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## AS-QUENCHED MICROSTRUCTURE OF A Cu-24.8Mn-30.0Al ALLOY

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### Introduction

Effects of manganese addition on the microstructural changes of Cu-Al binary alloys have been extensively studied by many workers[1-18]. Based on these studies, M. Bouchard and G. Thomas have established the Cu-Mn-Al metastable phase diagram[1]. In this phase diagram, it is seen that when the  $\text{Cu}_{3-x}\text{Mn}_x\text{Al}$  alloy with  $0.2 \leq x \leq 0.8$  was solution heat-treated at a point in the  $\beta$  phase region and then quenched rapidly, a  $\beta \rightarrow \text{B}_2 + \text{D}_0_3 + \text{L}_{21}$  phase transition would occur during quenching. It means that the as-quenched microstructure of the  $\text{Cu}_{3-x}\text{Mn}_x\text{Al}$  alloy with  $0.2 \leq x \leq 0.8$  was a mixture of  $(\text{D}_0_3 + \text{L}_{21})$  phases. When the manganese content in the  $\text{Cu}_{3-x}\text{Mn}_x\text{Al}$  alloy was increased to 25 at pct ( $x = 1$ ), the as-quenched microstructure became a single  $\text{L}_{21}$  phase[1-5]. The crystal structure of the  $\text{L}_{21}$  phase is similar to the  $\text{D}_0_3$  structure of  $\text{Cu}_3\text{Al}$ , and the only difference between them is that Mn replaces the Cu at a specific lattice site with the eight nearest Cu atoms in the  $\text{D}_0_3$  structure so as to form a stoichiometric composition of  $\text{Cu}_2\text{MnAl}$ [1].

Recently, we made transmission electron microscopy observations on the phase transformations of a  $\text{Cu}_{2.2}\text{Mn}_{0.8}\text{Al}$  alloy[18]. Based on this study, it is found that the microstructure of the alloy in the as-quenched condition or aged at  $300^\circ\text{C}$  was a mixture of  $(\text{D}_0_3 + \text{L}_{21} + \text{L-J})$  phases, where the L-J phase is a new phase having an orthorhombic structure with lattice parameters  $a = 0.413$  nm,  $b = 0.254$  nm and  $c = 0.728$  nm. This result is quite different from that reported by other workers[1]. However, to date, all of examinations were focused on the  $\text{Cu}_{3-x}\text{Mn}_x\text{Al}$  alloy with varying manganese content. Little information concerning the Cu-Mn-Al alloy with higher aluminum content has been provided. Therefore, the purpose of the present study is to investigate the as-quenched microstructure of the Cu-24.8Mn-30.0Al alloy.

### Experimental Procedure

The alloy was prepared by using 99.99% copper, 99.9% manganese and 99.99% aluminum in an induction furnace under a protective argon atmosphere. The melt was chill cast into a  $30 \times 50 \times 200$ -mm copper mold. After being homogenized at  $850^\circ\text{C}$  for 72 hours, the ingot was sectioned into 2-mm slices in thickness. These slices were subsequently heat-treated at  $850^\circ\text{C}$  for 1 hour and then rapidly quenched into iced brine.

Electron microscopy specimens were prepared by means of a double-jet electropolisher with an electrolyte of 70 percent methanol and 30 percent nitric acid. The polishing temperature was kept in the range from  $-40$  to  $-30^\circ\text{C}$  and the current density was kept in the range from  $3.0 \times 10^4$  to  $4.0 \times 10^4$  A/m<sup>2</sup>. Electron microscopy was performed on a JEOL 2000FX scanning transmission electron microscope (STEM) operating at 200 kV.

