PHASE TRANSFORMATIONS IN ORDERED, SPINODAL
Cu-Mn-Al ALLOYS

Masuo Okada
(M.S. thesis)

October, 1974

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

For Reference
Not to be taken from this room
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
PHASE TRANSFORMATIONS IN ORDERED, SPINODAL
Cu-Mn-Al ALLOYS

Contents

Abstract ......................................................................................... v

I. Introduction .................................................................................. 1

II. Experimental Procedures ............................................................. 4
   A. Materials and Heat Treatment ..................................................... 4
   B. Electron Microscopy ................................................................ 5

III. Results .................................................................................... 6
   A. "In Situ" Observation of Spinodal and Ordering Reactions ........ 6
      1. Determination of the Miscibility Gap Temperature ............... 6
      2. The Effect of Modulated Structure on APB Formation ........ 9
   B. Identification of the New Phase Appearing in Spinodally
      Transformed Cu-Al Rich Phase ................................................... 11
      1. Observation of the "New" Phase ......................................... 11
      2. Discussion of the Nature of the New Phase in the
         Cu-Al Rich Phase ............................................................... 13
      3. Analysis of Diffraction Patterns ......................................... 14
      4. Crystal Orientation Relationships ....................................... 15
      5. Stability of the γ' Phase ...................................................... 16

IV. Discussion ................................................................................ 18
   A. Spinodal and Ordering Reactions ............................................ 18
      1. Determination of the Miscibility Gap ................................. 18
      2. The Effect of Modulated Structures on APB Formation ....... 20
PHASE TRANSFORMATIONS IN ORDERED,
SPINODAL Cu-Mn-Al ALLOYS

Masuo Okada

Inorganic Materials Research Division, Lawrence Berkeley Laboratory and
Department of Materials Science and Engineering, College of Engineering;
University of California, Berkeley, California 94720

ABSTRACT

Alloys along the composition line Cu₃Al-Cu₂MnAl decompose spinodally
into a Cu₂MnAl rich phase and a Cu₃Al rich phase during aging at
temperatures below 350°C. Hot stage electron microscopy was applied
to determine the miscibility gap temperatures of the alloys by
monitoring the disappearance of satellites in the diffraction mode
and structure modulation in the image mode. The antiphase boundary
boundaries (APB's) developed during aging inside the miscibility gap were
found to inherit the same character as those above the miscibility gap.

The new phase (the γ' phase) appearing in the spinodally decomposed
Cu-Al rich phase was found to have an orthorhombic lattice with two
layer stacking sequence (2H), which is considered to be formed by a
shear along (110) planes of the parent β⁺-lattice (D₀₃). The
Cu-12.4% Al-4.68% Mn alloy which is almost at the edge of the miscibility
gap shows that slower quenching yields large amounts of γ' plates
(martensite). This observation is in good agreement with that of the γ'
phase in the Cu-Al rich phase, because the furnace cooled Cu₂.₅Mn₀.₅Al
alloy also gives a high density of γ' phase in the Cu-Al rich phase.
I. INTRODUCTION

Heusler\(^1\) discovered a series of ferromagnetic alloys composed only of paramagnetic or diamagnetic elements. Although the relatively low saturation magnetization of these materials reported to date suggests that the alloys are not commercially attractive, the alloy having the highest saturation magnetization, namely Cu\(_2\)MnAl, has been rigorously investigated to elucidate the origin of its magnetic properties. There is also academic interest surrounding its phase transformation and precipitation behavior.

The metallography of the Cu-rich portion of the Cu-Mn-Al system at temperatures above 450°C, has been studied by West and Thomas.\(^2\) Also the metallography of the alloys along the composition line Cu\(_3\)Al-Cu\(_2\)MnAl at temperatures below 350°C has been fully investigated by Bouchard and Thomas.\(^3\)-\(^5\) It is found that during decomposition along the Cu\(_3\)Al-Cu\(_2\)MnAl tie line, the system exhibits both ordering and spinodal reactions (Fig. 1).

The high temperature \(\beta\) phase, having a disordered bcc structure, orders rapidly during quenching. The ordering takes place in two stages, forming first a B2 structure, followed by a structure resembling an L2\(_1\) or DO\(_3\) superstructure (Fig. 2). During aging at temperatures below 350°C, the quenched structure decomposes and resulting microstructures show all the metallographic characteristics of spinodal decomposition, the theory for which has been developed in detail by Cahn\(^6\) and Hilliard.\(^7\) Low temperature aging also results in the appearance of extra reflections in selected area diffraction patterns. These extra spots have been indexed in terms of an L1\(_0\) structure, which emerges within one of the
spinodal products, the Cu$_3$Al rich phase.

The determination of the spinodal temperature has been carried out in the Al-Zn system by using small angle X-ray diffraction. A shortcoming of this and most other X-ray techniques, however, is the inability to produce a high resolution image of the (modulated) microstructures. Transmission electron microscopy enables a direct comparison of structure modulation and electron diffraction "satellite spots", with the additional option of dynamic observation of phase transformations. Nevertheless, no work has been done so far on determining the miscibility gap by "in situ" experiments in the Cu-Mn-Al system (or any other spinodal).

Since the (Cu-Mn)$_3$Al alloys decompose spinodally into a Cu$_2$MnAl rich phase and Cu$_3$Al rich phase during aging at temperatures below 350°C, this system is ideal for observing the spinodal reaction by "in situ" experiments with minor loss of image quality due to thermal instabilities. One objective of this investigation is to determine the miscibility gap temperature of (Cu-Mn)$_3$Al by monitoring the disappearance of satellites in the diffraction mode and structure modulations in the image as a function of aging temperature. This technique will also facilitate an estimation of the spinodal temperatures. Because spinodal and ordering reactions occur simultaneously in these alloys, this system also lends itself well to an investigation of the interactions between structure modulations and APB's (anti-phase domain boundaries), which will be also discussed in the light of hot-stage electron microscope experiments.
The mechanical behavior of spinodally decomposed and aged alloys has been investigated by several workers.\textsuperscript{9-12} The structure and mechanical properties of the Cu\textsubscript{2.5}Mn\textsubscript{0.5}Al alloy, which lies at the center of the miscibility gap along the Cu\textsubscript{3}Al-Cu\textsubscript{2}MnAl pseudo-binary have also been studied.\textsuperscript{13} Because of the extensive brittleness of the alloy, Vicker's hardness test was adopted to indicate the variation in strength with aging. These results reveal that a new phase tentatively identified as having an L\textsubscript{10} structure, plays an important role in increasing the Vicker's hardness. It is, therefore, important to classify the transformation DO\textsubscript{3} \rightleftharpoons L\textsubscript{10}. One possible mechanism of the transformation was proposed by Bouchard and Thomas.\textsuperscript{4} However, the stability of the L\textsubscript{10} phase is still unsolved.

In this paper other possibilities of the DO\textsubscript{3} \rightleftharpoons L\textsubscript{10} transformation will be discussed with respect to a martensitic transformation, since the composition of the original DO\textsubscript{3} structure is Cu\textsubscript{3}Al, a known candidate for a martensitic reaction. The stability temperature of the L\textsubscript{10} phase is estimated by hot-stage electron microscopy and the metallography of the L\textsubscript{10} phase is re-examined by high resolution dark field techniques.
II. EXPERIMENTAL PROCEDURES

A. Materials and Heat Treatment

Three alloys were chosen to determine the miscibility gap temperature. Table I shows the compositions of the alloys studied.

Table I. Atomic and chemical compositions of the alloys studied.

<table>
<thead>
<tr>
<th>Atomic Composition</th>
<th>Estimated Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wt% Cu</td>
</tr>
<tr>
<td>Cu$<em>{2.8}$Mn$</em>{0.2}$Al</td>
<td>82.5</td>
</tr>
<tr>
<td>Cu$<em>{2.5}$Mn$</em>{0.5}$Al</td>
<td>74.4</td>
</tr>
<tr>
<td>Cu$<em>{2.2}$Mn$</em>{0.8}$Al</td>
<td>66.3</td>
</tr>
</tbody>
</table>

The alloys were prepared from 99.999% Cu, 99.9% Mn and 99.999% Al by arc melting in helium atmosphere and were chill cast into a copper mold. Chemical analysis verified to within 1% the compositions given previously.

