PHASE TRANSFORMATIONS INDUCED BY IRRADIATION WITH IONS IN β Cu-Zn-Al SINGLE CRYSTALS

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***Abstract*— Single crystals of β Cu-Zn-Al alloys were irradiated with 30 keV Ar ions at room temperature to fluences in the range of 1 to 6 displacements per atom (dpa). The microstructural changes induced by the irradiation were investigated with transmission electron microscopy. Specimens with two different surface orientations, $(100)_\beta$ and $(011)_\beta$, were studied. In specimens with $(100)_\beta$ surface orientation a new phase with a hexagonal close packed structure was formed due to the ion irradiation. The orientation relationship with the matrix was of the type:**

$$(0001)_{Hex} \parallel (0\,\bar{1}1)_\beta\ ;\ [1\,\bar{1}0\,0]_{Hex} \parallel [011]_\beta$$

In specimens with $(011)_\beta$ surface orientation, the hexagonal structure was not observed. Instead, small precipitates of the γ phase with a mean size of 8 nm were found. The results are discussed in comparison with previous ion irradiation experiments and with similar phase transformations occurring in β Cu-Zn-Al alloys.

***Keywords*— Radiation effects, Cu-Zn-Al alloys, transmission electron microscopy, phase transformations, phase stability.**

I. INTRODUCTION

Phase stability in Cu-Zn-Al alloys is related to the electron concentration, that is, the number of conduction electrons per atom (e/a). At an e/a around 1.5, the equilibrium β phase at high temperature has a disordered body centered cubic (bcc) structure. At a lower e/a the α phase with a disordered face centered cubic (fcc) structure is found and at higher e/a the γ phase is formed, with a complex cubic structure.

On cooling the β phase from high temperatures, two ordering transformations occur: at about 800 K the B2 structure is formed which involves the ordering of nearest neighbours. At a lower temperature, which depends on composition, the $L2_1$ structure is formed which involves the ordering of second neighbours. The stability of the β phase at high temperature is due to the high vibrational entropy characteristic of the bcc structure. However, it is possible to retain the β phase at room temperature by quenching or even by air cooling (the latter is only possible at $e/a \approx 1.48$, which corresponds to the maximum stability of the β phase).

The metastable β phase at room temperature presents martensitic (diffusionless) transformations to close packed structures, named 6R, 18R and 2H, which differ in the stacking sequence of the close packed planes. They can be described as a face centered tetragonal (fct) lattice into which regular basal plane stacking faults are introduced every third plane (18R), or every second plane (2H). The 6R structure is that with no stacking faults. The transformation temperature is strongly composition dependent and can be varied between 0 and 400 K. These martensitic phases inherit the atomic order of the β phase. When diffusion is allowed in these phases, the degree of order is modified. This change is accompanied by changes in the lattice parameters and by an increase in the transformation temperature to the β phase. This process has been named stabilisation. More information about the phase stability of the β and martensitic phases can be found in the review by Ahlers (1986).

Irradiation with different kinds of particles (electrons, ions or neutrons) with energies in the keV or MeV range may be used to study phase stability in alloys (Wollenberger, 1994). One effect of irradiation is to introduce a high concentration of point defects, which substantially enhance diffusion. This enhancement may accelerate the evolution towards thermodynamic equilibrium. On the other hand, the flux of point defects to sinks may produce segregation, resulting in nonequilibrium microstructures. It is then possible to obtain information about the phase stability of a system by studying its evolution under irradiation.

Previous ion irradiation experiments in β phase Cu-Zn-Al have been carried out in order to study the influence of irradiation on the martensitic transformation and phase stability in these alloys (Tolley and Abromeit, 1995; Tolley and Abromeit, 1999). The β phase was irradiated at room temperature with a 300 keV Cu ion beam at the Hahn-Meitner Institute in Berlin. The microstructural changes were studied with transmission electron microscopy (TEM). Copper ions were chosen because they are the main component of the alloy. The energy of 300 keV produces an approximately homogeneous damage in a depth of about 100 nm, which is the typical thickness that is studied with TEM. The main results were the following:

a. Second neighbour order was completely destroyed and first neighbour order was partially reduced.
b. γ phase precipitates were formed.
c. A hexagonal close packed structure was formed on the surface of the irradiated specimens with 001 surface orientation.