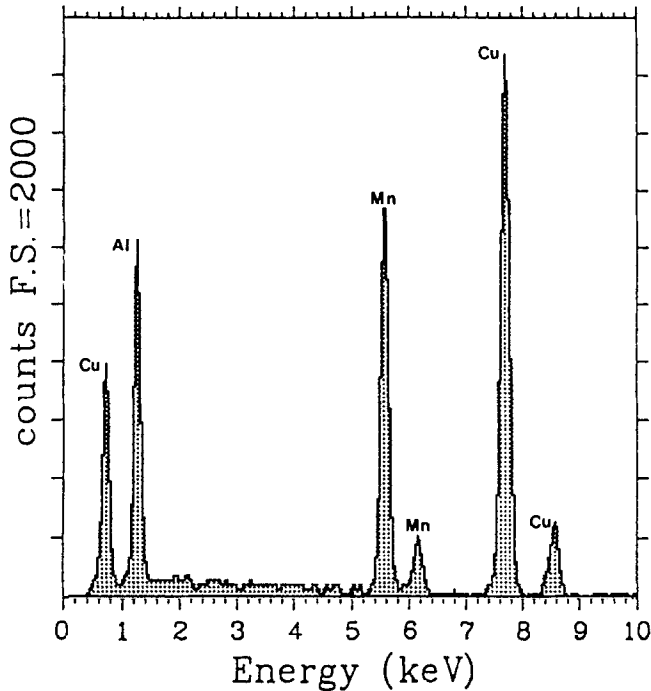


Figure 1. A typical EDS spectrum of the as-quenched Cu-24.8Mn-30.0Al alloy.

This microscope was equipped with a LINK-AN 10000 energy-dispersive X-ray spectrometer (EDS) for chemical analysis. Quantitative analyses of elemental concentrations for Cu, Mn and Al were made with the aid of a ZAF-corrected program on the LINK system ( where  $Z$  = backscatter coefficient;  $A$  = absorption coefficient; and  $F$  = fluorescence coefficient).

### **Results and Discussion**

Figure 1 is a typical EDS spectrum of the as-quenched specimen. The quantitative analyses of ten different spectra indicated that the average chemical composition was Cu-(27.0  $\pm$  0.6)wt pct Mn-(16.0  $\pm$  0.4)wt pct Al (Cu-(24.8  $\pm$  0.6)at pct Mn-(30.0  $\pm$  0.7)at pct Al).

Figure 2(a) is a bright-field electron micrograph of the as-quenched specimen, clearly exhibiting a modulated structure. Figures 2(b) through (e) show four different selected-area diffraction patterns (SADPs) of the as-quenched specimen. These SADPs consist of two sets of reflection reciprocal lattices: one derived from the matrix (brighter and well-arranged reflection spots) and another derived from fine precipitates (extra reflection spots indicated by arrows). Compared to our previous study in a  $\text{Cu}_{2.2}\text{Mn}_{0.8}\text{Al}$  alloy[18], it is found that these extra spots are of the L-J phase with two variants. The orientation relationship between the L-J phase and the matrix is  $(100)_{L-J} // (011)_m$ ,  $(010)_{L-J} // (111)_m$  and  $(001)_{L-J} // (211)_m$ . It is worthy to note here that the L-J phase has never been found by other workers in the Cu-Al, Cu-Mn and Cu-Mn-Al alloy systems before. In addition to the spots corresponding to the L-J phase, all of the reflection spots in Figures 2(b) through (e) can be indexed as either the  $\text{D0}_3$  or  $\text{L2}_1$  phase, since both of these two phases possess the same arrangement of the reflection spots[1], and the difference between their lattice parameters is only about two percent[20-21]. However, the chemical composition of the present alloy approximates to  $\text{Cu}_2\text{MnAl}$ . Therefore, these reflection