The ingots were then placed in stainless steel envelopes, homogenized for 3 days at 850°C and oil quenched in order to avoid quenching cracks. Thin slices, 0.5 mm thick, were the cut and homogenized at 850°C for 10 min under argon atmosphere in a vertical resistance furnace. Thin slices for determining the temperature of the miscibility gap were then quenched in an oil bath to develop a particular spinodal wavelength.

Samples for identifying the structure of the so called Ll$_0$ phase were furnace cooled because this treatment was found to produce well
defined $L_1$ reflections.\textsuperscript{13}

Specimens aged for 1000 min at 275°C in salt baths (50% potassium nitrate, 50% sodium nitrate) were also examined for comparison.

B. Electron Microscopy

Electron microscope disc specimens, 3.0 mm in diameter were spark eroded, followed by thinning in an automatic jet polisher using an electrolytic solution of 400 ml acetic acid, 20 ml water, 75 gr chromic oxide.

All "in situ" observations were made using a goniometer heating-holder in a Philips EM301 electron microscope. Photomicrographs were taken at temperature after the image had ceased drifting, using a short exposure time to avoid blurring. The hot stage was calibrated by the temperature at which a cobalt foil was observed to transform from hcp to fcc on increasing the temperature. At 450°C the microstructure consists of approximately 50% hcp and 50% fcc phase. The accuracy of the temperature given here is estimated to be better than ±5°C.

A high-angle tilt goniometer stage was used for determining the structure of the new phase transformed from the $D_0_3$ structure. The stability of this phase was also investigated using hot-stage analysis.
III. RESULTS

A. "In Situ" Observation of Spinodal and Ordering Reactions

1. Determination of the Miscibility Gap Temperature

On heating specimens from room temperature, crossing the spinodal limit results not only in the disappearance of satellites but also in the resolution of the characteristic spinodal structure modulations. Although the disappearance of the satellites can also be attributed to loss of coherency of the spinodal product, there are other diffraction effects which distinguish the break of coherency. These effects include the splitting of diffraction spots in a direction parallel to each reciprocal lattice vector $\mathbf{g}$. A further indication of loss of coherency is the generation of interfacial dislocations as a typical morphology. In the Cu$_{2.5}$Mn$_{0.5}$Al alloy, the loss of coherency occurs after aging at 300°C for approximately 1,000 min, and these conditions far exceed those employed in the present study. In addition, neither diffraction spot splitting nor the presence of interfacial dislocations was observed, hence coherency of the spinodal product is apparently maintained throughout "in situ" heating.

The temperature of the miscibility gap was determined by monitoring the disappearance of satellites and of modulated microstructures. The spinodal wavelengths were calculated from the satellite spacings in selected area diffraction patterns, and by direct measurements from the photographs. The former method is more accurate as it is independent of optical magnification. The closer the specimen temperature is to the miscibility gap temperature, the smaller the satellite spacing becomes. For longer wavelengths
(i.e., over 130 Å) a microdensitometer analysis was also carried out on photographically enlarged diffraction patterns to detect the satellite spots around the Bragg reflections.

Foils were oriented in an [001] direction to optimize detection of the changes of modulated structures and satellites around the (200) reflections. A temperature sequence of micrographs is shown in Fig. 3 for the asymmetrical alloy, Cu_{2.2}Mn_{0.8}Al. The imaging conditions for the best detection of the changes of modulated structures were utilized, and these are shown in the corresponding diffraction patterns of Fig. 4, which also depict changes in the satellites about the (200) reflection. The images show some contamination but the typical modulation contrast is clearly resolved at temperatures above 273°C in the sequence of Fig. 3.

During heating of the foil, well defined satellites are observed to develop from the original diffuse satellites. This is believed to arise from the preferential growth of a critical compositional wavelength along the elastically soft cubic directions from the range of initial wavelengths. The satellite spacing decreases with increasing temperature. In an asymmetrical alloy, the satellites are asymmetrical in intensity consistent with the volume fraction of Cu_{3}Al being lower than that of the major phase, Cu_{2}MnAl.

Below 307°C, well defined satellites were observed, but at 318°C, all reflections were streaked in a direction parallel to (100). Therefore, no measurement of the wavelength was made above 318°C from diffraction patterns. Micrographs reveal that the minor phase forms as thin platelets parallel to the cube planes of the matrix. This
suggests that the streaks in the associated diffraction pattern can be explained by the shape factor effect of these observed plate-like particles which produce rel-rods in a direction normal to the plate habit planes. Since above 318°C, no satellites were observed in the diffraction patterns, but composition modulations were seen in bright field images, it follows that 318°C lies inside the miscibility gap but outside the spinodal. Diffraction spot streaking disappeared at 328°C, but in the corresponding micrographs, the plate-like precipitates were not completely dissolved. The temperature of the miscibility gap is believed to be around 358°C, since this temperature corresponds to the complete dissolution of the plate-like precipitates in the bright field micrographs. A similar sequence of pictures was taken of the Cu$_{2.5}$Mn$_{0.5}$Al alloy and the temperature of the miscibility gap was determined as 350°C±5°C, by monitoring the dissolution of the modulated structures. However, for this alloy the temperature at which the modulated structure dissolved very nearly coincided with that of the disappearance of satellites. Therefore, the temperature of the miscibility gap, 350°C±5°C, for the Cu$_{2.5}$Mn$_{0.5}$Al alloy, is believed to be close to the spinodal temperature.

These results are summarized in Fig. 1 showing the limits of the miscibility gap, which are in good agreement with the previous results obtained by studying the constituents of the microstructures obtained after prolonged aging when the coarsening process has taken place.
2. The Effect of Modulated Structure on APB Formation

There are two possible types of APB vectors in both the \( \text{DO}_3 \) and \( \text{L}_2^1 \) structures, \( a/4\langle 111 \rangle \) and \( a/2\langle 100 \rangle \). The following table gives the phase change angle \( \alpha = 2\pi (\mathbf{g} \cdot \mathbf{R}) \) associated with phase contrast due to the presence of both types of APB's (\( \mathbf{g} \) is the operating reflection and \( \mathbf{R} \) is the anti-phase vector) and the values of extinction distances of \( \text{Cu}_2\text{MnAl} \) and \( \text{Cu}_3\text{Al} \), which are estimated by Marcinkowski\(^{14} \) and in this paper (see Appendix), respectively. There is no contrast when \( \alpha = 0 \) or \( n \cdot 2\pi \) and few fringes are obtained when \( t_0 \) is large.

Table II. Antiphase angle and extinction distances of the \( \text{DO}_3 \) and \( \text{L}_2^1 \) type superstructures.

<table>
<thead>
<tr>
<th>( \text{hk} )</th>
<th>Type of Reflection</th>
<th>( \alpha ) for ( 1/4a\langle 111 \rangle )</th>
<th>( \alpha ) for ( 1/2a\langle 100 \rangle )</th>
<th>( t_0 ) in ( \text{Cu}_2\text{MnAl} ) (Å)</th>
<th>( t_0 ) in ( \text{Cu}_3\text{Al} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>( S_I )</td>
<td>( \pm \pi/2 )</td>
<td>( \pm \pi )</td>
<td>2,700</td>
<td>3,160</td>
</tr>
<tr>
<td>200</td>
<td>( S_{II} )</td>
<td>( \pm \pi )</td>
<td>0</td>
<td>1,680</td>
<td>3,415</td>
</tr>
<tr>
<td>220</td>
<td>( F )</td>
<td>0</td>
<td>0</td>
<td>308</td>
<td>590</td>
</tr>
</tbody>
</table>

Referring to Table II, it is apparent that \( S_I \) type reflections give contrast for \( 1/4a\langle 111 \rangle \) and \( 1/2a\langle 100 \rangle \) APB's, but that with \( S_{II} \) type reflections, only the \( 1/4a\langle 111 \rangle \) APB's can be imaged. The energies of the two types of APB's in the \( \text{DO}_3 \) structure are small and nearly isotropic.\(^{14} \) No such calculations have been made for the \( \text{L}_2^1 \) structure but in view of the similarities with the \( \text{DO}_3 \) structure, the APB energies for the \( \text{L}_2^1 \) structure are also expected to be small. The extinction distances for \( S_I \) and \( S_{II} \) type reflections are large in comparison with foil thickness (i.e., 1000 Å), so that the contrast of an APB at \( s = 0 \) (where \( s \) is the deviation parameter) in \( \text{Cu}_2\text{MnAl} \)
and Cu$_3$Al would consist of a single broad band with a contrast comparable to that observed in Fe$_3$Al.$^{15}$

One of the necessary conditions of a system to undergo spinodal decomposition is that the structure of the two decomposed phases be nearly identical, in order to allow continuity in modulation. In the case of ordered structures, therefore, the types of APB of the decomposed two phases are expected to be nearly the same. If the extinction distances of the superlattice reflections for the two phases have the same value, the images of the APB's would be continuous through the decomposed two phases.