In order to continue studying these effects, new experiments were designed using the available ion irradiation facilities at Centro Atómico Bariloche. A 30 keV Ar ion beam was chosen, which produces displacement cascades in the material, and is therefore expected to produce qualitatively similar effects as those of 300 keV Cu ions. Differences could arise, however, due to the shorter penetration of the Ar beam of less than 30 nm. In this work the first results are presented. It is shown that similar effects to those produced by the 300 keV Cu ion beam are observed in the microstructure of β phase Cu-Zn-Al alloys.

II. EXPERIMENTAL

Single crystals of a Cu-22.7% Zn-12.7% Al alloy (atomic %) were used for the experiments. At this composition the martensitic transformation temperature (M_S) is around 80 K and the electron concentration is 1.48. The alloy was prepared by melting the pure metal components in sealed quartz capsules in an electrical resistance furnace. The single crystals were then grown by the Bridgman method. Specimens in the form of discs with a diameter of 3 mm and a thickness of 0.2 mm, suitable to fit the TEM specimen holder, were cut with a diamond wheel saw. Two kinds of specimens were prepared, with different surface orientation: (i) close to $(100)_\beta$ and (ii) close to $(011)_\beta$. The discs were annealed at 1123 K for 20 minutes and air cooled to room temperature.

The surface was prepared for irradiation by electropolishing using a TENUPOL double jet equipment, with one of the jets blocked. The electrolyte was a solution containing phosphoric acid, isopropyl alcohol, ethanol, water and urea. The polishing time was around 1 minute with a current of 80 mA, at a temperature between 278 K and 283 K. The specimens were irradiated at normal incidence at room temperature in an accelerator run by the Atomic Collisions Group at Centro Atómico Bariloche. A current density of 6.5 nA/mm^2 was used, which is equivalent to 4×10^{12} ions/cm^{2}s. After irradiation, the surface was covered with lacquer and polished from the opposite side to perforation. The lacquer was carefully removed in an acetone bath followed by rinsing with ethanol. The specimens were examined in Philips EM300 and CM200 TEMs.

The displacement cross section was obtained using simulation with the TRIM code (Biersack and Haggmark, 1980), using a displacement threshold of 25 eV. The average displacement cross section within the first 20 nm was found to be 2.1×10^{-15} cm^2, using an atomic volume of 13.4 Å^3. At larger thickness the cross section drops rapidly. The dose rate corresponding to the current density used in the experiments was of 8.8×10^{-3} dpa/s.

III. RESULTS

A. [100] Surface Orientation.

In Figs. 1 (a) and (b) the diffraction patterns corresponding to an unirradiated specimen and a specimen irradiated with 30 keV Ar to a fluence of 6.5 dpa (3×10^{15} ions/cm^2), respectively, are shown.

