FCC Surface Precipitation in Cu-Zn-Al after Low Angle Ga\(^+\) Ion Irradiation

Eugenia Zelaya\(^1,2\) and Dominique Schryvers\(^1\)

\(^1\)CAB, Av. Bustillo 9500, 8400 Bariloche, Rio Negro, CONICET, Argentina
\(^2\)EMAT, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium

The precipitation of a disordered FCC surface structure after low angle Ga\(^+\) ion irradiation during focused ion beam thinning of a B2 Cu-Zn-Al alloy with \(e/a = 1.48\) is reported. Conventional as well as high-resolution transmission electron microscopy techniques reveal FCC layers on both sides of the thinned sample. The occurrence of this structure is attributed to disordering and dezincification of the alloy resulting from the sputtering process during the irradiation. Changes in crystallographic sample orientation with respect to the incoming ion beam do not have a significant effect on the appearance of the FCC surface structure. [doi:10.2320/matertrans.M2010171]

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1. Introduction

The phase diagrams of metals of the 11th group such as Au, Ag or Cu with elements of the 12th group such as Zn and Cd present similar characteristics. The stability of the phases present is controlled by the electronic concentration \((e/a)\) defined as the average number of conduction electrons per atom.\(^1\) Alloys with an \(e/a\) ratio around 1.48 present a stable \(\beta\) phase with a bcc structure at elevated temperatures. On cooling, the first neighbor atoms become ordered into a B2 structure. In ternary alloys, a long range ordering at second neighbors is reached at lower temperature yielding L2\(_1\) or DO\(_3\) ordered structures depending on the percentage of the different constituents of the alloy.\(^2\)

Upon cooling, these structures transform martensitically to metastable close packed structures at a characteristic start temperature defined as Ms. In particular, in Cu-Zn-Al alloys with \(e/a < 1.5\) the material transforms martensitically from L2\(_1\) to 18R (AB\(_0\)CB\(_0\)CA\(_0\)CB\(_1\)A\(_0\)C\(_0\), with X and Y (\(X = A, B\) or C) denoting the same atom positions but a site occupation by different atom species, and from L2\(_1\) to 2H (AB\(_0\)) for alloys with \(e/a > 1.5\). The monoclinic 18R structure can be described by a stacking sequence of eighteen close packed planes, which are derived from a \([1\ 1\ 0]\)\(_p\) family of planes in the parent phase. The B plane is shifted over 1/3 \([100]\)\(_p\) while the C plane is shifted over 2/3 \([100]\)\(_p\) both with respect to the A plane. Similarly, the hexagonal 2H structure can be described as a stacking sequence of two planes derived from \([1\ 1\ 0]\)\(_p\). Since the martensitic transformation is a diffusionless first order transition, the resulting structure inherits the atom configuration or ordering of the \(\beta\) phase. However, the relative stability of the close packed phases can change if disorder is induced in the \(\beta\) phase.

In Ref. 3) it was shown that the transformation energy of the disordered structures differs from the ordered ones. Indeed, for disordered alloys with \(e/a\) lower than 1.48 a 2H structure is more stable until the electronic concentration reaches a value of 1.44 and the FCC structure becomes more stable. The disorder could, e.g., be induced by irradiation or quenching from high temperatures. The attenuation of the intensity of superlattice reflections with the increment of irradiation dose, implying a loss of long range order (LRO), was reported earlier.\(^4\)\(^,5\) As a result of the increase of the disorder by irradiation with Cu\(^+\) ions due to atomic mixing a 2H structure was detected for irradiation doses lower than 15 dpa\(^6\) and precipitation of an FCC structure was found for doses higher than 15 dpa.\(^7\) It should be reminded that the dpa is an irradiation unit used to quantify the dose and also indicates the number of times an atom receives the necessary energy to be displaced from its equilibrium position.

All the irradiation experiments cited above have been performed with the irradiation direction perpendicular to the surface sample. However, in present day transmission electron microscopy (TEM) sample preparation techniques, alloy samples are more and more being prepared by ion thinning, e.g., in a focused ion beam instrument operating with Ga\(^+\) ions in order to produce a well-focused beam allowing for site-specific sample preparation and cleaning. In such procedures the angle of the ion beam usually implies a grazing incidence. In the present work the remaining question of the influence of the irradiation direction is investigated, including crystallography of the structure.

2. Experimental

A Cu-22.7 at\%Zn-12.7 at\%Al alloy was prepared in an electric furnace using pure metals within a sealed quartz capsule. An \(e/a = 1.48\) and a \(\beta/\)monoclinic Ms transformation temperature of about 80 K\(^2\) correspond to this composition. A single crystal was grown by the Bridgman method. The single crystal of 6 mm diameter and 11 cm length was homogenized in a sealed quartz tube under an Ar atmosphere at 1073 K for 48 h. An orientation parallel to [001]\(_p\) was chosen using the Laue X-Ray method. Two parallel and consecutive oval shape slices were cut, one of 6 mm \(\times 7\) mm \(\times 5\) mm and the other one of 6 mm \(\times 7\) mm \(\times 1\) mm. The first slice was mechanically grinded from the round side until a flat surface of 2 mm \(\times 3\) mm appears perpendicular to [001]\(_p\). This polishing procedure was used in order to prepare a suitable probe to cut the FIB samples to be irradiated with Ga\(^+\) ions. The second slice was mechanically grinded until 0.2 mm thickness and a sample of 3 mm diameter (suitable for TEM) was cut. Further thinning for TEM observation was carried out by electropolishing using a double jet TENUPOL equipment with a solution of 500 ml distilled water, 250 ml ethyl alcohol, 250 ml orthophosphoric
acid, 50 ml propyl alcohol and 5 g urea operating at 12 V and 278 K. This reference sample was not irradiated.