In previous work,$^3$ it is reported that the APB's of the as-quenched alloys remained smoothly curved during brief aging at temperatures well inside the miscibility gap even though the microstructure is modulated. Figure 5(a) is a good example of this behavior. To enquire how APB's would behave when the specimen temperature exceeds that of the miscibility gap, hot stage sequences of the (111) dark field micrographs shown in Fig. 5 were taken of the Cu$_{2.5}$Mn$_{0.5}$Al alloy. The foil was oriented in a [110] zone where composition modulations parallel to [100] are imaged, along with the isotropic APB's. There APB's were shown to be of the type a/2(100) by taking a (200) dark field micrograph, in which no APB's were seen (See Table II). It should be noted that the $1/4a$(111) APB's generated at $T_c$(B2) ($750^\circ$C for Cu$_{2.5}$Mn$_{0.5}$Al) have a higher energy than the $1/2a$(100) APB's generated at $T_c$(L2$_1$-D0$_3$) ($600^\circ$C for Cu$_{2.5}$Mn$_{0.5}$Al). Therefore, it remains a possibility that $1/4a$(111) APB's exist within this structure, but, due to a large domain size, they lie outside the field of view of the micrographs in Fig. 5.
The [100] composition modulations lose contrast at 357°C (Fig. 5(d)), whereas the antiphase domain size increases as the temperature is increased. This observation indicates that the APB's developed during aging inside the miscibility gap inherit the same character above the miscibility gap. It is, therefore, believed that there is little interaction between the APB's and modulated structure. This observation can be explained on the basis of the reasons mentioned before; viz, (1) the types of APB's of the decomposed phases are the same as that of the ordered solid solution found above the miscibility gap, and (2) the APB energies in these structures are nearly isotropic. In addition, since this research relies on transmission electron microscopy, it is necessary that the imaging characteristics of the APB's be known, particularly any differences due to phase transformations. This problem is eliminated in the present study due to the similarity of the (111) extinction distances for the Cu₂MnAl and Cu₃Al phases and the L₂₁-D₀₃ solid solution.

B. Identification of the New Phase Appearing in Spinodally Transformed Cu-Al Rich Phase

1. Observation of the "New" Phase

The general morphology of the new phase has been reported previously,¹⁴ and in this paper its structure is reconsidered. The new phases are imaged in one of the spinodally decomposed products, which was shown to be the Cu₃Al rich-phase by Bouchard and Thomas.⁴

Figure 6(a) taken from the furnace cooled Cu₂.₅Mn₀.₅Al alloy reveals the modulated structure, with a wavelength of 210 Å. The corresponding diffraction pattern is shown in Fig. 7.
A dark field micrograph of the same area is shown in Fig. 6(b), obtained using the extra reflections marked N due to the new phase. The image shows that each small particle is elongated parallel to (111) which is the trace of {110} planes. The analysis of the morphology will be explained later. Figure 6(c) is a dark field micrograph using the diffraction spot marked M in Fig. 7. The random distribution of the particles having various sizes indicates that the reflection M is not simply due to a transformation in either Cu₃Al-rich phase or in Cu₂MnAl-rich phase, but is due to contamination, as demonstrated later.

The (310) micrograph taken from the aged specimen for 1000 min at 275°C shown in Fig. 8(a) is another example clearly imaging the new phase as black particles (B.F.) within the Cu₃Al rich phase. The micrograph clearly shows that the new phase is imbedded in the Cu₃Al phase and results from partial transformation of the DO₃ structure. The dark field micrograph of the new phase shown in Fig. 8(b) was obtained using the spot marked N in Fig. 9. The long axes of the imaged small particles are for the most part parallel to (133), which is also a trace of {011} planes as seen in Fig. 6(a) and (b). The dark field micrograph of Fig. 8(c) imaged with the reflection marked M in Fig. 9 illustrates that the small particles are dispersed throughout the area of the specimen, which is consistent with the morphology shown in Fig. 6(c).
2. Discussion of the Nature of the New Phase in the Cu-Al Rich Phase

It is well known that in binary Cu-Al alloys, Cu$_3$Al transforms martensitically to the 9R structure. The martensites are produced by a shear along one of the $(110)$ planes of the parent $\beta_1$ phase ($DO_3$ type), whose crystal structure consists of alternate stacking layers parallel to the $(110)$ plane, as shown in Fig. 10(b). The structure of the Cu-Al martensite varies with the Al content as shown in Table III below:

Table III.* Cu-Al martensite. 16-18

<table>
<thead>
<tr>
<th>Wt% Al</th>
<th>Symbol</th>
<th>Structure</th>
<th>Ms Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>11 Al</td>
<td>$\beta'$</td>
<td>fcc</td>
<td>450°C</td>
</tr>
<tr>
<td>11-13 Al</td>
<td>$\beta'_1$</td>
<td>9R</td>
<td>450°C-240°C</td>
</tr>
<tr>
<td>13-15 Al</td>
<td>$\gamma'$</td>
<td>2H</td>
<td>240°C</td>
</tr>
</tbody>
</table>

* $\beta'$ martensite is an ordered orthorhombic lattice consisting of units of 18 close-packed layers (9R) along the C direction. ($AB'CA'CA'BA'BC'BC'AC'AB'$). $\gamma'$ martensite consists of units of two close packed layers $AB'(2H)$ (see References 17 and 18).

It is possible that the new phase appearing in the Cu$_3$Al rich phase of the ternary Cu-Mn-Al alloys examined here would have this martensitic character. However, in the early stage of spinodal decomposition, the Cu$_3$Al rich component of the spinodal produce will contain Mn, which might have an effect on any subsequent transformation. It is reported that the structure of the martensite of Cu-12.5 wt% Al-4 wt% Mn alloy is based on an orthorhombic unit cell (2H structure). 19 Upon analyzing more diffraction patterns, the possibilities of those structures mentioned above were taken into consideration.
3. Analysis of Diffraction Patterns

A series of diffraction patterns representing several sections of reciprocal space (e.g., Figs. 7, 9, 20) was taken to determine the structure of the new phase. The result was best described by an orthorhombic structure, whose atom coordinates in the unit structure cell illustrated in Fig. 10(b) are:

\[
\begin{align*}
\text{Al} & \quad \text{Cu or Mn} \\
(000) & \quad (0, \frac{1}{2}, 0) \quad (\frac{1}{3}, 0, \frac{1}{2}) \\
(\frac{1}{3} \frac{1}{2} \frac{1}{2}) & \quad (\frac{1}{2}, 0, \frac{1}{2}) \quad (\frac{5}{6}, \frac{1}{6}, \frac{1}{2}) \\
(\frac{1}{3} \frac{3}{2} 0) & \quad (\frac{5}{6}, \frac{1}{6}, \frac{3}{2}) \\
\end{align*}
\]

The structure consists of two close-packed layers \( AB' \) (fundamentally a hexagonal close-packed structure), which is identical to the \( \gamma' \) phase in binary \( \text{Cu-13-15\% Al} \) alloys \(^{17}\) and \( \text{Cu-12.5 wt\% Al-4 wt\% Mn} \) alloys \(^{19}\), so it will also be called \( \gamma' \) by comparison. The reflections from the \( \gamma' \) phase and the \( \text{Cu}_2\text{MnAl} \) phase often superimpose, so that it is very difficult to uniquely determine the lattice parameter of the \( \gamma' \) phase. But the bright field shown in Fig. 8(a) illustrates that the \( \gamma' \) phase may be coherently imbedded in the \( \text{Cu}_3\text{Al} \)-rich phase. The lattice parameters of the \( \gamma' \) phase estimated from the \( \text{Cu}_3\text{Al} \) matrix unit cell are:

\[
\begin{align*}
A^* &= 4.12 \text{ Å} \\
B^* &= 5.84 \text{ Å} \\
C^* &= 4.03 \text{ Å}
\end{align*}
\]

Plane sections of the reciprocal lattice of the \( \gamma' \) phase are given in Fig. 11. Relative intensities are also indicated (from structure factor amplitudes only).
4. **Crystal Orientation Relationships**

