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A TEM STUDY OF DIFFUSION-INDUCED GRAIN BOUNDARY MIGRATION IN Ni-Cu DIFFUSION COUPLES

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ABSTRACT

A study was conducted on defect structures, orientation relationships, and compositional profiles at DIGM boundaries in Ni-Cu diffusion couples. TEM revealed dislocations at the initial grain boundary positions of the DIGM zones in the Ni substrate. The misorientation between the DIGM zones and the matrix (across the dislocation wall) was determined by electron diffraction and found to be less than 0.5°. Cu profiles across the DIGM zones were obtained by TEM/EDS analysis. The formation of the dislocation wall is discussed in terms of the misorientation and lattice misfit between the DIGM zones and the matrix.

INTRODUCTION

Diffusion-Induced Grain Boundary Migration (DIGM) is a well recognized phenomenon in which solute diffusion along grain boundaries gives rise to motion of the boundaries (1). Two different mechanisms have been proposed to explain DIGM. One of these, the coherency strain model (2), states that stresses due to compositional inhomogeneity in the vicinity of a boundary during diffusion provide a driving force for DIGM. The other (3) (4) is based upon grain boundary dislocation climb caused by unequal boundary diffusivities of solute and solvent atoms. However, neither model can explain all of the DIGM-related observations recorded in the literature. Although many theoretical and experimental papers on DIGM have been published, only a few have involved TEM studies such as the work on bulk samples of Fe-Zn(2), Cu-Zn(5) (6), Al-Zn(7) and Al-4.7% Cu alloy (8). The scarcity of TEM data in the literature is probably due to difficulties in preparing TEM foils, since the DIGM zone occurs within a few microns of the original interface between the two phases (9). The purpose of this paper is to report our initial TEM studies of DIGM in the Ni substrate of Cu-Ni diffusion couples after annealing.

EXPERIMENTAL

High purity Ni bars (99.999%) were reduced to a thickness of 250 μm by multiple-pass cold rolling. The Ni strips were annealed at 900°C for 24h in Ar. The recrystallized Ni strips were then electropolished in an electrolyte containing 90% methanol and 10% perchloric acid at -20°C to reduce the thickness to approximately 150μm. The electropolished Ni strips were then electrodeposited with Cu in a solution consisting of copper sulphate and sulphuric acid. A Cu layer, 15 μm thick, was coated on each side of the Ni substrate to form a Cu-Ni-Cu sandwich. The diffusion couples so produced were sealed in pyrex capsules filled with purified Ar and annealed at 615°C for 26h. Disks of 3 mm in diameter were then spark-cut from the annealed Ni-Cu strips. In order to study the DIGM region adjacent to the original Ni/Cu interface, the following perforation method was used. First, the disks were protected on one surface by a thin PTFE foil and jet electropolished in an electrolyte consisting of 400 ml acetic acid, 300 ml phosphoric acid, 200 ml nitric acid and 100 ml distilled water at -15°C for 2 min. As a result, one layer of Cu was dissolved and the Ni substrate was thinned to about 20 μm. The disks were cleaned in distilled water and methanol and then jet polished on both sides using the conditions described previously, until perforation occurred. The second stage of jet polishing requires about 5 to 10 sec.
The TEM microstructure was studied with a HITACHI H-800, 200 kV TEM which was equipped for EDS microanalysis. X-ray microanalysis of Cu profiles across DIGM zones was performed using a probe size of 50 nm. The take-off angle for the X-rays was 69.5°. The EDS processing was carried out using an Apple II computer and Dapple software. Convergent beam diffraction patterns with a spot size of 0.1 μm were recorded in the area where EDS analysis was to be performed in order to measure the foil thickness. The foil thickness was found to be less than the maximum allowable limit using the Cliff-Lorimer approach without an absorption correction. The maximum allowable limit for Ni was calculated to be 2160 Å according to Tixier and Philibert (10).