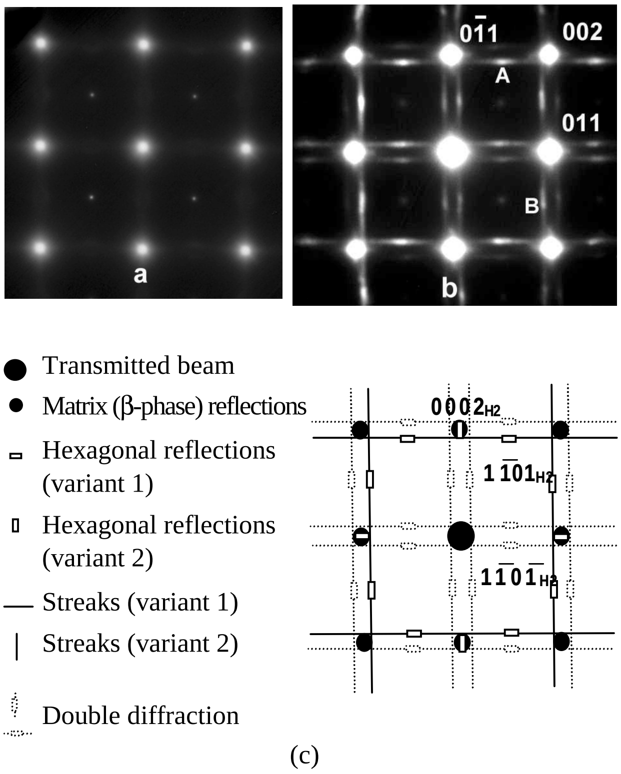


Figure 1. [100] zone axis diffraction patterns; (100) surface orientation. (a) Unirradiated specimen; (b) irradiated with 30 keV Ar ions to a fluence of 6.5 dpa. (c) Description of pattern (b).

Additional reflections to those of the matrix are clearly observed in between the 011 and 002 type reflections of the matrix (for example A and B). Streaks through the additional reflections, perpendicular to the 001 type planes, are also present.

In Fig. 2, dark field images obtained from reflections A and B are shown. The regions that contribute to each reflection have irregular shape and are complementary with each other. Within the regions, a contrast of fine striations is observed, which indicates a large density of stacking faults. These faults also cause the streaks in the diffraction patterns.

The additional reflections can be indexed as two perpendicular variants of a close-packed hexagonal structure, with the following orientation relationships with the matrix (Fig. 1 (c)):

Variant 1: $(0001)_{Hex} \parallel (011)_{\beta}$ and $[1\ \bar{1}\ 0\ 0]_{Hex} \parallel [0\ \bar{1}\ 1]_{\beta}$
Variant 2: $(0001)_{Hex} \parallel (0\ \bar{1}\ 1)_{\beta}$ and $[1\ \bar{1}\ 0\ 0]_{Hex} \parallel [011]_{\beta}$

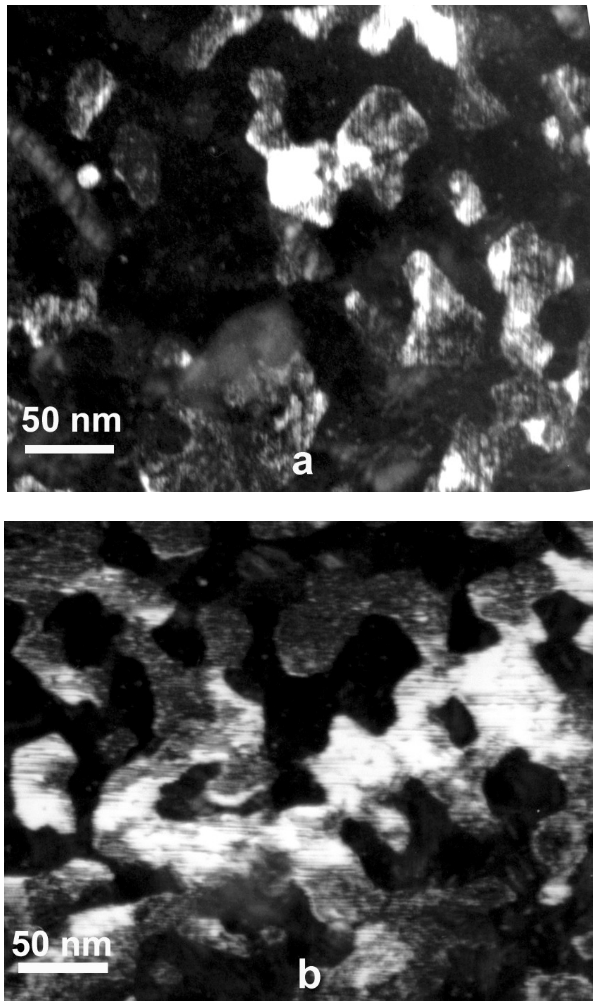
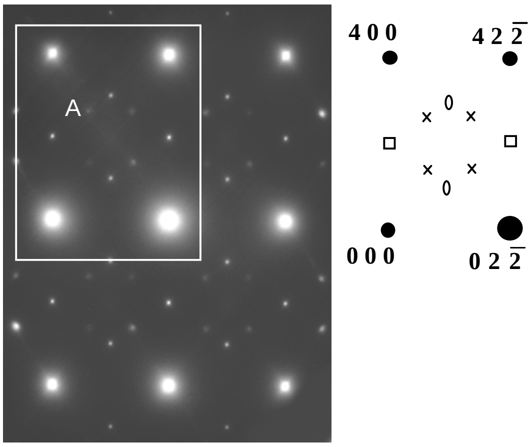