One way to determine an orientation relationship is to compare observed interplanar angles between a pair of planes of the matrix and the $\gamma'$ phase with those expected from the assumed orientation relationships for a number of pairs of planes. For indexing matrix reflections with respect to $\gamma'$ reflections in order to determine the orientation relationship, the following specific lattice correspondence was always taken:

$$\begin{align*}
\begin{bmatrix} 1 & 1 & 0 \end{bmatrix}_{\beta_1} + [100]_{\gamma'}, \\
[0 & 0 & 1]_{\beta_1} + [010]_{\gamma'}, \\
\begin{bmatrix} 1 & 1 & 0 \end{bmatrix}_{\beta_1} + [001]_{\gamma'}
\end{align*}$$

Because of the weak intensity of the $\gamma'$ reflection, the orientation relationship is not determined definitely. According to the proposed $\gamma'$ structure, the $(110)_{\beta_1}$ plane corresponds to the $(001)_{\gamma'}$ plane. The dark field micrograph of the $\gamma'$ phase shown in Fig. 6(b) illustrates the basal plane orientation. As discussed before, the small particles are elongated parallel to $[1\bar{1}1]_{\beta_1}$ and $[1\bar{1}1]_{\beta_1}$ directions. In corresponding diffraction patterns, the diffuse streaks lie in $[1\bar{1}2]_{\beta_1}$ and $[112]_{\beta_1}$. The stereographic projection shown in Fig. 12 indicates the correlation between the elongated particles and the origin of the diffuse streaks in the diffraction pattern. In the stereographic projection, marks $\Box$ correspond to the matrix $\beta_1$ ordered phase, marks $\bullet$ indicate those of $\gamma'$ expected from the assumption that $(110)_{\beta_1} \parallel (001)_{\gamma'}$, $[1\bar{1}1]_{\beta_1} \parallel [2\bar{1}0]_{\gamma'}$, and marks $\circ$ specify those when another relationship is assumed to be $(110)_{\beta_1} \parallel (001)_{\gamma'}$, $[\bar{1}\bar{1}1]_{\beta_1} \parallel [\bar{2}\bar{1}0]_{\gamma'}$. 
Assuming that (110)$_{\beta_1}$ || (001)$_{\gamma'}$ and [111]$_{\beta_1}$ || [210]$_{\gamma'}$, hold, the direction of the streaks, [112], is normal to the [111]$_{\beta_1}$ direction in which the $\gamma'$ particles are lengthened and is the trace of the (121)$_{\gamma'}$ or (121)$_{\gamma'}$ plane. However, identical diffraction effects will result for the alternative relationship, (110)$_{\beta_1}$ || (001)$_{\gamma'}$, [111]$_{\beta_1}$ || [210]$_{\gamma'}$. Experimentally it is very difficult to distinguish which relationship is more probable because of the diffuseness of the $\gamma'$ spots.

5. Stability of the $\gamma'$ Phase

The stability of the $\gamma'$ phase was studied by heating the foil in the microscope. Furnace cooled specimens were chosen for heat treatment because of their high density of the $\gamma'$ phase, as reported previously. In Fig. 13, the sequence of dark field micrographs was obtained with the $\gamma'$ reflections marked as $\gamma'$ in the corresponding diffraction patterns shown in Fig. 14. Figure 14(a) shows the regular array of fine particles of the $\gamma'$ phase within the Cu$_3$Al rich phase as in Fig. 6(b). The corresponding diffraction pattern given in Fig. 14(a) indicates that in addition to the $\gamma'$ spots, the extra spots marked M are formed.

At 157°C, the particles begin to be imaged poorly in the dark field micrograph, but the reflections due to the phase are still present. They disappeared at 205°C. This indicates that the reversion temperature of the $\gamma'$ phase developed during furnace cooling is around 205°C.

At higher temperature, 222°C, a diffuse ring pattern is formed along the M spots and the intensity of the M spots seem to increase. The dark field of the M spots is shown in Fig. 15(g), which shows that the small particles are distributed over all the thin specimen.

At 400°C, the equilibrium phases in this alloy are; Cu$_3$Mn$_2$Al, $\gamma$ and $\beta$Mn.
The precipitation of these phases can be suppressed by quenching. However, it has been reported that precipitation of the equilibrium phase may occur due to electron bombardment in the electron microscope as in the Cu-Sn system. In the present investigation, no evidences of the presence of $\beta_{\text{Mn}}$ and Cu$_3$Mn$_2$Al were found. The M spots appearing in (110) (as shown in Fig. 7) and (112) (not shown in this paper) diffraction patterns closely fit the lattice parameters of the $\gamma$ phase, but those in the (001) pattern did not. A further indication of the origin of the M spots was made by observing a thin specimen kept in air for two months at room temperature after being bombarded by electrons in the microscope. Figures 15(a), (b) and (c) were taken of the old specimen. In Fig. 15(c), strong M spots are observed, but the reflections due to the $\gamma'$ phase are absent. This substantiates the suggestion that M spots are due to some sort of contamination e.g., oxidation or phase transformation occurring characteristically in thin specimens at room temperature, because a bulk specimen kept in air for two months at room temperatures does not give M spots at all. Since the lattice spacings corresponding to the M spots are not found in the Cu or Mn or Al oxides listed in ASTM cards, M spots may arise from not merely simple one element oxides, but rather from complex two or three element oxides. More work is needed to establish the origin of M spots.
IV. DISCUSSION

A. Spinodal and Ordering Reactions

1. Determination of the Miscibility Gap

The dissolution at the higher temperature of a structure developed by aging at a lower temperature would possibly occur for one of the following three cases; 7 (1) the reversion temperature is within the coherent spinodal, (2) the reversion temperature is above the coherent spinodal but within the metastable region and (3) the reversion temperature is above the coherent phase boundary. Because there are apparently no experimental elastic constants and thermodynamic data available for the Cu-Mn-Al ordered solid solution, the coherent spinodal, which allows for the stabilizing effect of elastic energy on coherency strains, is not able to be estimated. However, the chemical spinodal curve can be calculated from the formula derived by Cook and Hilliard.21

\[
C_s - C_c = C_e - C_c [1 - 0.422(T/T_c)]
\]

\(C_s\) and \(C_e\) are the spinodal and equilibrium compositions at temperature \(T\), and \(C_c\) is the critical compositions at the critical temperature \(T_c\). Using \(T_c \sim 355^\circ C\) and \(C_c \sim 0.65\), which values were adopted from the estimated miscibility gap curve, the chemical spinodal is derived (Fig. 1).

The limits of the miscibility gap illustrated in Fig. 1 were obtained by monitoring the disappearance of satellites and of modulated structures. For the Cu_{2.2}Mn_{0.8}Al alloy, the temperature at which the satellites were not detectable even by a microdensitometer analysis, was not consistent
with that at which the modulated structure was dissolved. But for the
\( \text{Cu}_{2.5}\text{Mn}_{0.5}\text{Al} \) alloy, both temperatures were very close together. This
finding might be explained by referring to Fig. 1 showing the limits
of the miscibility gap and the chemical spinodal curves. For the
\( \text{Cu}_{2.2}\text{Mn}_{0.8}\text{Al} \) alloy, the satellites disappeared and all reflections
were streaked in a direction parallel to \( \langle 100 \rangle \), as shown in Fig. 3(b),
at 318°C, which is close to the temperature of the estimated chemical
spinodal (310°C). From the bright field micrograph at 318°C, the
wavelength \( \lambda \) was estimated to be \( \sim 230\text{Å} \), the corresponding satellites
of which should have been detected in the diffraction pattern since
satellites spacings of wavelength less than \( \sim 300\text{Å} \) were measurable. Instead
of the satellites, streaks were observed. This observation suggests that
the spinodal temperature for the \( \text{Cu}_{2.2}\text{Mn}_{0.8}\text{Al} \) alloy is around 318°C.
For the \( \text{Cu}_{2.5}\text{Mn}_{0.5}\text{Al} \) alloy the difference between the temperature of
the miscibility gap and the chemical spinodal temperature is \( \sim 14°C \).
This may explain why the satellites and the modulated structure
disappeared nearly at the same temperature for the \( \text{Cu}_{2.5}\text{Mn}_{0.5}\text{Al} \) alloys.

