RADIATION ORDERING IN QUENCHED ALLOYS OBSERVED “IN SITU” IN THE HIGH VOLTAGE MICROSCOPE

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(Received February 19, 1979)

Different alloys with a face centered cubic disordered structure have been electron irradiated in the quenched or short range order state under direct observation in a high voltage electron microscope. Ordering due to 1 MeV irradiation has been observed in Au,Mn, Ni,Mo and Cu,Pd. Care has been taken to avoid ordering due to the thermal effect of the electron beam. It has been demonstrated that although similar states of order can be achieved by thermal and irradiation ordering, the path followed can be different however.

1 INTRODUCTION

Upon irradiation with electrons of sufficient energy most alloys will disorder progressively as a result of displacements and replacements of atoms. This disordering process can be followed in the electron microscope either by observing the gradual disappearance of the superstructure spots in the diffraction pattern or by the increase in spacing between superdislocations in the image. Displacement damage is usually observed as small clusters or dislocation loops and has been studied extensively by various laboratories.

The reverse phenomenon, i.e. ordering upon irradiation of disordered or short range ordered alloys is also possible. Indirect evidence for this phenomenon was first obtained by studying the changes in electrical resistivity in quenched alloys under neutron irradiation. In a number of cases an initial drop in the resistivity is observed, followed by an increase of it on continued neutron irradiation. We examined the most relevant examples Cu-11.5 at.% Zn, and Cu-17 at.% Mn which exhibit this type of behaviour by means of electron microscopy but irradiation at different temperatures and with different doses did not produce any visible ordering effect. A quite general survey of irradiation-induced phase transitions updated to 1963 is given by Hauser and Schenk. More recently, radiation ordering under electron irradiation has been observed in an Au–Ag alloy, in FeNi and in Ni–Mo but the number of examples remains very limited.

We have studied three different alloys which can be obtained in the SRO state by fast quenching and which are known to order on heat treatment: Au,Mn, Ni,Mo and Cu,Pd. For the Ni,Mo and Au,Mn alloys it is known that the LRO reflections do not coincide with the initial SRO spots so that any long range ordering effect or the formation of any transition state between SRO and LRO can clearly and unambiguously be observed. Careful annealing experiments have shown that the thermal ordering of these alloys proceeds through a number of transition stages. It appears that irradiation with 1 MeV electrons is a very convenient alternative way of studying “in situ” the gradual ordering of these alloys. The first intermediate stages between SRO and LRO are clearly revealed by the diffraction evidence they produce.

Since all of the investigated alloys order on heat treatment outside the electron microscope one might argue that beam heating may be the reason for the observed ordering. However, this is very improbable for a number of reasons. Specimen areas only 10 micron away from the irradiated area did not show any ordering effects, whereas the irradiated areas already exhibited pronounced changes in the diffraction pattern. Taking into account the good thermal conductivity of these alloys it is unlikely that large temperature gradients would be present. Moreover, we previously tried in vain to order the same alloys by heat treatment in the heating holder of the electron microscope. Also irradiation below the threshold voltage for atom displacement even at
FIGURE 1  Sequence of [001]* diffraction patterns of the same area of splat cooled Au₅Mn (a) and irradiated for different times between 10 and 300 s at a dose rate of $1.5 \times 10^{19}$ e/cm²s. The irradiation temperature was 320°C.
dose rates as high as $10^{19}$ e/cm²/s for 30 min did not produce any ordering effect.

The temperature rise in thin metallic foils due to electron irradiation has been calculated by Fisher\textsuperscript{10} for a number of pure metals. For copper irradiated with 1 MeV electrons and a beam flux of $10^{20}$ e/cm²/s the calculated temperature rise for a 6 micron beam radius is less than 50°C. For nickel the corresponding temperature rise was found to be approximately 150°C. Since the temperature rise is approximately proportional to the beam current,\textsuperscript{10,11} the actual temperature increase for a beam flux of $2 \times 10^{19}$ e/cm²/s, as used for our experiments would be drastically lower. Moreover, according to Makin \textsuperscript{2} and Snykers and Janssens\textsuperscript{11} who experimentally measured the temperature rise for 316-steel, the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{Subsequent ordering steps upon irradiation of quenched Ni₅Mo at a dose rate of $1.5 \times 10^{19}$ e/cm²/s at a temperature of 400°C. The (001)-diffraction patterns were recorded with approx. 1 min intervals.}
\end{figure}
values of Fisher may be considered as upper limits. For these various reasons we believe that the observed phenomenon is not a beam heating effect but has to be considered as radiation induced.

We will now briefly discuss the evolution of ordering as revealed by the selected area diffraction patterns of the three mentioned alloys, irradiated for various periods of time with 1 MeV electrons.