The irradiations of the samples were performed with a FIB/SEM Nova 200 FEI dual-beam system, in which double-sided thinning is carried out by a focused Ga⁺ ion beam. The irradiation doses were varied between 0.001 dpa and 15 dpa (six different samples), with an angle between the beam and the surface plane of 5°. The dose could be varied in this equipment by changing the energy of the Ga⁺ ions and varying the current (a detailed calculation is given elsewhere). Also, two other samples with a calculated dose of 13 dpa were prepared. In one sample, the angle between the sample surface and the ion beam was 10° while in another sample the crystallographic orientation was changed from $[001]_b$ to $[102]_b$. Both of the latter samples yield information on the variation of irradiation direction in two perpendicular directions. All TEM slices prepared by FIB were also covered by the regular Pt protection layer, deposited by smooth ion beam induced deposition.

TEM characterization was carried out using an FEI CM20 microscope operated at 200 kV and HRTEM measurements were obtained on an FEI CM30 FEG, operated at 300 kV.

3. Results and Discussion

Two kinds of frequently observed $[001]_b$ diffraction patterns in a sample prepared by FIB using 30 keV of Ga⁺ ions at 1 nA current (13 dpa), are shown in Fig. 1. Both selected area diffraction (SAD) patterns could be observed in every sample prepared with FIB, though the first one (Fig. 1(a)) was more frequently recorded in all samples. In the first SAD pattern, basic reflections of the $β$ phase along $[001]_b$ are observed including some weak B2 ordering reflections as well as a single variant of a disordered FCC structure along $[101]_{FCC}$. This single variant is presented as grey circles in the schematic of Fig. 1(d), including a dashed line to guide the eye and pointing out the line of symmetry. Also, double diffraction produced by the overlapping of the FCC precipitating on both sides of the sample is visible. The second diffraction pattern shows additional reflections corresponding to pairs of twin related $[101]$ variants of the FCC structure. The second variant is represented in Fig. 1(d) by open circles, from which the twin relation with the first variant along the $\overline{1}1\overline{1}$ direction can be concluded. In Fig. 1(c), a dark field image produced with the $020_{FCC}$ reflection is shown revealing a typical dark field image of a compact phase over a $β$ phase. This type of microstructural image covers the entire irradiated sample. The electro-polished reference sample obtained from the same crystallographic orientation of the sample was different from $[001]_b$, only precipitation of FCC was observed, i.e. no 2H stacking was found.

These diffraction patterns and micro features were detected in all eight different samples irradiated with Ga⁺ ions with doses varying from 0.001 dpa to 15 dpa, the former being obtained in the cleaning processes with energies of 1 keV. Also, in samples in which the inclination of the beam was larger than 5° or the crystallographic orientation of the sample was different from $[001]_b$, only precipitation of FCC was observed.

Figure 2(a) shows a high resolution TEM (HRTEM) image of the border of the sample prepared with 30 keV and 3 nA (15 dpa). As a result of this high irradiation dose, the protective layer of Pt has disappeared. Therefore, the thinner parts of the sample (that correspond to the area closer to the Ga⁺ ion source) exhibit only the precipitated closed packed phase. As the sample becomes thicker, a Moiré contrast produced by the matrix and the FCC covering both sides of the matrix can be distinguished. Figure 2(b) shows the FFT produced by the thinner side of the sample which can indeed be associated with the $[101]_{FCC}$ zone axis of the FCC structure.