Because the misfit between the coherent particles in this system
is large (\( \sim 2\% \)), the coherent spinodal is expected to be depressed
below the chemical spinodal. However, as an example, the \( \text{Cu}_{2.5}\text{Mn}_{0.5}\text{Al} \)
alloy is very brittle as shown by the tensile data reported previously. \( ^{13} \)
Young's modulus estimated from the stress-linear strain curve is
\( \sim 5\times10^8 \text{ (dyn/cm}^2 \text{)} \) (\( Y_{(100)} \text{ Cu} \sim 1.15\times10^{12} \text{ dyn/cm}^2 \)), assuming the deformation
occurred not along the grain boundary but uniformly within the grain.
It should be noted that the estimation of Young's modulus made here is
subject to a great uncertainty since the polycrystal specimens are
surely deformed along the grain boundary regions. If Young's modulus is very small, a strain energy term \( \eta^2 Y \), in which \( \eta = (1/a) (da/dc) \) and \( Y \) is Young's modulus, is also small. Therefore the coherent spinodal, given by the locus of \( f'' + 2\eta^2 Y = 0 \), may be in approximately the same position as the chemical spinodal. As discussed above, metallographic features on heating the system are well explained by the position of the chemical spinodal, which also suggests that the coherent spinodal and the chemical spinodal coincide.

2. The Effect of Modulated Structures on APB Formation

Morral and Cahn 22 extend the theory of spinodal decomposition to ternary systems and show the possibility of spinodal decomposition and continuous ordering occurring simultaneously. Also, in binary systems, it has been reported that Fe-Be alloys decompose into a periodic, modulated structure containing Fe-Be particles with the ordering CsCl structure. 23-25 M. J. Richards and J. W. Cahn 26 examined the ground state energy and superstructures of bcc and fcc using Ising model systems by taking account of second neighbor interactions and demonstrated that ordering and clustering are not mutually exclusive even for binary alloys.

One of their results is illustrated in Fig. 16 to show the curve of the energy of mixing of various states as a function of composition, where first and second neighbor interaction parameters, \( V_1 \) and \( V_2 \) are positive and \( 4/3 > V_2/V_1 > 2/3 \). The ordered structure in the ground state up to 25% (and between 75 and 100%) is of the \( \text{Fe}_3\text{Al}(\text{Fm3m}) \) type. There are two superstructures that are candidates for the ground state between 25 and 50% B; (a) a superstructure with symmetry \( \text{Fm}3\text{m} \) and 16 atoms per cell with sites in position II of the \( \text{Fe}_3\text{Al} \) lattice (\( \text{DO}_3 \) structure)
being progressively filled by B; (b) a superstructure with the lower symmetry of space group F\textsuperscript{4}3m and 16 atoms per unit cell, with sites either in position I or III being progressively filled by B.

By extending this idea to the pseudo-binary phase diagram composition along the Cu\textsubscript{3}Al-Cu\textsubscript{2}MnAl alloy shown in Fig. 1, Fig. 16 indicates the possible metastable transition phases that might form during transformation from the disordered state to the equilibrium state following a quench from high temperatures. Figure 16 is well followed by the sequence of ordering reactions occurring in the alloys along the composition line Cu\textsubscript{3}Al-Cu\textsubscript{2}MnAl. Referring to Fig. 1 and Fig. 2, a disordered bcc structure first orders to a B2 structure and further orders to a DO\textsubscript{3}-L\textsubscript{2}1 structure. The non-stoichiometric superstructure up to 25% Mn would form the superstructure resembling an L\textsubscript{2}1 structure because excess Mn atoms favor type II sites in place of Cu atoms according to Fig. 16 showing Fm\textsuperscript{3}m in the ground state. On the Cu\textsubscript{2}MnAl side (between 75 and 100% Mn), excess Cu atoms tend to replace type II sites instead of Mn atoms. Thus DO\textsubscript{3}-L\textsubscript{2}1 structures are stabilized through the composition line Cu\textsubscript{3}Al-Cu\textsubscript{2}MnAl above a certain temperature. The DO\textsubscript{3}-L\textsubscript{2}1 structure is in the ground state up to 25% Mn (and between 75 and 100 Mn), so that the superstructure is relatively stable at lower temperature near these compositions (below 350°C). The superstructure in the ground state between 25 and 50% is space group F\textsuperscript{4}3m.

From the symmetry of the curve in Fig. 16, the same arguments hold also between 45 and 100% B. Excess Mn atoms in the Cu\textsubscript{3}Al alloy progressively fill up positions I or III rather than position II shown in Fig. 2. For
the Cu$_2$MnAl side in this range (between 50 and 75% Mn), Cu atoms are in excess and Mn atoms are deficient with respect to the L2$_1$ structure. These excess Cu atoms may diffuse to the Cu$_3$Al phase to form the nearly stoichiometric crystal (DO$_3$) and further reduce the energy of mixing. On the other hand, the excess Mn atoms in the Cu$_3$Al phase may tend to diffuse to form the nearly stoichiometric L2$_1$ structure. This may explain the origin of Cu rich or Mn rich sinusoidal compositional modulations which develop inside the miscibility gap. However, it is uncertain whether the superstructure within the miscibility gap possesses the Fm3m or the F43m space group symmetry. X-ray diffraction techniques cannot be used to experimentally distinguish between these two superstructures. Even if the superstructure within the miscibility gap is F43m, it is expected that the APB configuration of F43m is the same as that of Fm3m (DO$_3$). This model supports the observation that APB's developed during aging inside miscibility gap inherit the same character above the miscibility gap.

B. Identification of the New Phase Appearing in Spinodally Transformed Cu-Al Rich Phase

1. Classification of the DO$_3^{\gamma'}$ Transformation (previously DO$_3^{\gamma^{LL}}$)\textsuperscript{4,13}

It was reported that a slower quench results in the appearance of a new phase ($\gamma'$) in the Cu$_3$Al rich phase. Increasing the quench rate decreases the amount of the new phase.\textsuperscript{13} This observation can be explained by the character of a thermoelastic martensite expected in Cu-Al based alloys.

The martensite which emerges in an Fe-30% Ni alloy is normally formed by a high degree of undercooling, but thermoelastic martensite
(e.g. Au-47.5% Cd) requires little driving force for the transformation to occur. The conventional martensite transforms by "bursting" to a final size at a high under-cooling, but thermoelastic martensite grows in length and width with cooling. There is also significant differences in As (austenite start temperature) and Ms (martensite start temperature) between conventional and thermoelastic martensites. The difference between As and Ms is large (400°C for the Fe-30% Ni alloy) in the former case, but is small (15°C for Au-47.5% Cd) in the latter case.

As shown in Table 2, the Ms temperature of the γ' phase appearing in the Cu-Al system is 240°C or below and decreases with the increasing Al content. The Ms temperature of the γ' phase in the Cu-Al system is in quite good agreement with the reversion temperature of the γ' phase (205°C), estimated from the furnace cooled specimen (Cu_{2.5}Mn_{0.5}Al) by hot stage analysis. Because it is expected that the difference between Ms and As is very small for thermoelastic martensite, the Ms temperature of the γ' phase in the Cu_{3}Al rich phase would be close to the reversion temperature of the γ' phase.

However, in an early stage of spinodal decomposition, one of the spinodal products, the Cu_{3}Al rich phase, will contain some amount of Mn. The effects of Mn addition on the phase transformation of the β Cu-Al alloys have been investigated by several workers.

Tarora reported that Mn additions depress the temperature of eutectoid decomposition $\beta \rightarrow \alpha + \gamma_2$ and tend to suppress the occurrence of the decomposition. The Ms temperature of the $\beta_1 \rightarrow \beta'_1$ transformation is also lowered by the addition of Mn and Al. Sugino, Nakanishi and Mitani also studied the effects of Mn addition on martensite in Cu-Al...
alloys by means of specific heat and X-ray measurements. It was found that two types of martensite, \( \beta'_1 \) and \( \gamma' \), were formed in a Cu-11.8% Al-4% Mn alloy. After iced brine quenching, only the \( \beta'_1 \) martensite peak was detected around 385°C on specific heat vs temperature curves for the alloy. But in slowly cooled specimens (i.e., a furnace cool or an air cool), a martensite peak was found at 170°C in addition to the \( \beta'_1 \) martensite. As the quenching rate is reduced, the peak corresponding to \( \gamma' \) martensite becomes stronger and the \( \beta'_1 \) peak becomes weaker.

