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OF SURFACE-REACTIVE METALS PREPARED BY
VACUUM WELDING

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GRAIN BOUNDARIES IN THIN-FILM BICRYSTALS
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ABSTRACT

A technique for preparing thin-film bicrystal specimens of surface-reactive metals containing grain boundaries of controlled geometry was developed. Epitaxial films were deposited on oriented substrates and were then welded together face-to-face in situ under vacuum. Low angle twist boundaries in copper and aluminum prepared by this technique contained grids of primary dislocations as shown by transmission electron microscopy. Grids of secondary grain boundary dislocations were detected in high angle $\langle 111 \rangle$ twist boundaries at twist angles near the high coincidence density $\Sigma=3$ misorientation. The potential use of the technique in the study of interphase interfaces was pointed out.

1. INTRODUCTION

An extensive series of electron microscope studies of grain boundaries (see Balluffi, Komen and Schober, 1972; Balluffi, Woolhouse and Komen, 1972) has been carried out in our laboratory using thin-film bicrystal specimens of controlled geometry which are fabricated by pressure welding. In order to prepare these specimens single crystal thin-films of the required orientation are first grown on oriented single crystal substrates using vapor deposition (Wagner 1974). Thin-film bicrystals of the desired geometry are then obtained by pressure welding these films, while still on their substrates, together face-to-face at the required misorientation at a moderate temperature (Schober and Balluffi 1969). The misorientation between crystals and the orientation of the grain boundary plane can be controlled to within approximately $\pm 0.5^\circ$ (see Wagner 1973). The substrates are then dissolved away, and the bicrystal specimens can then be studied conveniently at normal incidence by transmission electron microscopy.

So far, the welding step has been carried out in air, and the technique has therefore been restricted to non-surface reactive materials such as the noble metals gold and silver.

In the present note we describe an extension of the technique in which the entire process is carried out in situ in vacuum. Applications of the technique to the study of several low and high angle grain boundaries in aluminum and copper are described.

2. EXPERIMENTAL

The apparatus, which is entirely enclosed in vacuum, is shown schematically in Fig. 1. Two oriented rocksalt substrates, clamped to individual heaters, are located symmetrically around the retractable central evaporation source. Epitaxial thin films are then deposited simultaneously on the substrates, and the evaporation source is retracted. The two thin-films are finally welded together by forcing the pressure plate assembly against the fixed backplate assembly. After cooling, the welded sandwich is removed from the vacuum system, and the substrates are dissolved away.

For example, in order to produce bicrystals of aluminum containing $\langle 001 \rangle$ twist boundaries {100} cleaved rocksalt substrates were mounted on the heaters at various twist angles and were maintained at 400°C . A vacuum of 1×10^{-9} Torr was achieved in an all-metal system with an oil diffusion pump and a Granville Phillips cold trap. Also, a 500 l/sec titanium sublimation pump operated in the main chamber. Optical baffles retarded titanium contamination, and the titanium filaments were not flashed once evaporation had commenced. A pre-measured amount of aluminum was evaporated from the source by means of resistance heating. Through careful positioning of the substrate assemblies an equal epitaxial film of aluminum, about $2000 \text{ \AA}$ thick, was deposited on both substrates at 400°C . After the evaporation of the aluminum film it was necessary to wait

until the substrates had cooled to 125°C before welding. (If higher temperatures were used, the grain boundary in the mid-plane of the specimen was lost as a result of grain boundary migration.) Since it took over an hour to cool to this temperature, the ultra high vacuum environment was needed to prevent the formation of any oxide film. After welding the compression was maintained during cooling to room temperature.

Boundaries in aluminum and copper of the types listed in the Table were produced by this general technique.

Aluminum grows epitaxially on {100} NaCl either in the form of {100} single crystal films or else as {111} large-grained polycrystals (Pashley 1956). In the latter case the individual grains are rotated around $\langle 111 \rangle$ with respect to each other by angles which are multiples of 30°. For copper, {001} films may be grown at a temperature of 200°C by a modification of a method described by Schober (Schober 1969). Of particular interest were high angle $\langle 111 \rangle$ twist boundaries in aluminum having twist angles near the critical angles $\theta_c = 27.8, 38.2$ and 60.0° which correspond to exact high density coincidence site situations with $\Sigma = 13, 7$ and 3 respectively (Brandon, Ralph, Ranganathan, Wald 1964). Here Σ = density of atoms divided by the density of coincidence lattice points. Such boundaries would be expected to contain grids of secondary grain boundary dislocations (GBD's) which might be visible by transmission electron microscopy (Balluffi, Komen and Schober 1972).

