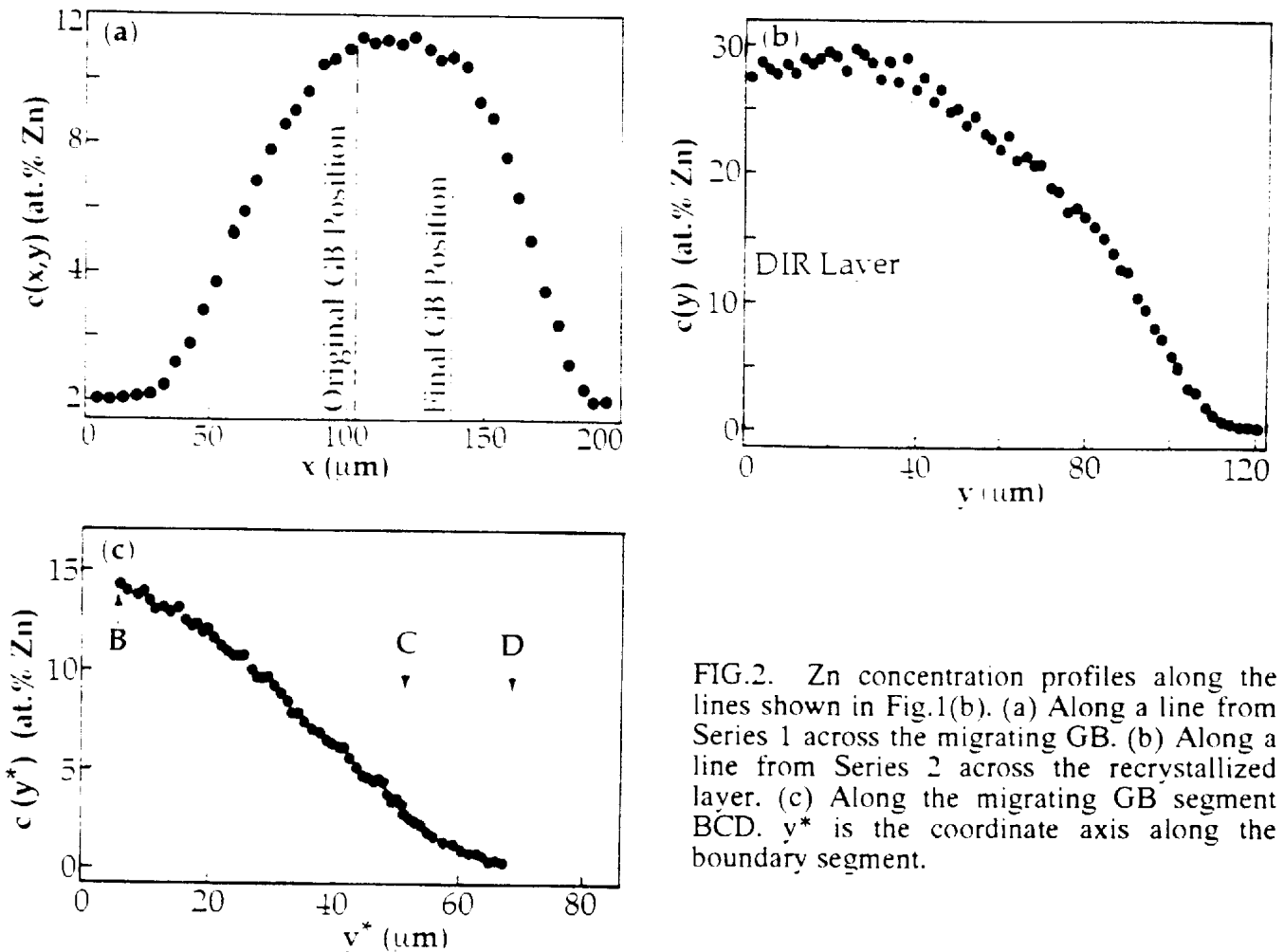

FIG.2. Zn concentration profiles along the lines shown in Fig.1(b). (a) Along a line from Series 1 across the migrating GB. (b) Along a line from Series 2 across the recrystallized layer. (c) Along the migrating GB segment BCD. y^* is the coordinate axis along the boundary segment.