RESULTS

In the present study, TEM observations were made in the Ni substrate in which fifteen boundaries were observed to migrate either in a single direction or in opposing directions by DIGM. Fig. 1 shows a representative boundary which has moved by DIGM in one direction. The initial grain boundary position is marked by a dislocation wall. The Cu concentrations along AB, CD and EF in Fig. 1 were obtained using EDS. These composition profiles gave similar patterns illustrated in Fig. 2, in which the zone swept by DIGM is seen to be Cu-rich.

Fig. 1 (left): A segment of grain boundary showing the initial position XY and the final position PQ after migration by DIGM. Note the dislocation wall at XY.

Fig. 2 (right): Cu concentration profiles along AB in Fig. 1 showing a Cu rich region in the DIGM zone. Cu profiles along CD and EF in Fig. 1 showed a similar pattern.
Fig. 3 shows grain boundary dislocations, ledges and the dislocation wall in the central area of the DIGM band shown in Fig. 1. The dislocations at the original grain boundary position were tangled, and some of them extended into either the DIGM zone or the matrix. The image was checked in different g vectors; the majority of the dislocations still remained visible, indicating that the Burger's vector of the dislocations is not unique. Misorientations between the DIGM zones and the matrix across the dislocation walls were measured using Kikuchi line analysis as shown in Fig. 4(a) and (b). Three different beam directions were chosen at positions DP1 and DP2 as shown in Fig. 3. The measured misorientations were 0.14°, 0.11° and 0.18° corresponding to the [002], [114] and [223] beam directions respectively. The misorientation measurements were also carried out at three different positions (AB, CD and EF) as indicated in Fig. 1, using a [114] beam direction. The results showed misorientations of 0.32°, 0.28° and 0.46° at AB, CD and EF, respectively.

Fig. 3 (left): Dark field image of the central part of the DIGM band in Fig. 1, showing the dislocation wall at the original boundary position, grain boundary dislocations and ledges at the migrated grain boundary.

Fig. 4(a) and (b) (right): A pair of Kikuchi/spot patterns taken at DP1 (matrix) and DP2 (DIGM zone) in Fig. 3 using a [114] beam direction. Fig. 4(a) was recorded by overlapping the Kikuchi and spot centres. Fig. 4(b) shows a small deviation between the two centres, corresponding to a 0.11° misorientation between the DIGM zone and the matrix.

A typical bi-directional migration of DIGM is shown in Fig. 5. Initially, the boundary migrated from position ABC to position EFC, leaving behind a dislocation wall at the original boundary position. Then, the part PC together with boundary CD moved backwards to form an S-shaped DIGM zone.

Fig. 5: The original boundary position is shown as ABCD. Initially, a boundary segment ABC moved by DIGM and stopped at position EFC. Then, segment PC migrated backwards, combining with the unmigrated segment CD and leaving a dislocation wall at FCD.
Cu concentration profiles along PQ and XY in Fig. 5 are plotted in Fig. 6(a) and (b) respectively. A peak concentration (22 wt% Cu) occurred just behind the dislocation wall in the second DIGM zone (line XY) which is higher than the value of 15.5 wt% Cu in the first DIGM zone (line PQ). The measured misorientations across the dislocation wall in the first DIGM zone (PQ) are 0.21° and 0.18° using beam directions of [114] and [002] respectively. Fig. 7 shows relatively uniform arrays of dislocations at an original boundary position in another DIGM region. Cu concentrations across the wall were found to be 4.5 wt% in the matrix and 19.5 wt% in the DIGM zone. The misfit parameter was estimated to be 0.4%, and the misorientation across the wall was found to be 0.2° in a [114] beam direction.

Fig. 6(a) (left): Cu concentration profile measured by EDS along the line PQ in the first DIGM zone shown in Fig. 5. Note the peak (15.5 wt% Cu) at the dislocation wall in the DIGM zone.