As shown in Table III, increasing the Al content varies the structure of the martensite in the Cu-Al system. In the Cu-Al-Mn system, the structure of the martensite is additionally subject to heat-treatment, as well as composition variations. Figures 17, 18 and 19 were taken from Cu-12.4% Al-4.68% Mn alloy which is almost at the end of miscibility gap for the Cu-Al rich phase. The former two specimens were oil quenched and the latter one was furnace cooled. Oil quenching yields the ordered \( \beta'_1 \) single phase as shown in Fig. 17, although some areas contain the twinning plates shown in Fig. 18. Furnace cooling produces a plate-like morphology, having internal striations. The diffraction pattern shown in Fig. 19(a) was taken from the plate marked (a) in the bright field micrograph. The structure of the plate found here is analysed to be identical with that of the \( \gamma' \) phase in the Cu-Al rich phase. The direction of strong streaking in the diffraction pattern is perpendicular to the direction of the striations in the bright field micrograph, so that the striations are due to a high density of stacking faults. The striations in the plate marked (b) are normal to
those in the plate marked (a). The diffraction pattern taken from the area marked C, including both plates (a) and (b), gives the same pattern as that taken from the furnace cooled \( \text{Cu}_2.5\text{Mn}_{0.5}\text{Al} \) alloy shown in Fig. 20. The (001) diffraction pattern of the furnace cooled \( \text{Cu}_2.5\text{Mn}_{0.5}\text{Al} \) alloy is indexed in terms of the two variants of the \( \gamma' \) phase. The morphology of the two variants of the \( \gamma' \) phase in an (001) orientation has been discussed extensively in previous papers.\(^4\),\(^13\)

The density of plates observed in Fig. 19 increases with decreasing quenching rate. This implies that the plates are formed from the ordered \( \beta_1 \) phase because slower quenching results in developing a higher degree of ordering. Cahn and Coll\(^29\) confirmed that an \( \text{Fe}_3\text{Al} \) alloy with the \( \text{DO}_3 \) type structure shows resistance to twinning if the degree of order is increased, and that the alloy does not exhibit twinning if it is fully ordered. This is consistent with the observation made here.

Since those plates (possibly the \( \alpha' \) martensite) emerging in the \( \text{Cu-12.4}\%\text{Al-4.68}\%\text{Mn} \) alloy obey the observed \( \alpha' \) phase behavior in the \( \text{Cu}_3\text{Al} \) rich phase, and since the alloy is located near the \( \text{Cu}_3\text{Al} \) rich side of the miscibility gap, the \( \gamma' \) martensite in \( \text{Cu-12.4}\%\text{Al-4.68}\%\text{Mn} \) may have the same origin as the \( \gamma' \) phase in the \( \text{Cu}_3\text{Al} \) rich material.

The structure of this new phase (\( \gamma' \)) was previously proposed\(^4\) to be of the \( \text{L}_1^0 \) type, which is generated from the \( \text{DO}_3 \) structure by the partial disordering of the \( \text{DO}_3 \) lattice to the \( \text{B}_2 \) lattice, followed by the ordering of only one set of the \( \{110\} \) planes of the \( \text{B}_2 \) structure. However, this mechanism would fail to explain the observation that the amount of the \( \text{L}_1^0 \) phase increases with decreasing quenching rate, on
the basis of the arguments which follow:

(1) The proposed mechanism involves the generation of non-conservative APB's of the DO₃ structure parallel to every (220) plane of the structure.

(2) The surface energies of non-conservative APB's will be higher relative to conservative APB's due to the change in local composition across non-conservative

(3) The APB energy of both types are also proportional to $S^2$ where $S$ is the degree of long range order. Consequently the relative difference in energies will be small in partially ordered alloys and may effectively vanish in as-quenched alloys. This implies that conservative APB's are more stable than non-conservative APB's when the degree of order, represented by $S$, is high.

Therefore, it is expected that iced-brine quenched alloys would produce a high density of the Ll₀ phase due to the stabilization of non-conservative APB's which is required for the nucleation of the Ll₀ phase. Slowly quenched alloys would have a lower density of the Ll₀ phase due to destabilization of the non-conservative APB's ($S$ is large).

The experimental observations, however, are inconsistent with the prediction made above, based on the previously proposed mechanism. Instead, the origin of the γ' phase is proposed in this paper to be the transformation of the ordered DO₃ phase, by homogeneous (110) shear, to an orthorhombic Cu₃Ti type structure shown in Fig. 10, which is similar to the γ' martensite in Cu-Al-Mn (or in Cu-Al).
2. Metallography of the $\gamma'$ Phase

The structure of the $\gamma'$ phase in the Cu$_3$Al rich phase was determined to be orthorhombic, with lattice parameters of $A = 4.12\,\text{Å}$, $B = 5.84\,\text{Å}$ and $C = 4.03\,\text{Å}$. However, the lattice parameters of the $\gamma'$ phase in Cu-12.5% Al-4% Mn and in Cu-13% Al, have been reported to be $a = 4.45\,\text{Å}$, $b = 5.30\,\text{Å}$, $c = 4.24\,\text{Å}$ and $a = 4.51\,\text{Å}$, $b = 5.20\,\text{Å}$, $c = 4.22\,\text{Å}$ respectively. It is considered that the $\gamma'$ martensite in the Cu-Al system is formed by a shear along (110) planes of the parent $\beta_1$-lattice, accompanied by shuffling on alternate layers. But the Cu$_3$Al rich phase in which $\gamma'$ imbedded is surrounded by the ternary Cu$_2$MnAl rich phase, so that the mode of DO$_3$$\gamma'$ would be restricted by the strain due to the misfit between the Cu$_3$Al phase and the Cu$_2$MnAl phase. This may be the reason why the lattice parameters of the $\gamma'$ phase in the Cu$_3$Al rich phase differs from those in Cu-Mn-Al or Cu-Al, and why the structure of the phase is close to tetragonal ($a = 4.12\,\text{Å}$ and $c = 4.03\,\text{Å}$).

The orientation relationship between the L1$_0$ phase ($\gamma'$ phase) and Cu$_2$MnAl have been reported as followed:

\[
\begin{align*}
(010)_{\text{L}1_0} & \parallel (001)_{\text{L}2_1} \\
[001]_{\text{L}1_0} & \parallel [110]_{\text{L}2_1}
\end{align*}
\]

This orientation relationship is basically the same as the lattice correspondence explained before. But previous observation of the particles in a [110] foil has shown that the L1$_0$ particles are distributed in platelets lying in the (001) plane of the matrix. The present high resolution dark field micrograph shown in Fig. 6(b) reveals, however, that the $\gamma'$ particles are not elongated along the (001) plane of the
matrix, but rather along the (111) directions of the matrix. The trace analysis of this direction yields the following orientation relationship.

\[(001)_\gamma \parallel (110)_\beta', \quad [\overline{1}1\overline{1}]_\beta \parallel [\overline{2}10]_\gamma', \]

or \([\overline{1}1\overline{1}]_\beta \parallel [\overline{2}10]_\gamma', \]

A similar orientation relationship was reported in Cu-Sn martensite.\(^\text{30}\)

In the Cu-Sn system, two kinds of martensite were observed, banded (\(\beta'\)) and wedge-shaped (\(\beta''\)), depending on the heat treatment. The former was found to be an orthorhombic lattice of \(AB'AC'\) type with stacking faults in the quenched state. The latter was found to be the orthorhombic lattice of \(AB'\) type, which is equivalent to the structure of the \(\gamma'\) phase found in this investigation, when the alloy was subzero-cooled.

The orientation relationship obtained in the latter case was \((001)_\beta \parallel (110)_\beta_2\)

and \([\overline{2}10]_\beta \parallel [\overline{1}1\overline{1}]_\beta_2\), which holds good when the twinning plane is expected as \((121)\) and the stacking fault plane as \((\overline{1}2\overline{1})\).

Also in the present investigation the same relationship is found to hold. The particles are lengthened along the \((121)\) or \((\overline{1}2\overline{1})\) plane and the direction of the streaks in the diffraction pattern is normal to the trace of the \((121)\) or \((\overline{1}2\overline{1})\) plane. This analysis suggests that the \((121)\) or \((\overline{1}2\overline{1})\) plane would be the twinning plane or stacking fault plane in the \(\gamma'\) phase.