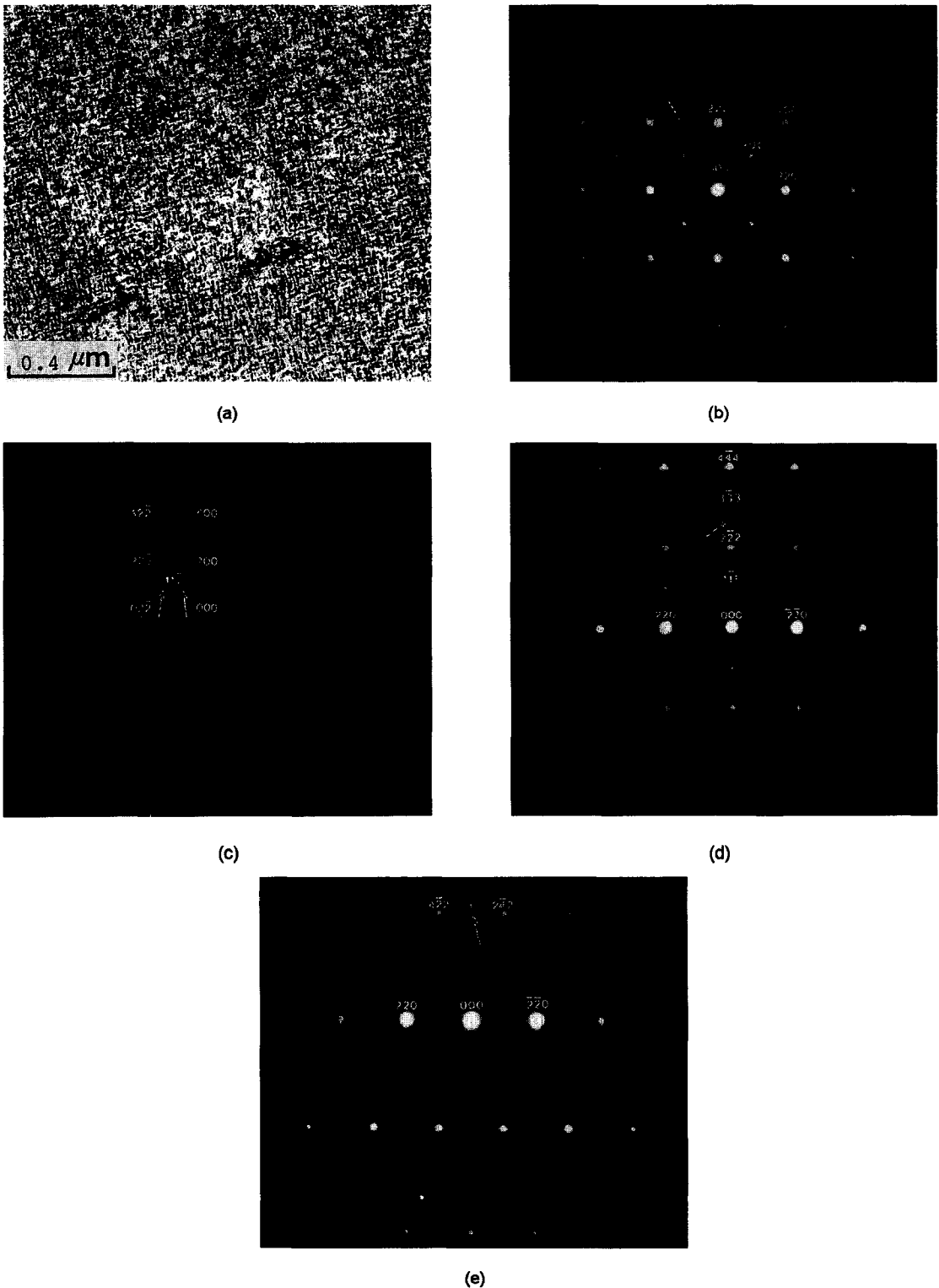
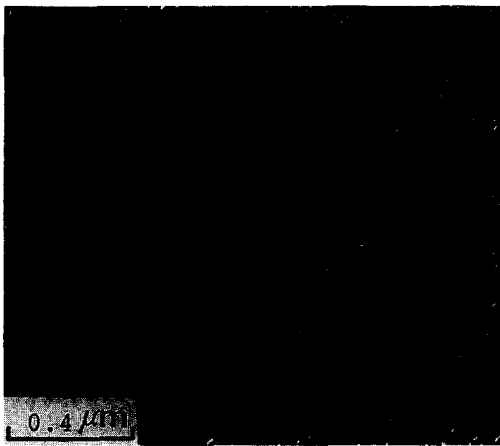
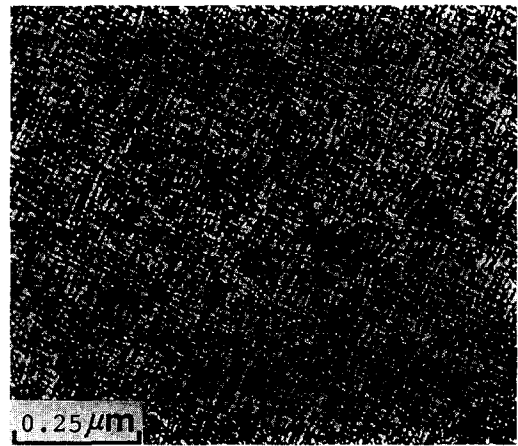