Although the precipitation of an FCC structure after ion irradiation was reported before, this is the first time that it could be found after an irradiation dose as low as 0.001 dpa, typical for final FIB thinning or cleaning processes. The main difference between the previous works and the present one is the low angle between the sample surface and the ion beam in our studies, which is again important in TEM sample preparation procedures. Previous reports, with a normal ion beam incidence, show the precipitation of a 2H structure instead of the FCC structure for low doses. This behavior was
attributed to the disorder induced by the irradiation which yielded the precipitation of 2H for $e/a$ higher than 1.44 and FCC for $e/a$ lower than 1.44 (see e.g. Fig. 2). The disorder produced by irradiation was already reported in the same Cu-Zn-Al alloy with starting $e/a = 1.48$ for a 0.1 dpa dose after 300 keV Cu$^+$ ion irradiation and the formation of 2H and FCC was attributed to the decrease of the electronic concentration resulting from the dezincification of the alloy (FCC below $e/a = 1.44$). This dezincification process can be produced by preferential sputtering during irradiation as such or by temperature increase. For the latter case, the formation of 2H areas was observed in a Cu-Zn alloy with a starting $e/a = 1.5$ due to the evaporation of the Zn after annealing at 450°C for 14 min. Following a local overheating produced in the sample due to the focused ion beam could favor a depletion of Zn. It should indeed be noticed that in all irradiation experiments performed with Cu$^+$ or Ar$^+$ ions the diameter of the beam was orders of magnitude higher than the Ga$^+$ ion beam of the FIB. While the beam diameter of the Ar$^+$ ions is $\approx 2\, \text{nm}$, the beam diameter of the FIB varies between 23 and 400 nm. The small area of heat transfer as well as the lower implantation range due to the low angle of irradiation decrease the volume of heat transfer increasing the local temperature of the sample surface. Indeed, the total implantation range calculated by SRIM for 30 keV Ar$^+$ ion irradiation perpendicular to the irradiation surface is 20 nm while the penetration range for Ga$^+$ ions at 5° from the irradiation surface is always lower than 5 nm. However, irrespective whether a stationary state solution of the heat transfer equation or a time dependent solution is chosen, the raise does not produce temperatures above 90°C even for the higher doses produced by FIB. To solve the heat transfer equation for this sample the sample was considered as a semi-infinite medium and a constant irradiation flux at the sample surface was assumed. As a result, the following expression for the maximum of the temperature raise in the sample was obtained:

\[
T(0, t) - T_i = \frac{2q_0^0}{K} \sqrt{\frac{at}{\pi}}
\]

where $q_0^0$ is the heat flux that can be calculated multiplying the current by the energy of irradiation per unit area, $K$ is the thermal conductivity (315 W·m$^{-1}$·K$^{-1}$) and $\alpha$ the thermal diffusivity (95.46 $10^{-6}$ m$^2$·s$^{-1}$) of the bronze. Using eq. (1) the raise of temperature as a function of the dose shows a linear behavior as shown in Fig. 3 and yielding the following parameters:

\[
T(0, t) - T_i = a + b \cdot \text{dose},
\]

where $a = (0.3 \pm 0.6)\, ^\circ\text{C}$ and $b = (4.16 \pm 0.06)\, ^\circ\text{C} \cdot \text{dpa}^{-1}$.

Even the highest temperatures obtained for the higher doses are considered to be too low for any dezincification. As a result of this calculation, even the present low doses of Ga$^+$ irradiation are apparently sufficient to reduce $e/a$ below 1.44 by dezincification from preferential sputtering rather than by heating. At the same time, however, they induce lattice disordering of the sample surface thus yielding FCC on the surface of the thinned TEM samples.

Another aspect worth to consider is the crystallographic orientation of the surface with respect to the irradiation direction of the beam. The dependence of the type of
structure with surface orientation on a Cu-Zn alloy with a starting $e/a = 1.48$ and irradiated with 30 keV of Ar$^+$ ions was investigated before. After an irradiation with 5 dpa, a close packed mixture of 2H and FCC stacking sequences was found in a sample with a surface normal of [001]$_g$ along the normal irradiation direction. However, when the orientation of the surface normal along the irradiation was [110]$_g$ only a single variant of an FCC structure was found. Moreover, two FCC variants in mutual twin relation were detected for a [112]$_g$ surface normal. Due to the experimental setting inside the FIB, in this work the irradiation direction was close to a [310]$_g$ surface normal, taking into account that the direction of the beam was nearly perpendicular to the edge of the sample covered with Pt. Although the direction of [310]$_g$ is closer to [100]$_g$, than to [110]$_g$, the remaining the [110]$_g$ component could contribute to the precipitation of the FCC due to surface orientation. Nevertheless, only an increase on the amount of precipitated FCC was detected in the sample where the crystallographic orientation of the irradiation sample was changed to [102]$_g$. Moreover, in Ref. 8) the formation of FCC after Ar$^+$ ion milling for a sample prepared with a crystallographic orientation between [102]$_g$ and [001]$_g$ is reported. These tendencies show that the formation of the FCC after low dose irradiation is more related to the low irradiation angle as such than to the crystallographic orientation of the surface with respect to the incoming beam. However, a certain influence on the formation of the twin FCC due to local variations of the surface orientation should not be disregarded. In Ref. 16) an atomic force microscopy analysis of the surface of polycrystalline Cu indeed shows that the topography after FIB sputtering depends on grain orientation. Some grains were almost featureless whereas others had a rippled or dotted topography due to structural modifications.

4. Conclusions

Even extremely low irradiation doses with Ga$^+$ focused beams as applied in final thinning processes for TEM samples can produce surface restructuring in certain Cu-Zn-Al alloys. The observation of a disordered FCC surface lattice transformed from an ordered B2 bulk phase indicates a lowering of the $e/a$ ratio by dezincification. The latter is considered to be a preferential sputtering effect as local heating does not reach sufficiently high temperatures for lowering of the Zn content. The accompanying disorder further shifts the stability region for the 2H structure, yielding only FCC in the present case. No effect from crystallographic orientation of the sample normal with respect to the incoming beam was observed.

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REFERENCES