THE MICROSTRUCTURE OF THE $\zeta \rightarrow \beta'$ TRANSFORMATION IN THE Ag-Cd SYSTEM

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Summary

The $\zeta \rightarrow \beta'$ isothermal transformation in Ag-Cd was studied using X-rays and the development of ζ/β' interphases was observed using high resolution optical microscopy (1680x-0.4μm resolution).

Interphases showing macroledges ($\simeq$1μm) were observed to grow by lateral movement of these macroledges. A value of 75kJ/mol was obtained for the activation energy of this process. It is suggested that barriers to growth exist that give rise to the formation of this macroledges.

The significate of the value of the activation energy Q_r = 67kJ/mol obtained by Kittl, Serebrinsky and Gomez from resistivity measurements of the same trasnformation is discussed on the light of these results.

Introduction

Since Aaronson (1) first developed his theory of crystal growth, introducing the idea of plane interfaces with microledges and postulating their lateral motion, many studies of the interfaces in different solid state transformation have been completed and confirmed his assertions.

In the Ag-Cd alloys at about 50% at. (2), we may notice remarkably neat macroledges of about 1 μm in the plane interphases ζ/β' developed during the transformation ζ (disordered hcp) $\rightarrow \beta'$ (ordered bcc).

An analysis is made in the present work of the frequency and thickness of the observed macroledges, and also of the way they move. Results are discussed considering the X-ray observations and the values of Q_r obtained by resistivity (3) and hot stage observations (4).

Experimental

a. Alloys 49, 50 and 51% at.Cd were prepared from Ag and Cd 99.999% (6). Metallographic observations were performed upon disk 3 mm in height, after mechanical polishing and then electropolishing with a 10% CNK solution in water (4). Samples were annealed in a silicone oil bath at 290°C for 30 minutes and quenched in carbon tetrachloride at 0°C, so as to hold the high temperature ζ phase, from which the $\zeta \rightarrow \beta'$ transformation started. The grain size obtained was of about 1 millimeter.

b. In order to observe the motion of the several ζ/β' interphases, high magnification optical observations (1680x-0.4μm resolution) were made after each successive isothermal annealing (30-10 minutes) at low temperatures (70°C-50°C). There was not intermediate polishing. Both the morphology of the interphases and the form in which they advance became evident through these experiments carried out in a Gebrüder Haake thermostat model FT ($\pm$ 0.01°C).

c. Orientation relationships between the initial ζ phase and the final β' phase were determined with X-ray (5). An hexagonal monocrystal (a ζ grain of approximately 1 mm^2 separated from a polycrystalline disk 0.3 mm thick of a sample 49% at.Cd) mounted on a goniometric head coupled to a Laue chamber, was used. The monocrystal suffered successive annealings "in situ" at 80°C, 30 minutes long each. The advance of the transformation was followed by corresponding reflection diffraction diagrams. Radiation of a cobalt tube was employed.

Results

a. X-ray

Fig. 1 shows the diffraction diagram obtained after 120 minutes "in situ" heating of a monocrystal, in which the [0001] direction was approximately parallel to the incident beam. It is clear how begin to appear Debye rings (which result from diffraction of Co K_α and K_β lines on planes of the β' phase) that coexistent with the initial diagram. The rings, that become more intense as the non-transformed fraction decreases, indicate that most β' crystal grow from a ζ crystal hold by quenching without orientation relationship (*). A certain texture may be noticed, however, (the regions of

(*) It is interesting to remark that, despite this result, the angles formed by the interphases under which the β' phase advances, attain only certain particular values: 90°, 113°, 140° and 153° (6).

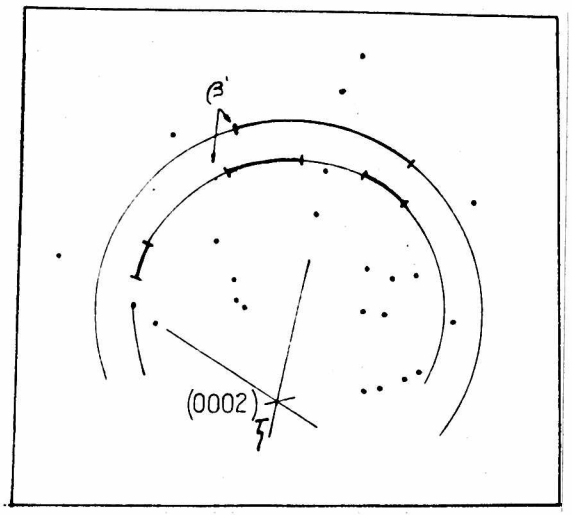

Fig. 1 Diffraction diagram obtained after 120 min. "in situ" heating of a ζ monocrystal.

