

Chapter 1.

General Introduction



Phase transformations of copper-aluminum (Cu-Al) binary alloys have been extensively studied by many workers [1-10]. Based on their studies, it was found that when the Cu-Al binary alloys with a chemical composition ranging from 20 to 30 at.% Al were solution heat-treated at a point in the single β phase (disordered body-centered cubic) region and then quenched into room-temperature water or iced brine, a $\beta(A2) \rightarrow \beta_1(D0_3)$ phase transition would be occurred during quenching by an ordering transition, as shown in Figure 1.1. Figure 1.1 is a Cu-Al binary phase diagram [6-7], two kinds of martensite phases, β_1' (18R) and γ_1' (2H), are occurred during quenching by a martensitic transformation in the different composition ranges. The martensitic transformation temperature would decrease with increasing the Al content. In addition, in order to suppress the martensitic transformation, manganese (Mn) was added to the Cu-Al binary alloys [11-21]. Effects of the Mn content on the microstructure of Cu-Al binary alloys have been studied by many researchers, too [12-16, 19-42]. According to their studies, it was found that the addition of Mn to the Cu-Al alloy is effective in decreasing the martensitic transformation temperature (M_s) and stabilizing the β phase region [12-26, 40-42]. In 1975, M. Bouchard and G. Thomas have established the metastable phase diagram of the $Cu_{3-x}Mn_xAl$ alloys with $0 \leq X \leq 1.0$ ($0 \leq Mn \leq 25.0$ at.%), as shown in Figure 1.2 [25]. Based on their reports, it is seen that when the $Cu_{3-x}Mn_xAl$ alloys with

$0.1 \leq X \leq 0.8$ ($2.5 \leq \text{Mn} \leq 20.0$ at.%) were solution heat-treated at a point in the single β phase region and then quenched into iced brine rapidly, a $\beta \rightarrow \text{B2} \rightarrow (\text{D0}_3 + \text{L2}_1)$ transition would occur during quenching by an ordering transition and a spinodal decomposition. The as-quenched microstructure of the $\text{Cu}_{3-x}\text{Mn}_x\text{Al}$ alloys with $0.1 \leq X \leq 0.8$ was a mixture of $(\text{D0}_3 + \text{L2}_1)$ [25, 35, 38, 39]. When the Mn content of the $\text{Cu}_{3-x}\text{AlMn}_x$ alloys was increased to $X=1.0$ (Mn=25 at.%), the as-quenched microstructure of the alloys became a single L2_1 (Cu_2MnAl) phase [22-28, 33, 38-41]. The crystal structure of the L2_1 phase is similar to the D0_3 structure (Cu_3Al), and the only difference between them is that Mn replaces Cu at a specific lattice site with the eight nearest Cu atoms in the D0_3 structure so as to form a stoichiometry composition of Cu_2AlMn [19, 25, 39], as illustrated in Figure 1.3. Recently, Kainuma et al by using X-ray diffraction measurement found that when the Mn content of the $\text{Cu}_{3-x}\text{Mn}_x\text{Al}$ alloys with $X \leq 0.32$ ($\text{Mn} \leq 8.0$ at.%), the as-quenched microstructure of the alloys was a single D0_3 phase[39].

It is well-known in the previous studies of Fe-Al, Fe-Al-Ti, Fe-Al-Mn and Fe-Al-Mn-C alloys that if the D0_3 phase was formed by continuous ordering transition during quenching. It was always occurred through an $\text{A2} \rightarrow \text{B2} \rightarrow \text{D0}_3$ transition [43-49]. The $\text{B2} \rightarrow \text{D0}_3$ transition produced $a/2\langle 100 \rangle$ anti-phase boundaries (APBs) and the $\text{A2} \rightarrow \text{B2}$ transition produced $a/4\langle 111 \rangle$ APBs

[43-45, 49]. Similarly, a number of workers also found this phenomenon in Cu-Al, Cu-Al-Ni and Cu-Al-Mn alloy systems [7, 21, 25, 50], that is, the $D0_3$ phase in these alloy systems could also be formed by the $A2 \rightarrow B2 \rightarrow D0_3$ continuous ordering transition during quenching from the single β phase region. However, in contrast to the result above, some workers claimed that the $D0_3$ phase was occurred through an $A2 \rightarrow D0_3$ transition, rather than the $A2 \rightarrow B2 \rightarrow D0_3$ transition [6-7, 51-52]. The reason for this discrepancy between them is that, up to now, the existence of B2 phase-field was investigated by means of differential scanning calorimetry (DSC), differential thermal analysis (DTA) and X-ray diffraction method, no $a/4\langle 111 \rangle$ APBs could be observed by transmission electron microscopy (TEM). It means that no direct evidence confirmed the existence of the B2 phase-field in these Cu-Al base alloys.