3. RESULTS

All of the boundaries produced by the present techniques appeared "normal" in every respect. No evidence was found for oxide inclusions or any other features which could be attributed to the surface-reactive characteristics of aluminum or copper.

The low angle $\langle 100 \rangle$ twist boundaries in both aluminum and copper consisted of square grids of lattice screw dislocations with Burgers vectors $a/2\langle 110 \rangle$ and were indistinguishable from those observed previously (Schober and Balluffi 1969) in gold bicrystals which were welded in air.

The low angle $\langle 111 \rangle$ twist boundaries in aluminum consisted, as expected (Schober and Balluffi 1969), of hexagonal networks of lattice screw dislocations with Burgers vectors $a/2\langle 110 \rangle$ as seen in Fig. 2 (see Fig. caption for details).

In the high angle $\langle 111 \rangle$ twist boundaries hexagonal networks of secondary screw GBD's were found at twist angles in the vicinity of $\theta_c = 60.0^\circ$ corresponding to the $\Sigma = 3$ coincidence situation. These dislocations have Burgers vectors $a/6\langle 211 \rangle$, and the appearance of a typical grid under a $\vec{g} = \langle 220 \rangle$ diffraction condition is shown in Fig. 3 (see Fig. caption for details). Despite considerable effort, we were unable to detect secondary dislocation networks at twist angles near $\theta_c = 38.2^\circ$ ($\Sigma=7$) or $\theta_c = 27.8^\circ$ ($\Sigma=13$).

4. CONCLUSIONS

We conclude that thin-film bicrystals of surface-reactive metals containing grain boundaries of controlled geometry can be fabricated successfully by the present method. In general, the technique should be applicable to any material that can be epitaxially deposited on a suitable substrate. We also note that it should be possible to fabricate a wide variety of interphase boundaries as well as grain boundaries, by the method.

The observation of the secondary GBD networks near $\theta_c = 60.0^\circ$ ($\Sigma=3$) is of interest, since this represents the first observation of networks of this type. Other secondary GBD networks were undoubtedly present at angles near $\theta_c = 27.8$ and 38.2° . However, it appears that they were not detected because of their smaller Burgers vectors (Balluffi, Komen and Schober 1972) and difficulties caused by the long extinction distance of aluminum (Thölen 1970).

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Table. Types of boundaries produced in the present work

Metal	Boundary Description	θ (deg)	Σ
Al	low angle $\langle 100 \rangle$ twist	0-2	-
	low angle $\langle 111 \rangle$ twist	0-3	-
	high angle $\langle 111 \rangle$ twist	≈ 27.8	13
		≈ 38.2	7
		≈ 60.0	3
Cu	low angle $\langle 100 \rangle$ twist	0-7	-

FIGURE CAPTIONS

- Figure 1 Apparatus for producing thin-film bicrystal specimen. Entire apparatus is enclosed in vacuum manifold.
- Figure 2 Hexagonal network of lattice screw dislocations with $\vec{b} = a/2\langle 110 \rangle$ in low angle $\langle 111 \rangle$ twist boundary in aluminum. (Middle) A segments parallel to $\vec{g}$ in strong contrast. (Bottom) B and C segments in contrast, and A segments (perpendicular to $\vec{g}$) out of contrast.
- Figure 3 Hexagonal network of secondary screw grain boundary dislocations with $\vec{b} = a/6\langle 211 \rangle$ in high angle $\langle 111 \rangle$ twist boundary in aluminum. $\theta \approx 60^\circ$, $\Sigma=3$. Hexagonal network in same orientation as top of Fig. 2. B and C segments in contrast, and A segments (perpendicular to $\vec{g}$) out of contrast. (Note similarity to Fig. 2 (Bottom)).

Figure 1

Figure 2

Figure 3