Figure 2. Dark field images obtained from additional reflections in Fig. 1(b). (a) Reflection A (hexagonal variant 1); (b) reflection B (hexagonal variant 2).

These results indicate that the irradiation induced a phase transformation from the β phase to a new phase with a hexagonal structure. Two variants are formed with their basal planes perpendicular to each other.

B. [011] Surface Orientation.

In specimens with (011) surface orientation only irradiations to fluences of about 1 dpa were studied. In Fig. 3, a diffraction pattern along the [011] matrix zone axis obtained in a specimen irradiated to 1.3 dpa (6.4 x 10^{14} ions/cm^2) is shown. Additional reflections to those of the β phase are present, which correspond to γ phase precipitates (Lovey *et al.*, 1984). In Fig. 4, a dark field image obtained from reflection A (Fig. 3) is shown. Small spheroidal precipitates with a mean size of 8 nm can be seen.



- ● Transmitted beam
- • Matrix fundamental reflections
- □ First neighbour order reflections (B2)
- 0 Second neighbour order reflections ($L2_1$)
- × Additional γ phase reflections.

Figure 3. Diffraction pattern along the [011] matrix zone axis, obtained in a specimen with (011) surface orientation irradiated with 30 keV Ar ions to a fluence of 1.3 dpa.

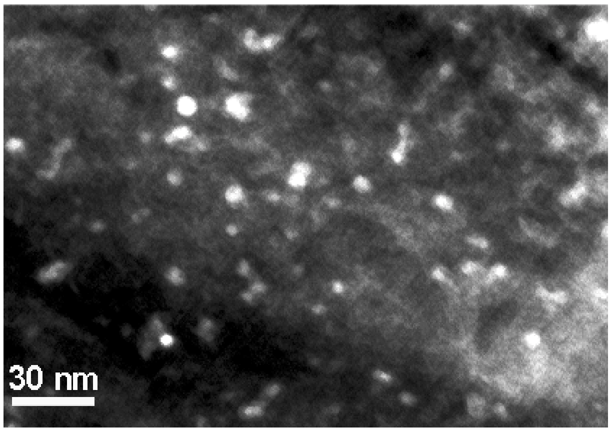


Figure 4. Dark field image obtained from a γ phase reflection. The specimen was irradiated with 30 keV Ar ions to a fluence of 1.3 dpa. γ phase precipitates with a mean size of 8 nm are observed.

IV. DISCUSSION

In the specimens with (100) surface orientation, a transformation to a new phase with a hexagonal structure was observed. Two variants with perpendicular basal planes were formed. The shape of the variants is irregular, and there is no preferred orientation of the interface between them. Due to the strong diffraction effects it is concluded that the thickness of the irradiation induced hexagonal phase is comparable to that of the irradiation affected zone (20 nm).

A transformation with identical characteristics (orientation relationship, morphology, high stacking fault density), has been previously observed in single crystals with (100) orientation of Cu-Zn-Al alloys with the same composition, irradiated with 300 keV Cu ions, up to fluences above about 1 dpa (Tolley and Abromeit, 1995; Tolley and Abromeit, 1999).