Fig. 6(b) (right): Cu concentration profile measured by EDS along the line XY in the second DIGM zone in Fig 5, showing a higher peak (22.5 wt% Cu) at the dislocation wall in comparison with that (15.5 wt% Cu) in Fig. 6(a).

Fig. 7: A dislocation wall at the original boundary position in a DIGM zone. The dislocation arrays have a misfit of 0.4% and a misorientation of 0.2° between the DIGM zone and the matrix.

DISCUSSION

Dislocation walls at the original grain boundary position have been observed in several DIGM systems (2),(5),(9). Hillert and Purdy (2) reported that the dislocation wall contained a misfit array in the Fe-Zn system. However, Grovenor (11) argued that the dislocations constituted a low angle boundary in the Au-Cu thin film samples. Recently, Hackney et al (5) pointed out that there was a small misorientation across the dislocation wall in the Cu-Zn system, although no experimental measurements were reported. In the present study, the steep Cu concentration gradient at the original grain boundary positions and the small misorientations (less than 0.5°) across the dislocation walls indicate that these dislocation arrays appear to have both lattice misfit and misorientation characteristics.

The presence of the dislocation wall at the original boundary position may be rationalized in terms of Hillert's coherency strain model on the basis of stress relaxation leading to the initiation of boundary migration. According to Hillert, the coherency strain energy can be estimated as follows (8):
\[ \Delta G = \frac{E \eta^2}{1 - \nu} (X_2 - X_1)^2 \]  

(1)

where \( E \) is Young's modulus, \( \eta \) is the coherency strain, \( \nu \) is Poisson's ratio, \( X_1 \) is the bulk concentration of the solute, and \( X_2 \) is the concentration at the grain boundary. For Ni, \( E = 2.07 \times 10^5 \text{MPa} \) (12) and \( \nu = 0.3 \) (13), with the measured compositions \( X_2 = 0.184 \) (19.5\% Ni), \( X_1 = 0.042 \) (4.5\% Cu), and the calculated value of \( \eta = 0.2\% \).

For Ni, the DIGM zone value indicated by the present results. Hackney et al. (5) estimated the coherency strain energy of one order of magnitude too small as defined previously, \( \delta \) is the boundary energy, \( K \) is the boundary curvature. They also found a value of coherency strain energy of one order of magnitude too low for the observed curvature. However, they pointed out that the coherency strain energy calculation result does not invalidate the coherency strain theory, and suggested that an additional driving force may be present.

Cu concentration steps across the original grain boundary positions shown in Fig.6(a) and (b) resulted in a 0.28\% coherency strain at the initially migrated DIGM segment of the boundary and a 0.46\% coherency strain at the second. The larger coherency strain (0.46\%) may not be necessary to provide a larger coherency strain energy, since the driving force would also depend on the orientation dependence of the elastic modulus (15). The DIGM directions in the neighboring grain were not determined, so that the exact elastic moduli in the two directions are unknown. However, it is clearly shown that the direction of initial movement (from P to Q in Fig.5) corresponds to the smaller coherency strain (0.28\%).

The phenomenon of the same boundary moving in both the forward and backward directions is difficult to explain by the dislocation climb model. This model predicts that the structure of the boundary determines the direction of migration. A reversal in the direction of migration would require change in the dominant set of grain boundary dislocations at various positions of the same boundary.

SUMMARY

This paper reports on the first TEM study of DIGM in a Cu-Ni bulk system. The grain boundaries in the Ni substrate were observed to move either in a single direction or in opposing directions by DIGM. The initial boundary positions are outlined by dislocation walls which have both misfit (0.2 to 0.4\%) and misorientation (<0.5\%) characteristics. The coherency strain energy (driving force) was estimated as \( 1 \times 10^5 \text{j/m}^3 \), which is one order of magnitude smaller than that required for the DIGM process. It is suggested that an additional driving force for the initiation of the DIGM process may be required.

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