The \(\gamma'\) martensites shown in Figs. 18 and 19, in the Cu-12.5 wt% Al-4.68 wt% Mn alloy located at the Cu\(_3\)Al rich side of the miscibility gap, indicate that oil quenching produces twinning plates (Fig. 18) and furnace cooling gives highly faulted plates (Fig. 19). Figure 19 is very similar to faulted martensite structures observed in binary Cu-Al alloys (e.g., References 16 and 17). Thus, the \(\gamma'\) phase which emerges in the
Cu₃Al rich spinodal product, might have the same features (i.e., internal faulting or twinning). However, the γ' phase of the furnace cooled Cu₂.₅Mn₀.₅Al alloy is expected to have a faulted character, since slower quenching results in the faulted structure for the alloy near the end of miscibility gap. The diffuse streaks in the diffraction pattern shown in Fig. 7 may, therefore, be due to the internally faulted structure of the γ' phase.

3. γ' Phase and Spinodal Decomposition

The γ' phase would vary its structure and Ms temperature due to changes in Mn or Al content and heat-treatment. Complications in uniquely identifying the γ' phase arise from the fact that the wavelength (λ) of the sinusoidal composition modulations show strong variation with aging, so that Mn or Al concentration changes with aging inside the miscibility gap.

It has been reported that at the early stages of coarsening, the structure of the binary phase is mostly that of γ' phase. In the intermediate stages of coarsening the volume fraction of the γ' phase within the binary phase decreases by about a factor of 3 between 300 to 3000 min aging. By aging at temperatures above 275°C, the binary phase has mainly the D₀₃ structure, with a relative absence of γ' particles.

These observations could be explained by the pseudo-binary phase diagram along composition line Cu₃Al–Cu₂MnAl shown in Fig. 1. The composition of the equilibrium phase at the Cu₃Al rich side after aging at 225°C is estimated as Cu-12.5 wt% Mn-4.6 wt% Al from the figure. Since composition itself is responsible for producing the Cu–Mn–Al martensite as seen in Figs. 18 and 19, it is expected that the γ' phase would appear even after long time aging at 225°C. However, 275°C and 325°C
aging for long times (i.e., 10,000 min) would not give rise to the \( \gamma' \) phase, simply because the expected compositions of Cu-Al rich side after long time aging are Cu-12.5 wt% Al-6.12 wt% Mn and Cu-12.6 wt% Al-10.26 wt% Mn respectively. Higher Mn contents tend to depress the Ms temperature.

Moreover, in the early stages of spinodal decomposition, some amount of Mn atoms do not diffuse from the binary rich phase. Consequently in the initial spinodal reaction the Mn concentration in the binary phase would be higher than that at the later stage of aging, so that the \( \gamma' \) phase would not appear within the binary phase. It has been reported that the \( \text{Cu}_3\text{Al} \) rich phase is distorted to a tetragonal symmetry before losing coherency\(^3\). This tetragonal structure of the \( \text{Cu}_3\text{Al} \) undergoes compression along cubic directions, as set up by the ternary phase. These misfit compression stresses could then be relieved by \( \langle 110 \rangle \) shearing if the elastic constant \( 1/2(C_{11} - C_{12}) \), corresponding to \( \{110\}\langle 110 \rangle \) shear, would decrease to zero.

Although there is no data about the elastic constant of \( \text{Cu}_3\text{Al} \), it is expected that lattice softening might occur just before the Ms temperature. This condition might also explain the occurrence of the \( \text{DO}_{3} \rightarrow \gamma' \) transformation, even when the Cu-Al rich phase contains a high Mn content.
The following results and conclusions have been drawn from this investigation:

1. The miscibility gap temperatures of the \((\text{Cu-Mn})_3\text{Al}\) alloy were determined by "in situ" hot stage experiments. The results summarized in Fig. 1 are in agreement with previous studies.

2. The position of the chemical spinodal estimated from the miscibility gap curves, is reinforced by the metallographic observations of the \(\text{Cu}_{2.5}\text{Mn}_{0.5}\text{Al}\) and \(\text{Cu}_{2.2}\text{Mn}_{0.8}\text{Al}\) alloy in "in situ" experiments. The coherent spinodal curve of the alloys is believed to be in the nearly same position as the chemical spinodal.

3. The APB's in \(\text{Cu}_{2.5}\text{Mn}_{0.5}\text{Al}\) developed during aging inherit the same character as those above the miscibility gap, having little interaction with the modulated spinodal structure.

4. The new phase (\(\gamma'\)) which emerges within the spinodally transformed Cu-Al rich phase is identified as having an orthorhombic lattice of AB' type, (i.e., two layer stacking \(\{110\}_{\beta_1}\) phase) and results from partial transformation of the \(\text{DO}_3\) structure.

5. The orientation relationships between the \(\gamma'\) phase and the parent \(\beta_1(\text{DO}_3)\) phase are

\[(100)_{\beta_1} (001)_{\gamma'}, \quad [\overline{1}11]_{\beta_1} [\overline{2}10]_{\gamma'},\]

or \([\overline{1}1\overline{1}]_{\beta_1} [2\overline{1}0]_{\gamma'}\)

6. The reversion temperature of the \(\gamma'\) phase in furnace cooled \(\text{Cu}_{2.5}\text{Mn}_{0.5}\text{Al}\) alloys was determined to be \(\approx 205^\circ\text{C}\) by the hot stage work, and his is close to the \(\text{Ms}\) temperature (240°C) for \(\gamma'\) martensite in a
Cu-13-15% Al alloy. However, the Ms temperature decreases with increasing Mn and Al content.

7. The Cu-12.4% Al-4.68% Mn alloy, which is almost at the end of miscibility gap near the Cu-Al rich phase, shows that oil quenching results in nearly all single phase material, except for small regions of twinned γ' plates (martensite), but furnace cooling yields a high number of densely faulted γ' plates (martensite). This observation is in good agreement with that of the γ' phase in the spinodally decomposed Cu-Al rich phase, because slower quenching gives a high density of γ' phase in the Cu_{2.5Mn0.5}Al alloy.
ACKNOWLEDGEMENTS

The author is deeply grateful to Professor Gareth Thomas for his guidance, encouragement, unending patience and support during this work. He is indebted to Dr. R. Sinclair and Mr. R. Gronsky for many helpful discussions and for reviewing the manuscript. He is also thankful to Dr. Omer Van der Biest for his help in computer programming.

This research was performed under the auspices of the U. S. Atomic Energy Commission through the Inorganic Materials Research Division of the Lawrence Berkeley Laboratory.
APPENDIX: CALCULATION OF THE VALUES OF THE EXTINCTION DISTANCE ($t_0$) OF Cu$_3$Al

The general procedure to obtain extinction distances is discussed with an example by Thomas. 31

The values of $t_0$ are obtained using the following expression derived by Hirsch et al.: 32

$$ t_0 = \frac{\pi V \cos \theta}{\lambda F} = \frac{\pi a_0^3 \cos \theta}{\lambda F} $$

($s = 0$ where $s$ is deviation parameter from the exact Bragg reflection)

where $\lambda$ is the wavelength of the incident beam, $V$ is the volume of the unit cell of edge length $a_0$ and $F$ is the structure factor for the unit cell. The structure factors associated with DO$_3$ type superlattice are given by the following:

$$ F_{DO_3} = 4(3f_{Cu} + f_{Al}) $$

for $h, k, l$ all even and $\left( \frac{h + k + l}{2} \right)$ even

$$ F_{s} = 4(f_{Cu} - f_{Al}) $$

for $h, k, l$ all odd, and

$$ F_{s} = 4(3f_{Cu} + f_{Al}) $$

for $h, k, l$ all even and $\left( \frac{h + k + l}{2} \right)$ odd

where $f_{Cu}$ and $f_{Al}$ are the electron scattering factor of Cu and Al, respectively. The calculated values of $f_{Cu}$ and $f_{Al}$ are listed in Table IV.
Table IV. Atomic scattering amplitudes for electrons $f$ in Å (after the appendix of Ref. 33).