new grains and between them and the underlying grains of the bicrystal measured with the aid of EBS do not exceed 6 - 7°. This means that only subgrain boundaries with little misorientation are formed during this DIR. The boundaries between these subgrains are eventually also wet by the Zn-rich melt

Figure 2 shows the Zn concentration profiles taken from the regions indicated in Fig.1(b). As can be seen from Fig.2(a) the profile c(x,y) (y = const) across a segment of the migrating GB along a line from Series 1 in Fig.1(b) shows that extensive diffusion occurred up to about 60 μm ahead of the migrating GB and that extensive interdiffusion of Zn and Fe occurred across the plane corresponding to the initial GB position. Within the region left behind the migrated GB the Zn concentration remained fairly constant at about 11 at.% at this depth. This enrichment of the material left behind the migrated GB in Zn plus the morphology of migration shown in Fig.1(a) strongly suggest that the GB and liquid film have migrated by DIGM [3] and LFM [4], respectively. From Fig.2(b), which shows the Zn concentration profile through the recrystallized layer along a line from Series 2 in Fig.1(b), it can be seen that the Zn concentration is fairly constant through the recrystallized grains at about 28 at.% Zn, although it exhibits some scatter about this value. Beyond the boundary of the last recrystallized grain there is a gradual drop-off in the Zn concentration with increasing depth. These observations are indicative of DIR [3], however, DIR with appreciable volume diffusion ahead of the last grain in the DIR layer.

Figure 2(c) shows the Zn concentration profile along the migrating boundary segment BCD, which was obtained from the Zn profiles along the line in Series 1 in Fig.1(b). As can be seen, the Zn content drops off almost linearly with increasing depth. It should be pointed out that the Al content along the various profiles was constant, indicating that Al did not play a role in the observed DIGM, LFM and DIR.

Considering the large amount of volume diffusion observed ahead of the migrating GB in Fig.1(a), the GB migration can be classified as the high temperature form of DIGM described by Tashiro and Purdy [5]. Until recently most reports of DIGM involved GB migration at such low temperatures that little if any volume diffusion of the diffusing element occurred in advance of the migrating GB [3]. In fact in the Fe-Zn system [6-8] the highest temperature for which DIGM was reported was 650°C [7]. For these temperatures the diffusion distance of Zn into the grain ahead of the migrating GB is estimated to be less than 0.2 nm [7].

In order to determine the volume interdiffusion coefficient D ahead of the migrating boundary and the GB diffusivity $s\delta D_b$ (here s is the GB segregation factor, δ is the GB width and D_b is the GB diffusion coefficient), Mishin and Razumovski's [9] steady state solution for the problem of diffusion along and out of a boundary migrating with a constant velocity v was used to analyse the Zn concentration profiles (Fig.2). According to [9] a more or less steady state concentration profile of diffusant develops ahead of a migrating GB whenever the GB migrates with a constant velocity v which is a least three times greater than the effective diffusional velocity $v_D = 2(D/t)^{1/2}$, of the diffusant atoms in the bulk. Here t is annealing time. Under the above condition, which exist for the GB in Fig.1(a), the concentration profile ahead of the boundary is given by