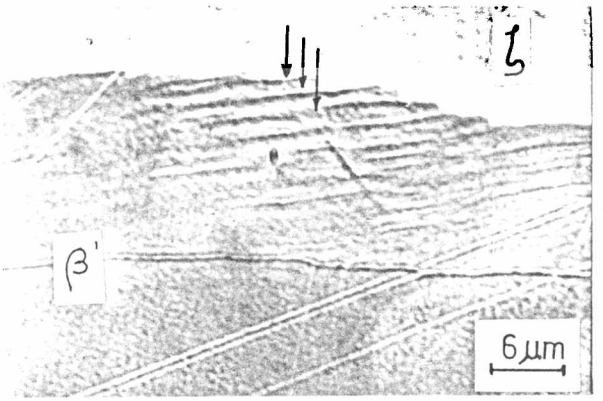

Fig. 2 Interface ζ/β' . Arrows indicate relief marks between the macroledges.

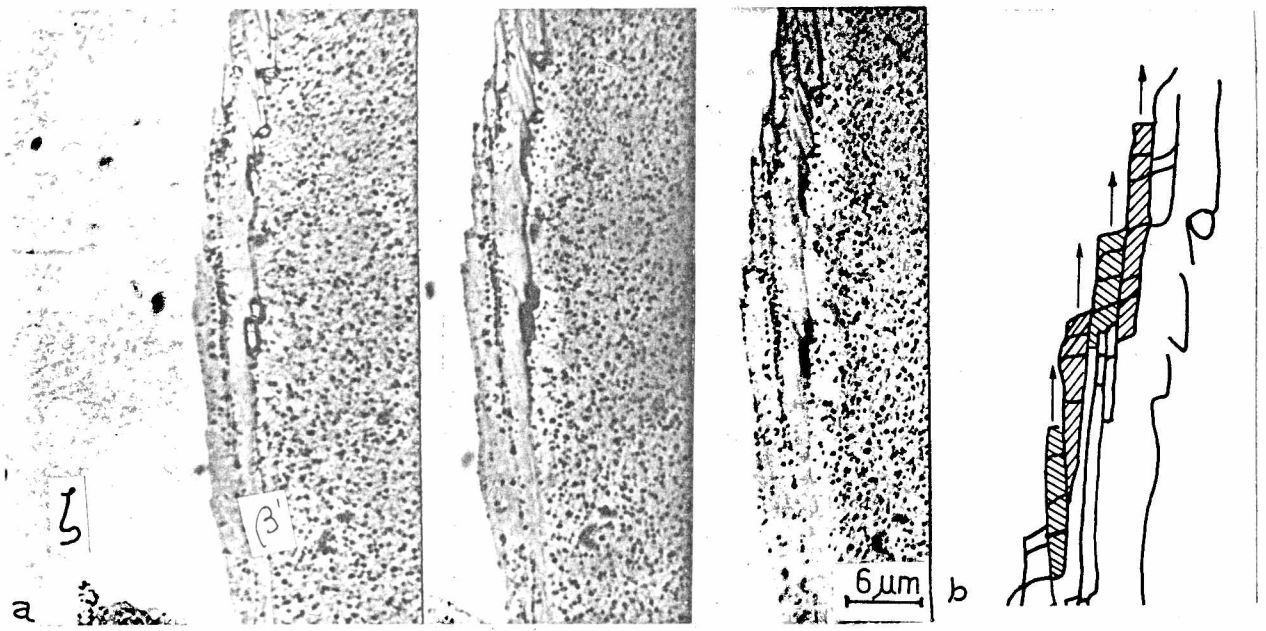

Fig. 3 a. The same interphase of Fig. 2 after annealing in air at 70°C. A preferential attack may be seen in the boundary of each macroledge. Photography each 10 minutes.

b. Successive positions of the macroledges.

greater intensity within each ring) and may be associated to higher frequency of β' crystals that growth with orientation relationship (5).

b. Observations under high magnification.

