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Lattice Transitions and Flickering Images in Aged Cu-Mn Alloys

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Abstract. Distinctive "flickering" movements are observed in TEM images of the microstructure of Cu-Mn alloys after aging within the miscibility gap. Analyses of two-beam image extinction and electron diffraction streaks indicate that the underlying tweed and "V-shaped" images involve a static displacement field of the type $\{110\} \langle 1\bar{1}0 \rangle$. Atomic force microscopy and other microanalyses show the presence of Mn-enriched colonies of 15-40 nm, formed throughout the microstructure, in which twinned fct crystallites are induced and confined. The flickering movements are interpreted as a direct manifestation of the $\text{fcc} \Rightarrow \text{fct}$ transformation event and in particular of a rotation of the fct c-axis, these effects being caused by an inelastic interaction between $\langle 110 \rangle \langle 1\bar{1}0 \rangle$ phonons and the accelerated electrons of the incident TEM beam.

1. INTRODUCTION

In Cu-Mn alloys of nearly stoichiometric composition, aging inside the miscibility gap causes phase decomposition of the γ -fcc solid solution into Mn-rich and Mn-poor regions [1-3]. As well, near the Mn-rich end of the Cu-Mn system it is well-known that an $\text{fcc} \Rightarrow \text{fct}$ diffusionless transformation [4,5] and a paramagnetic $\Rightarrow$ antiferromagnetic transition [6] take place upon cooling. Technologically, a combination of the phase decomposition during aging and the lattice transitions upon cooling form the basis of high damping capacity [1-3], and microstructurally they enable a remarkable dynamical effect in TEM called "flickering" [7,8], which occurs in tweed and other characteristic contrast images.

"Flickering" consists of repetitive and consistent contrast movements at specific locations, with the extent of the relevant contrast, both in terms of the scale of the feature and the amount of movement, being on the order of 5 to 20 nm [7]. However, detailed examinations of the microstructure and interpretation of this unusual dynamical effect have not yet been reported. While a more comprehensive report has been prepared for dissemination elsewhere [9], a condensed outline of the analysis and the resultant hypothesis regarding the flickering effect is presented here.

2. EXPERIMENTAL

In the present work, the procedures by which 53.1% Cu- 44.8% Mn- 1.6% Al (wt.%) alloys were aged and thin-foils prepared for TEM observation were as reported previously [7]. It is noted that because of the two-phase character of the aged alloys and the occasional presence of α -Mn particles at longer aging times, conventional electropolishing procedures were unable to produce the requisite brilliancy of thin-foil surfaces. Thus, a two-stage electropolishing procedure was developed, although this method still leaves slight microscale irregularities on the surface, as shown later.

A Digital Instruments "Nanoscope III" scanning probe microscope was used in a tapping mode to monitor the surface topography. A Hitachi IMA-3 secondary ion mass spectrometer (SIMS) was used with Cs^+ primary ions to inspect the composition profile in the direction of the specimen depth. The approximate sputtering rate may be estimated from that for pure Cu, about 10 nm/min. TEM observations were made using JEOL JEM-120CX and JEM-2000EX microscopes.

3. RESULTS AND DISCUSSION

Aging at 723°K for longer than 5 hours develops a remarkable microstructure in TEM images, which contains dashed, V-shaped, or W-shaped contrast features aligned in similar orientations, as shown typically in Fig. 1(a). This microstructure, which we may term "V-shaped" images, is obtained at a more advanced stage of aging than an earlier stage that produces striated tweed contrast; the latter appears at lower aging temperatures or shorter aging times.

3.1. Image extinction and diffraction features of V-shaped images

In the V-shaped images, the bisector of the V-angles is always lying along the trace of $\{110\}$ planes. In Fig. 1(a) is shown an example with two V-alignment directions. One of these disappears when the $0\bar{2}2$ reflection is excited, as shown in Fig. 1(b). Various two-beam image analyses indicate that the V-shaped images follow the same extinction rules which apply to tweed microstructures [10]. The image extinction is well explained by assuming a static displacement field on $\{110\}$ planes in $\langle 1\bar{1}0 \rangle$ directions, with image extinction occurring when the displacement direction involved in the image is exactly perpendicular to the g-vector. For example, the two V-alignment directions observed with $g=020$ excitation near $[100]$ orientation, as in Fig. 1(a), are associated with $(011)[0\bar{1}1]$ and $(0\bar{1}1)[011]$ shear displacements, respectively. Of these, the one with $(0\bar{1}1)[011]$ vanishes for the $g=0\bar{2}2$ excitation condition of Fig. 1(b), since the g-vector is normal to the shear direction.