$$c(x,y) = c_0 \exp [-y(v/s\delta D_b)^{1/2}] \exp (-xv/D) \qquad (1)$$

In this equation c(x,y) is the Zn concentration at some distance x ahead of the migrating GB and some depth y below the surface and c_0 = c(y = 0). Figure 3(a) shows a plot of ln c(x,y) versus x for the part of the profile in Fig.2(a) ahead of the migrating GB. This GB segment migrated an average of 35 μm in 23 h. Thus v = $4 \cdot 10^{-6}$ m/s. Knowing the slope of the curve in Fig.3(a) to be 0.023 μm^{-1}, D is then found to be $7.9 \cdot 10^{-15}$ m^2/s. For comparison with the above value of D we determined D values from Zn concentration profiles formed at the initial position of the GB along a line from Series 1 in Fig.1(b) (D = $2.3 \cdot 10^{-15}$ m^2/s) and below DIR grains along a line from Series 2 in Fig.1(b) (D = $1.4 \cdot 10^{-14}$ m^2/s) using the error function solution for a pair of semi-infinite solids of different compositions [10]. These values of D agree within an order of magnitude of the values of $3.2 \cdot 10^{-15}$ m^2/s for Zn diffusion in α-Fe [11] and $1.6 \cdot 10^{-14}$ m^2/s for Zn diffusion in an Fe-5 at.% Si alloy [1]. The differences between the D values determined above probably result from assumptions such as that of a constant migration rate for the boundary. Perhaps the boundary initially migrated rapidly and then slowed down before reaching its final position. Also, those parts of the boundary near the surface probably migrated faster than those deeper in the specimen and D is proportional to
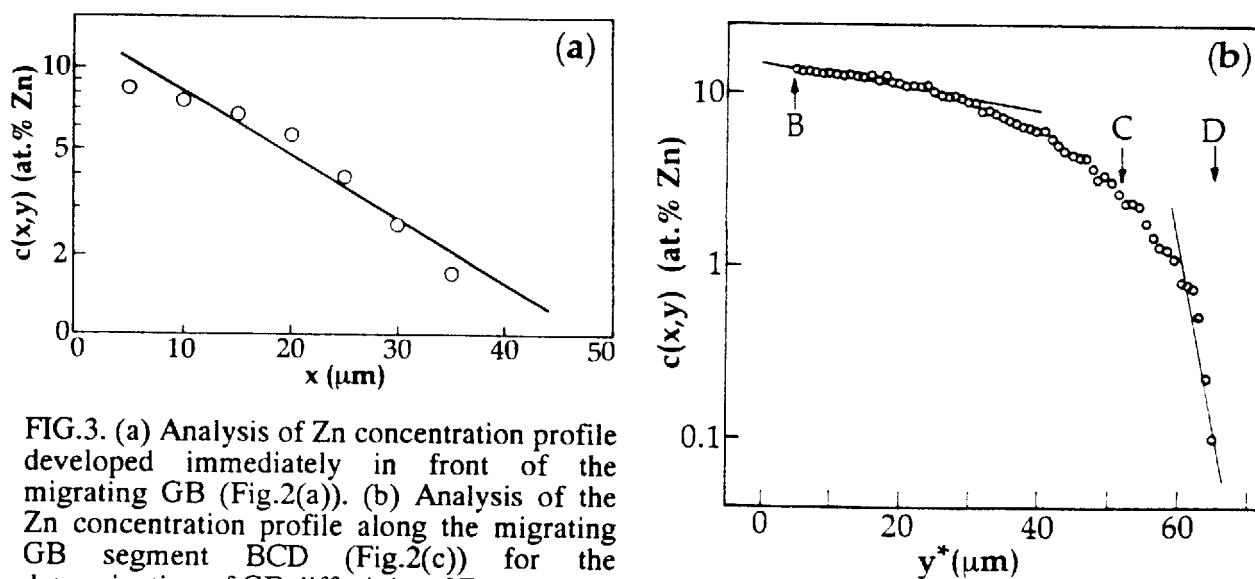
FIG.3. (a) Analysis of Zn concentration profile developed immediately in front of the migrating GB (Fig.2(a)). (b) Analysis of the Zn concentration profile along the migrating GB segment BCD (Fig.2(c)) for the determination of GB diffusivity $s\delta D_b$.

the assumed value of v. The deviations from the constant velocity assumption can account for about one order of magnitude in the calculated D values.

From equation (1) it can be seen that one can determine the GB diffusivity $s\delta D_b$ from the slope of a plot of ln c(y) versus y for the Zn concentration profile along the GB (Fig.3(b)) from B to D in Fig.1(b)) provided that one knows the GB migration rate v. Here the coordinate y^* denotes the position along the line BCD. As can be seen ln $c(y^*)$ exhibits a nonlinear dependence on y^* similar to that observed in [1,2]. Unlike α-Fe-Si alloys, however, no sharp transition from high diffusivity to low diffusivity is observed. From the slopes of the straight line segments fitted to data points in Fig.3(b) and the GB migration rate, $s\delta D_b$ values were determined. For the high diffusivity region $s\delta D_b$ is $1.6 \cdot 10^{-18}$ m³/s; for the low diffusivity region, $3.2 \cdot 10^{-20}$ m³/s. These values are about a factor 10 lower than the corresponding values ($1.5 \cdot 10^{-17}$ m³/s and $3.0 \cdot 10^{-19}$ m³/s) for the GB diffusion of Zn in an Fe-5 at.% Si alloy [1]. As $s\delta D_b$ is proportional to v, this may be the result of too low of an assumption for v.

ACKNOWLEDGEMENTS

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