These observations (1680x) suggest two groups of ζ/β' interphases: 1) irregular interphases and 2) interphases presenting certain geometrical characteristics with predominance of plane interphases with macroledges (heigth ap-

proximately 1 μm).

Fig. 2 shows an interphase obtained after 270 minutes annealing at 100°C in silicon oil.. A typical macroledges growth may be seen. Arrows indicate reliefs marks between successive macroledges positions.

Fig. 3 shows the same interphase of Fig. 2 after further annealings in the thermostat at 70°C. A preferential attack may be seen in the boundary of each macroledge positions. The motion of the interphase is due only to the lateral advance of macroledges.

The experimental activation energy for the lateral advance of macroledges was calculated from these experiments at 50°C and 70°C (Fig. 3b). The result was 75 kJ/mol ± 15 kJ/mol.

Discussion

a. Interphases

Relief mark appearing on plane interphases after each ledge has passed (Fig. 2), together with the preferential attack on the border during annealing in air (Fig. 3) and the independent lateral advance of each ledge allow us to postulate that each macroledge is a "layer" of β' phase that grows by incorporating atoms to its edge. To explain this morphology of growth, barriers must be assumed and must account the fact that perpendicular growth stops during the period of lateral growth. Experimental results (6) allow us to reject the following phenomenon as origin of the barriers: a) α and γ precipitates; b) ζ phase defects and c) thermical effects. This, together with the fact that certain of β' grains are observed to growth orientated with respect to the initial ζ grain, lead us to postulate in this case the existence of certain crystallographic configurations of boundary energy low enough, as the origin of barriers (primary barriers (B_p)). These configurations might be well matching interfaces with a high density of coincidence sites (1). These primary barriers enable microledges formation and from that moment onwards the microledges would start growing laterally. Lateral growth would stop, however, when the edge of the microledge found an obstacle (another low energy ζ/β' configuration, for example) constituting a secondary barrier (Bs). This might stop the lateral growth of successive microledges until the whole set attained such a size that the new front might start, again, growing laterally. We may say then that the observed successive macroledges are formed by aggregates of microledges which advance simultaneaously after breaking the secondary barrier (the energy associated to the new volume of β' phase being formed < the energy associated to the secondary barrier). Their frequency and height in different interphases would depend on the quotient between the energies E_p and E_s associated to the barriers B_p and B_s respectively (E_p being always less than E_s). Taking into account the angular dispersion corresponding to regions of greater intensity in the X-rays diagram, and considering they are associated to the diffraction that results from β' crystals growing by interphases with ledges, we may assume that successive macroledges in an interphase are slightly disorientated.

b. Activarion energy.

Activation energies were calculated from perpendicular displacement of different interphases from measurements performed in hot stage (40x-100x) at different temperatures (4). The mean value obtained for the experimental activation energy is 78 kJ/mol. Comparing this result with the activation energy computed from measurements of resistivity (Q_r) for the $\zeta \rightarrow \beta'$ transformation (3), the values coincide within the experimental error.

This same value of Q_r also coincide within the error with the activation energy Q measured for the lateral motion of ledges. Thus, the activation energy computed from measurements of resistivity might be interpreted as a mean value resulting from averaging the Q_i associated to the motion of the different interphases, or as the activation energy of the basic interphase motion process. This last alternative becomes more relevant by observing that coincident values of Q have been found for the same transformation from variations of different volumentric magnitudes (3).

Conclusions

a. Some ζ/β' interphases developed during the $\zeta \rightarrow \beta'$ transformation show macroledges approximately 1 μm high.

b. The observed macroledges may be considered as β' phase "layers" slightly disoriented, which grow independently by lateral motion with an activation energy of 75 kJ/mol. Each layer would be formed by microledges of certain net parameters in height developed along planes corresponding to low energy interfaces which might constitute a primary barrier to growth. Macroledges formation would be the result of a secondary barrier.

c. There might exist a fixed orientation relationship between the ζ phase and β' crystals presenting macroledges in the interphases.

d. The activation energy computed from measurements of variations different volumetric magnitudes might be interpreted as the activation energy of the basic interphase motion process.

References

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