2 OBSERVATIONS

2.1 $Au_4Mn$

The diffraction pattern in Figure 1a is from splat cooled material. Apart from the FCC spots it only exhibits diffuse intensity along the lines $ik0$ and $h00$. It was shown in Ref. 9 that this diffraction pattern is characteristic of a transition state in which the pre-

![FIGURE 3](image-url) $\{00\}^*$ diffraction pattern of Cu$_2$Pd before (Figure a) and after room temperature irradiation with 1 MeV electrons.
dominant cluster is a tetrahedron containing three gold atoms and one manganese atom.

On irradiation at 200°C or at 320°C at a dose rate of $1.5 \times 10^{19}$ e/cm²s the endpoints of the streaks become more intense (Figure 1b and 1c) and gradually one family of such points breaks up into two maxima which are the precursors of the superlattice spots due to the two coaxial variants (Figure 1e and 1f). No further ordering occurs on continued irradiation. Comparing this diffraction pattern series with the one obtained by thermal annealing (Figure 2 of Ref. 9) it is obvious that thermal treatment and irradiation produce somewhat different diffuse intensity patterns; the ordering process proceeds along somewhat different paths.

While during thermal annealing an intermediate phase is formed with a characteristic diffraction pattern (Figure 2 of Ref. 9), this phase has not been observed during irradiation of the splat cooled material (see Figure 1). Along the diffuse intensity segments: $h,k = 1; l = 0$. Maxima are only observed at both ends of each segment but no clear superstructure is revealed.

2.2 Ni₄Mo

The diffraction pattern of the quenched alloy in Figure 2a exhibits the well known $(1 \frac{1}{2} 0)$ spots attributed to SRO. On irradiating at 400°C (or at 550°C) at a dose rate of $1.5 \times 10^{19}$ e/cm²s one observes, in a much more gradual manner than on annealing, the evolution towards the transition state (Figure 2b and 2c). This state is revealed by a more or less circular ring of diffuse intensity. This ring, already observed during thermal annealing at 800°C⁸ is much more pronounced here. The final state of ordering (Figure 2d) is similar to the one observed for Au₄Mn. Again the precursors of the eight superstructure spots due to the two coaxial variants become prominently visible.

Different from the thermal treatment case (see Ref. 8) is the presence of the segments $h,k = 1; l = 0$

**FIGURE 4** Dark field micrographs corresponding to Figure 3(b) and 3(d) respectively obtained by selecting the 110 satellites in the objective diaphragm.
which upon thermal annealing at 800°C are extremely weak and disappear already upon slight annealing. Upon irradiation ordering they remain till the LRO state is almost completely formed, indicating the importance of the tetrahedral clusters of nearest neighbours during the ordering process. Ordering in quenched Ni−Mo alloys has also been studied by Carpenter and Kenik. They also observe the development of the long range order state upon irradiation with 1 MeV electrons in the temperature range between 300 K and 750 K. Irradiation at 520 K yields an incomplete transformation of the SRO areas into the LRO state.

At both irradiation temperatures they observe weak satellite spots around the FCC matrix reflections which they attribute to the presence of a new unidentified phase. In none of our experiments, even after prolonged irradiation, we found evidence for this new phase.

2.3 Cu₃Pd

Cu−Pd alloys with a composition around Cu₃Pd are known to form a one-dimensional and two-dimensional long period superstructure. The as quenched state shows weak diffraction spots centred around 110 and 100 reciprocal lattice positions (Figure 3a). Upon irradiation at room temperature (even at 750 kV) the superstructure reflections become more intense as can be judged from the time sequence in Figure 3. Dark field micrographs obtained by selecting in the objective aperture all four 110 satellites reveal small ordered microregions after a few minutes of irradiation at a dose-rate of 2.1×10¹⁹ e/cm²s (Figure 4a). These ordered domains grow after prolonged irradiation (Figure 4b). In the bright field micrograph of the same area, dislocation loops can be easily recognized (Figure 5).

3 DISCUSSION

The process of radiation ordering can simply be understood. The activation energy for diffusion by means of vacancies, which is relevant also for ordering, consists of two parts: the activation energy for the formation of vacancies and the activation energy for migration.

Under electron irradiation the instantaneous concentration of vacancies (and of interstitials) is much larger than in thermal equilibrium at the

FIGURE 5 Bright field micrograph of Cu₃Pd after irradiation. Dislocation loops are clearly visible.

irradiation temperature. As a result the effective activation energy for ordering is decreased since only the migration energy has to be supplied thermally. Alternatively one might say that the effective temperature that determines the rate of diffusion is in fact higher than the temperature measured on the microfurnace in the microscope.

REFERENCES