<table>
<thead>
<tr>
<th></th>
<th>(111)</th>
<th>(200)</th>
<th>(222)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_{Cu}$</td>
<td>3.47</td>
<td>3.00</td>
<td>2.01</td>
</tr>
<tr>
<td>$F_{Al}$</td>
<td>2.14</td>
<td>1.76</td>
<td>1.11</td>
</tr>
</tbody>
</table>

Thus, for 100 kV electrons ($\lambda = 3.7\times10^{-10}$), and taking $\cos\theta = 1$, $t_o$ of the (111) reflection for Cu$_3$Al is obtained as follows:

$$t_o(111) = \frac{3.14\times(5.83\times10^{-8})^3}{3.7\times10^{-10}\times4(3.47 - 2.14)\times10^{-8}}$$

$\sim 3160\text{Å}$

$t_o(200) \sim 590\text{Å}$

$t_o(222) \sim 3415\text{Å}$
REFERENCES

1. O. Heusler, Phys. Gesel, 1399 (1903).


28. Tarora, J. Japan Inst. of Metals 8, 6 (1944); 13, 3 (1949).


Fig. 1. The pseudo binary phase diagram along Cu$_2$MnAl and Cu$_3$Al (after Bouchard). The temperatures of the miscibility gap obtained in this investigation are illustrated. The chemical spinodal was calculated using $T_C \sim 355^\circ C$ and $C \sim 0.65$ from Ref. 21. The Curie temperatures of the quenched alloys were taken from Ref. 13.

Fig. 2. Schematic representation of the ordering sequence during the quenching of the alloy Cu$_{2.5}$Mn$_{0.5}$Al (vertically) and its isothermal decomposition (horizontally).

Fig. 3. Bright field micrographs from the alloy Cu$_{2.2}$Mn$_{0.8}$Al. Showing the gradual increase in the wavelength of the composition modulation parallel to the cube planes and dissolution of the modulated structures.

Fig. 4. Sections of the corresponding (001) diffraction pattern. The figure illustrates the gradual emergence of the well defined satellites and the gradual decrease of the intersatellite spacing to yield diffraction spot streaking. The temperature of the miscibility gap is believed to be around 358°C.

Fig. 5. Dark field micrographs taken with (111) reflection of the alloy Cu$_{2.5}$Mn$_{0.5}$Al in (110) orientation. The figure shows that the smoothly curved 1/4a(100) APB's have little interaction with the composition modulation even when the specimen temperature exceeds the miscibility gap temperature.
Fig. 6. (a) Bright field micrograph of the alloy Cu$_{2.5}$Mn$_{0.5}$Al cooled in the furnace. (b) Dark field micrograph of the same area imaged with the reflection marked N in Fig. 7 showing γ' particle elongation along (111) directions. (c) Dark field micrograph of the same area obtained with the reflection marked M in Fig. 7, showing that M spots are not due to the Cu-Al rich transformation.

Fig. 7. (110) corresponding diffraction pattern of Fig. 6. The extra reflections marked M are indexed in terms of the proposed γ' phase structure.

Fig. 8. (a) Bright field micrograph of the alloy Cu$_{2.5}$Mn$_{0.5}$Al aged at 275°C for 1,000 min, showing the γ' phase imbedded in the Cu$_3$Al rich phase. (b) Dark field micrograph of the same area imaged with the spot marked N in the corresponding diffraction pattern shown in Fig. 9. The γ' particles are elongated along (133) directions. (c) Dark field micrograph obtained using the reflection marked M in Fig. 9.

Fig. 9. The corresponding (310) diffraction pattern of Fig. 8. Symbols are the same as in Fig. 7.

Fig. 10. (a) Crystal structure of the matrix DO$_3$ type (β$_1$). (b) The proposed orthorhombic structure of the γ' phase, showing the lattice correspondence in the transformation from the β$_1$ matrix to the γ' phase.

Fig. 11. Reciprocal lattice section of the proposed γ' phase, with the calculated structure factors.
Fig. 12. Stereographic projection, showing the orientation relationships between $\beta_1$ matrix and $\gamma'$ phase. Marks $\square$ and $\bullet$ correspond to the main lattice planes of the $\beta_1$ matrix and the $\gamma'$ phase, respectively. Marks $\bullet$ indicate those of the $\gamma'$ phase expected from the assumption that $(001)_\gamma\| (110)_{\beta_1}$, $[\bar{2}10]_\gamma\| [\bar{1}11]_{\beta_1}$. Marks $\bigcirc$ indicate those when the second orientation relationship is assumed to be $[\bar{2}10]_\gamma\| [\bar{1}11]_{\beta_1}$.

Fig. 13. A sequence of dark field micrographs of the $\gamma'$ phase in the furnace cooled $\text{Cu}_{2.5}\text{Mn}_{0.5}\text{Al}$ alloy, imaged with the $\gamma'$ reflection, indicating the stability of the $\gamma'$ phase. (g) is the dark field micrograph obtained using the reflection marked M in Fig. 14.

Fig. 14. The corresponding diffraction patterns for the Fig. 13. The reflections due to the $\gamma'$ phase disappeared around 205°C.

Fig. 15. (a) The bright micrograph of the oil quenched $\text{Cu}_{2.2}\text{Mn}_{0.8}\text{Al}$ alloy aged at room temperature for two months. The foil yields a general morphology which may be due to contamination. (b) The dark field micrograph imaged with the reflection marked M in the diffraction pattern shown in (c). (c) The corresponding (110) diffraction pattern, showing no $\gamma'$ spots, but strong M spots.

Fig. 16. The energy of mixing vs composition of various states on the bcc structure from Ref. 26, indicating that an Fe$_3$Al (Fm3m) type is in the ground state up to 25% B, but a Fd$\bar{4}3m$ structure is in the ground state between 25 and 50% B.
Fig. 17. Bright field micrograph from the oil quenched Cu-12.4% Al-4.68% Mn alloy in an (001) orientation, showing a large extent of ordered $\beta_1(DO_3)$ single phase.

Fig. 18. Bright and dark field micrographs from the oil quenched Cu-12.4% Al-4.68% Mn alloy, indicating regions containing twinned plate.

Fig. 19. Bright field micrograph from the furnace cooled Cu-12.4% Al-4.68% Mn alloy in an (010) orientation, showing two variants of plates with internal striations. The diffraction patterns (a), (b) and (c) were taken from the corresponding area marked (a), (b) and (c) in the bright field micrograph. The streaks are normal to the striations in the plates are are believed to be due to stacking faults within the plates.

Fig. 20. (001) diffraction pattern of the furnace cooled Cu$_{2.5}$Mn$_{0.5}$Al alloy, indexed in terms of the two variants of the $\gamma'$ phase. The symbols are the same as in Fig. 7.
\( \beta \) (Disordered BCC)

\( T_c (B2) \)

\( B2 \)

\( T_c (DO_3-L2_1) \)

\( T_c L2_1 \)

\( T_c DO_3 \)

\( M_S \)

Curie Temp.

Chemical Spinodal

\( \text{Cu}_2\text{MnAl} \)

\( \text{Cu}_3\text{Al} \)

(1) After Bouchard

(2) Present investigation

Fig. 1

ATOMIC COMPOSITION \( \text{Cu}_{3-x} \text{Mn}_x \text{Al} \)

XBL 749-7148
Fig. 2
Fig. 5
Fig. 6
Fig. 7

[110]_{\beta_1} // [001]_{\gamma'}

DO_3 △ FUNDAMENTAL
(\beta_1) ▲ SUPERLATTICE
\gamma' ● FUNDAMENTAL
o SUPERLATTICE
x DOUBLE REFLECTION

XBB 748-5443

Fig. 7
Fig. 9

\[ [310]_β_1 \parallel [102]_γ' \]
Cu₃Al (DO₃) ORTHORHOMBIC STRUCTURE

- Al ATOMS
- Cu ATOMS

Fig. 10
\[
\begin{align*}
\ell = 2n + 1
\end{align*}
\]

**FUNDAMENTAL**
- \(2(3\text{fu} + f\text{Al})\)
- \(\sqrt{3} (3\text{fu} + f\text{Al})\)
- \(3\text{fcu} + f\text{Al}\)

**SUPERLATTICE**
- \(2(f\text{cu} - f\text{Al})\)
- \(\sqrt{3} (f\text{cu} - f\text{Al})\)
- \(f\text{Cu} - f\text{Al}\)

Fig. 11
(001)_{γ'} \parallel (110)_{β_1}

- $β_1$
- $γ'$

--- $[2\overline{1}0]_{γ'} \parallel [\overline{1}1\overline{1}]_{β_1}$

--- $[\bar{2}\bar{1}\bar{0}]_{γ'} \parallel [\bar{1}1\bar{1}]_{β_1}$

XBL749-7147

Fig. 12
Fig. 17
Oil Quench

Fig. 18
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.