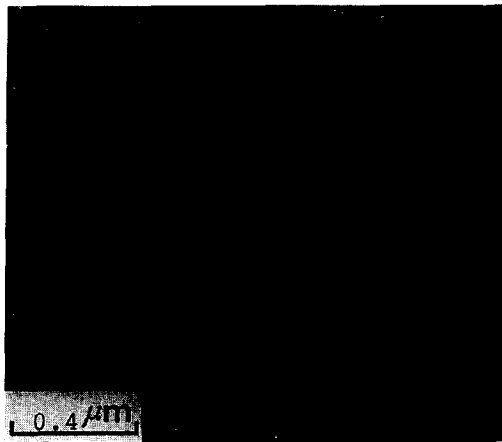
Figure 2. Electron micrographs of the as-quenched Cu-24.8Mn-30.0Al alloy. (a) Bright-field. (b)-(e) Four selected-area diffraction patterns (SADFs). The zone axes of the  $L_{2_1}$  phase are (b)  $[001]$ , (c)  $[011]$ , (d)  $[\bar{1}12]$  and (e)  $[\bar{1}13]$ , respectively. ( $hkl = L_{2_1}$  phase).



(a)



(b)



(c)

Figure 3. (a)-(b) 111 and 200  $L_{21}$  dark-field electron micrographs, (c) A dark-field micrograph taken with the reflection spot marked as 1 in Fig. 2(e).

spots are considered to be of the  $L_{21}$  phase, rather than the  $D0_3$  phase. Although these reflection spots could be analyzed as  $L_{21}$  phase, the  $L_{21}$  reciprocal lattices contain all the B2-type reflections[19-22]. Therefore, in order to decide whether the ordered B2-type phase coexists with the  $L_{21}$  phase, both electron diffraction method and dark-field technique were used. Intensity of reflection spot is proportional to  $|F|^2$ , where the  $F$  is structure factor[23]. The structure factors  $F_{111}$ ,  $F_{200}$  and  $F_{222}$  of the  $Cu_2MnAl$   $L_{21}$  can be expressed as follows [24]:  $F_{111} = 4f_{Mn} - 4f_{Al}$ ,  $F_{200} = 8f_{Cu} - 4f_{Mn} - 4f_{Al}$  and  $F_{222} = 8f_{Cu} - 4f_{Mn} - 4f_{Al}$ . Using the atomic scattering factors of  $f_{Cu}$ ,  $f_{Mn}$  and  $f_{Al}$ [25], the values of  $|F_{111}|^2$ ,  $|F_{200}|^2$  and  $|F_{222}|^2$  were calculated to be 29.72, 12.91 and 19.78, respectively. This indicates that the 111 reflection spot should be stronger than the 200 and 222 reflection spots. However, the reverse result can be observed in Figures 2(c) and (d). Accordingly, it is suggested that the 200 and 222  $L_{21}$  reflection spots derived from not only  $L_{21}$  phase but also B2 phase, since the 111 reflection spot comes

from the L<sub>21</sub> phase only; while the 200 and 222 reflection spots can come from both the L<sub>21</sub> and B2 phases (the 200 and 222 L<sub>21</sub> reflection spots are equal to the 100 and 111 B2 reflection spots, respectively). Figures 3(a) and (b) are 111 and 200 L<sub>21</sub> dark-field electron micrographs of the same area in the as-quenched specimen. It is clearly seen that the bright region in 200 dark-field image is much more than that in the 111 dark-field image. This demonstrates that both B2 and L<sub>21</sub> phases are present, rather than single L<sub>21</sub> phase; otherwise these two dark-field images should be morphologically identical. Shown in Figure 3(c) is a dark-field electron micrograph taken with the reflection spot marked as 1 in Figure 2(e), revealing the presence of extremely fine L-J precipitates. By comparing with our previous study[18], it is found that the amount of the L-J precipitate is much more than that observed in the as-quenched Cu<sub>2.2</sub>Mn<sub>0.8</sub>Al alloy.

In summary, the as-quenched microstructure of the Cu-24.8Mn-30.0Al alloy is a mixture of (L<sub>21</sub> + B2 + L-J) phases. The increase of aluminum content in the Cu-Mn-Al alloy will enhance the formation of the L-J precipitate.

### **Acknowledgement**

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