The diffraction characteristics have also been examined to confirm the close analogy between the V-shaped images and conventional tweed contrast in TEM images. The $\langle 110 \rangle^*$ relrods, with the extinction rule that two for $\{h00\}$, one for $\{hh0\}$ and three for $\{hhh\}$ reflections do not appear [10], are observed exactly as reported for tweed microstructures. The $\langle 110 \rangle^*$ relrods are formed owing to a shear displacement field of the type $\{110\} \langle 1\bar{1}0 \rangle$ involved in the V-shaped images. Among the various indications of the $\langle 110 \rangle^*$ relrods as streaks around diffraction spots, streaks along $\langle 112 \rangle$ around $\{1\bar{3}3\}$ spots are shown in Fig. 2(a). Note the absence of streaks in $\pm [01\bar{1}]$ direction for the $\{1\bar{3}3\}$ spots, as this extinction confirms that the $\langle 110 \rangle^*$ relrods are derived from the static displacement field but not from the shape factor due to platelets of the tetragonal phase or precipitates.

Apart from the $\langle 110 \rangle^*$ relrods, $\{110\}^*$ relwalls appear to exist, in that there are $2/3 \langle 11\bar{2} \rangle^*$ extra spots observed in $[\bar{1}11]$ zones, Fig. 2(b). Three $\{110\}^*$ relwalls intersect at $2/3 \langle 11\bar{2} \rangle^*$ in $[\bar{1}11]$ zones to cause an appreciable intensity. In addition, weak extra spots at $\langle 110 \rangle^*$ in $\langle 100 \rangle$ zones and very weak streaks connecting diffraction spots in $\langle 011 \rangle$ zones have been observed, as the indications of the $\{110\}^*$ relwalls [9]. The origin of the $\{110\}^*$ relwalls in fcc crystals is ascribed to the dynamic displacement of atomic chains along the close-packed $\langle 1\bar{1}0 \rangle$ directions [11]. The examination of the image and diffraction characteristics of aged Cu-Mn alloys leads to the conclusion that both static and dynamic $\{110\} \langle 1\bar{1}0 \rangle$ shear waves exist underlying the V-shaped microstructure.

Fig. 1. V-shaped images observed in a Cu-Mn alloy aged at 723°K for 10 hours. taken at two-beam excitation near $[100]$ direction.

Fig. 2. SAD patterns indicating the presence of (a) $\langle 110 \rangle^*$ reldrods as streaks in $[011]$ zone and (b) $\{110\}^*$ relwalls as extra spots in $[\bar{1}11]$ zone.

3.2 Dynamical "flickering" effect and microanalysis

In the V-shaped images the most distinctive "flickering" activity was observed, although it was observed in the tweed images as well. Various movements observed in the V-shaped morphologies are shown schematically in Fig. 3. The flickering effect consists of spacially consistent and repetitive contrast variations. The regions which flicker are around 5~20 nm in size. Under certain diffraction conditions this dynamical movement was converted to an "on-off" nature in dark field images, so that it could be recorded in micrographs taken successively, as shown in Fig. 4. Here, bright spotty contrasts appear or disappear from place to place with elapsing time during observation, indicating clearly the dynamical movements taking place in the specimen.

Fig. 3. Schematic diagram of flickering. Upper and lower diagrams indicate the images before and after a change of contrast.

Fig. 4. Dark-field images taken successively in a Cu-Mn-Al alloy aged at 723°K for 10 hours. Flickering bright spots are indicated.

Figure 5 shows TEM-EDX profiles taken from the matrix and the V-shaped region, respectively. The Mn concentration in the V-shaped region is clearly higher than in the matrix. Since these V-containing regions are embedded in the matrix, the actual Mn concentration is probably much higher than measured. When the Mn concentration is greater than 80 wt.%, fct martensite is reputed to be stable at room temperature [4]. When constrained in very small coherent segregated volumes, the M_s temperature may well be modified. Thus, the Mn-enriched colonies are considered to be capable of transformation $\text{fcc} \Rightarrow \text{fct}$ with the progress of the phase separation.

Fig. 5. EDX profiles of Cu and Mn for (a) matrix and (b) V-shaped regions. Sample aged at 723°K for 10 hours.

TEM-specimen surface topography was examined by using atomic force microscopy (AFM). As supposed from the difficulty of electropolishing or ion-milling to obtain a brilliant surface, AFM inspection of a well-polished surface yet revealed a corrugated surface with a maximum height gap around 10 nm or so, as shown in Fig. 6. This type of microirregularity is assumed to result from different etching rates of Mn-rich and Mn-poor regions along a specimen surface during electropolishing. Protruding portions of the surface are assumed to be Mn-rich if referred to the results of SIMS measurements, Fig. 7. The yield of Mn ions decreases and that of Cu ions increases as primary Cs^+ ions induce sputtering into the depth of the specimen. Thus, from the sectional surface profile of AFM in Fig. 6 the Mn-concentration modulation is estimated to be on the scale of 30-80 nm. This gives the size of the Mn-enriched colonies to be around 15-40 nm.