In the specimens with (011) surface orientation, the formation of γ phase precipitates was observed. No other transformation was observed up to a fluence of 1.3 dpa. The precipitation of the γ phase has also been previously observed in Cu-Zn-Al single crystals irradiated with 300 keV Cu ions, as from fluences of about 0.5 dpa (Tolley and Abromeit, 1995). The latter was observed both in specimens with (100) and (011) surface orientation. The reason why no γ phase precipitates are observed in specimens with (100) surface orientation by irradiation with 30 keV Ar ions in the present work may be due to the shorter penetration of the Ar ion beam. In the 300 keV Cu ion irradiations, the region modified by the irradiation is about 100 nm, which corresponds to the thickness observed in TEM. A fraction of this irradiated thickness is transformed to the hexagonal structure, while the other remains in the β phase. The γ phase precipitates, which are coherent with the β phase, are formed in the region of the irradiated matrix, which does not transform to the hexagonal structure. In the Ar ion irradiations, the damage extends to a thickness of only about 20 nm, most of which transforms to the hexagonal phase. Since the γ phase is cubic, precipitates of this phase within a close packed structure are expected to have a large interfacial energy, and are therefore not formed.

The results presented in this work show that irradiation with 30 keV Ar ions produces similar effects to those of 300 keV Cu ions in β Cu-Zn-Al single crystals at room temperature. In both cases, the formation of the hexagonal structure was found to depend on the surface orientation of the specimen.

In β phase Cu-Zn-Al single crystals, additional reflections in electron diffraction patterns have been reported (Lovey *et al*., 1980, Lovey *et al*., 1981). The positions of these extra reflections were found to depend on the surface orientation of the specimen. It was shown that they arise from a thin layer of martensite formed on the specimen surface. In specimens with (011) surface orientation, 18R martensite is formed, while in specimens with (111) surface orientation, 2H martensite is formed. In specimens with (100) surface orientation, no additional reflections were observed, that is, no martensite is formed on this surface. All these features could be explained by assuming that the undistorted (or little distorted) habit plane between the matrix and the martensite is nearly parallel to the specimen surface. In the present results the surface orientation was shown to influence the formation of a new phase with a hexagonal structure. The additional reflections observed in specimens with (100) surface orientation in the [100] diffraction pattern are similar to those of 2H martensite. However, no martensite is formed spontaneously on specimens with this surface orientation. This suggests that the mechanism for the formation of the hexagonal phase under irradiation is not displacive. Instead, it may be speculated that the enhancement of diffusion during irradiation plays a significant role in the transformation.

Recently, small hexagonal precipitates were found in β Cu-Zn single crystals with (100) surface orientation, which were annealed at 450°C under vacuum in order to evaporate the Zn component (dezincified). The orientation relationship with the matrix was the same as that found in the present work, but the morphology was that of small, irregular shaped precipitates (Troiani *et al.*, 1999). A high density of stacking faults was also found in the precipitates. Irradiation experiments in β Cu-Zn are being carried out to explore the possible relation between both transformation processes.

Equilibrium phases with hexagonal structure have not been reported at electron concentrations around 1.48 in noble metal alloys, although they are common at higher electron concentrations. An interesting problem is then to analyse the stability of the hexagonal phase relative to the bcc β phase at room temperature and at such low electron concentration. Further ion irradiation experiments are expected to provide useful information on this point.

V. CONCLUSIONS

Cu-Zn-Al single crystals of the β phase were irradiated with 30 keV argon ions. Phase transformations induced by irradiation were obtained.

1. In specimens with (100) orientation, a hexagonal phase is formed. The transformation mechanism is not displacive. The orientation relationship between the matrix and the hexagonal phase is:

$$(0001)_{Hex} \parallel (0\,\bar{1}1)_{\beta}\;;\;\; [1\,\bar{1}0\,0]_{Hex} \parallel [011]_{\beta}$$

2. In specimens with (011) surface orientation, precipitation of the γ phase is observed.
3. In β Cu-Zn-Al alloys, the irradiation with 30 keV Ar ions produces similar effects than those of 300 keV Cu ions.

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