Fig. 6. AFM image of TEM-foil surface and line scan profile across points A and B. Sample aged at 723°K for 10 hours.

Fig. 7. Depth profile of secondary ions in SIMS surface analysis. Sample aged at 723°K for 10 hours.

From these observations it follows that each bright spot in the dark field images of Fig. 4 corresponds to an fct crystallite confined in the segregated Mn-rich colony, the bright spot being produced because the slight misorientation of the fct crystallites causes stronger diffraction of the beam than does the surrounding matrix. In Fig. 4 the fct crystallites are sized 5-40 nm, aligned in similar orientation, and appear to exist in groups with gaps between them. This observation is suggestive that in the Mn-rich colonies fct crystallites of different orientation are arranged alternately, in similar fashion to the self-accommodating pairs that occur in martensitic microstructures.

Figure 8 shows a high resolution TEM image of V-shaped regions observed from the [011] direction. Various lattice planes are noticed to be rotated and curled at many locations. Although this effect can be partly attributed to the aforementioned thickness variations, some of these fringe modifications, such as those seen in the encircled area, may be caused by the presence of fct crystallites of different c-axis orientations.

Fig. 8. HREM image observed in [011] orientation showing irregular lattice planes due to surface irregularities and to possible involvement of fct crystallites. Region of significant rotation of (111) is encircled.

3.3. Mechanism of "flickering"

In Cu-Mn alloys of near-stoichiometric composition, aging within the miscibility gap activates decomposition of the γ -phase into Mn-rich and Cu-rich fractions and produces a microstructural modulation, as shown schematically in Fig. 9. When the Mn-enrichment is sufficient in the segregated colonies, the twinned fct phase is supposed to develop in a self-accommodating manner. The tetragonality gradually decreases to naught in the transient area around the Mn-rich colony. Therefore, the twin boundary, which should otherwise have formed on {110}, greatly deviates from {110} and tapers in the Mn-rich colony to lead to the V-shaped morphology. Across the V-delineations are crystals of alternating c-axis directions.

Fig. 9. Assumed structure of the V-shaped morphology within a Mn-enriched colony, consisting of fct crystallites of alternating c-axis directions.

With the segregated microstructure as described, the dynamical flickering movements may be postulated as the rotation of the tetragonal axis, displacement of twin boundaries, and the transformation event between fcc and fct, all taking place in the Mn-rich colonies. The driving force to initiate these events is supplied from the electron-phonon interaction as follows. The elastic constant $C' = (C_{11} - C_{12})/2$ of Mn-rich Cu-Mn alloys is reported to decrease significantly as the temperature decreases toward the phase transformation temperature [12, 13]. The presence of high-amplitude transverse acoustic waves with wave vector $\vec{q} // \langle 110 \rangle$ and displacement vector $\vec{\epsilon} // \langle 1\bar{1}0 \rangle$ is likely, especially in the segregated Mn-rich colonies in the present alloys. Thus, we may envision that the accelerated electrons of 100-200 keV would inelastically interact with the lattice to induce phonons of 0.01-0.1eV. The induced $\langle 110 \rangle \langle 1\bar{1}0 \rangle$ phonons would couple and cause in effect simultaneous double shears of $\{110\} \langle 1\bar{1}0 \rangle$ which produce the fcc $\Rightarrow$ fct phase transformation according to the Bowles-Barrett-Gutmann double shear theory [14]. Moreover, the couplings of $\langle 110 \rangle \langle 1\bar{1}0 \rangle$ phonons are related to the rotation of c-axis according to their combination. For example, coupling of the $[101][10\bar{1}]$ and $[011][01\bar{1}]$ phonons would cause the c-axis contraction to produce the fcc $\Rightarrow$ fct transformation, whereas if the $[011][01\bar{1}]$ phonon is absorbed and the $[\bar{1}10][\bar{1}\bar{1}0]$ phonon is excited the c-axis of this fct would be rotated by 90 degrees. This mechanism of flickering is summarized in Table 1.

Table 1 Interpretation of the Mechanism of Flickering

<u>Phonon Interaction</u>	<u>Crystallographic Change</u>	<u>Flickering Mode</u>
$[101][10\bar{1}] + [011][01\bar{1}] \equiv P_1$	fcc $\Rightarrow$ fct forward transformation	creation, displacement
$P_1 - [101][10\bar{1}] - [011][01\bar{1}]$	fct $\Rightarrow$ fcc reverse transformation	disappearance, displacement
$P_1 - [011][01\bar{1}] + [\bar{1}10][\bar{1}\bar{1}0]$	fct c-axis reorientation	rotation

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