When the as-quenched $Cu_{3-x}Mn_xAl$ alloy was aged at temperatures ranging from 300°C to 650°C for moderate times, γ -brass, β -Mn and T_3 phases would be precipitated within the matrix during aging. The γ -brass (Cu_9Al_4) has a $D8_3$ (ordered body-centered cubic) structure with lattice parameter $a=0.872$ nm [23-24, 26, 29, 31]. The orientation relationship between the γ -brass and the matrix was cubic to cubic [16, 33]. The β -Mn has an A13 (simple cubic) structure with lattice parameter $a=0.641$ nm [26, 29, 31]. The T_3 phase has a C15 structure (ordered fcc) with lattice parameter $a=0.691$ nm that the

stoichiometry composition corresponds to $\text{Cu}_3\text{Mn}_2\text{Al}$ [26, 29, 31]. In 1987, R. Kozubski reported that the orientation relationship between the $\beta\text{-Mn}$ and L_{21} matrix was $[011]_{\beta\text{-Mn}}//[013]_{\text{L}_{21}}$, $(100)_{\beta\text{-Mn}}//(100)_{\text{L}_{21}}$ with a plate-like shape at 460°C and $[001]_{\beta\text{-Mn}}//[001]_{\text{L}_{21}}$, $(210)_{\beta\text{-Mn}}//(100)_{\text{L}_{21}}$ with a irregular shape at 560°C [33].

Recently, the present workers performed TEM observations on the phase transformations of the Cu-Mn-Al alloy systems. Based on our experimental results, it is found that the as-quenched microstructure of a Cu_2MnAl alloy was a mixture of ($\text{L}_{21} + \text{L-J}$) phases (the L-J phase is a new type of precipitate, which was firstly observed and identified by Liu and Jeng (designated L-J phase) in a $\text{Cu}_{2.2}\text{Mn}_{0.8}\text{Al}$ alloy) [53]. The L-J phase has an orthorhombic structure with lattice parameters $a=0.413\text{nm}$, $b=0.254\text{nm}$ and $c=0.728\text{nm}$. The orientation relationship between the L-J phase and the matrix was $(100)_{\text{L-J}}//(0\bar{1}1)_m$, $(010)_{\text{L-J}}//(1\bar{1}\bar{1})_m$ and $(001)_{\text{L-J}}//(211)_m$ [54]. The rotation axis and rotation angle between two variants of the L-J phase were $[021]$ and 90° , respectively. It is worthwhile 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. When the Cu_2MnAl alloy was aged at 460°C and 560°C , the $\beta\text{-Mn}$ precipitates were formed within the L_{21} matrix. TEM examinations indicated that the orientation relationship between the $\beta\text{-Mn}$ and the L_{21} matrix would still

maintain the same, in spite of the morphology change, and it could be the best stated as follows: $(210)_{\beta\text{-Mn}} // (100)_{L2_1}$, $(\bar{1}20)_{\beta\text{-Mn}} // (010)_{L2_1}$ and $(001)_{\beta\text{-Mn}} // (001)_{L2_1}$. This finding is in disagreement with that reported by R. Kuzobski et al. in the aged Cu_2MnAl alloy [33].

To date, it is apparent that the phase transformations in the $\text{Cu}_{3-x}\text{Mn}_x\text{Al}$ alloys with $0.5 \leq X \leq 1$ have been studied by many researchers, however, the information concerning about the microstructural changes of the alloys with Cu-Mn-Al alloys with Mn content less than 12.5 at.% ($X < 0.5$) is very deficient. Therefore, the purpose of these studies is an attempt to investigate the microstructural changes of the $\text{Cu}_{3-x}\text{Mn}_x\text{Al}$ alloys with low Mn content. In addition, the addition of the Mn content higher than 35 at.% on the phase transformations of Cu-Mn-Al alloy will also be investigated by TEM and energy-dispersive X-ray spectrometer analyses (EDS). The detailed experimental results are presented in Chapters 2~4, respectively.

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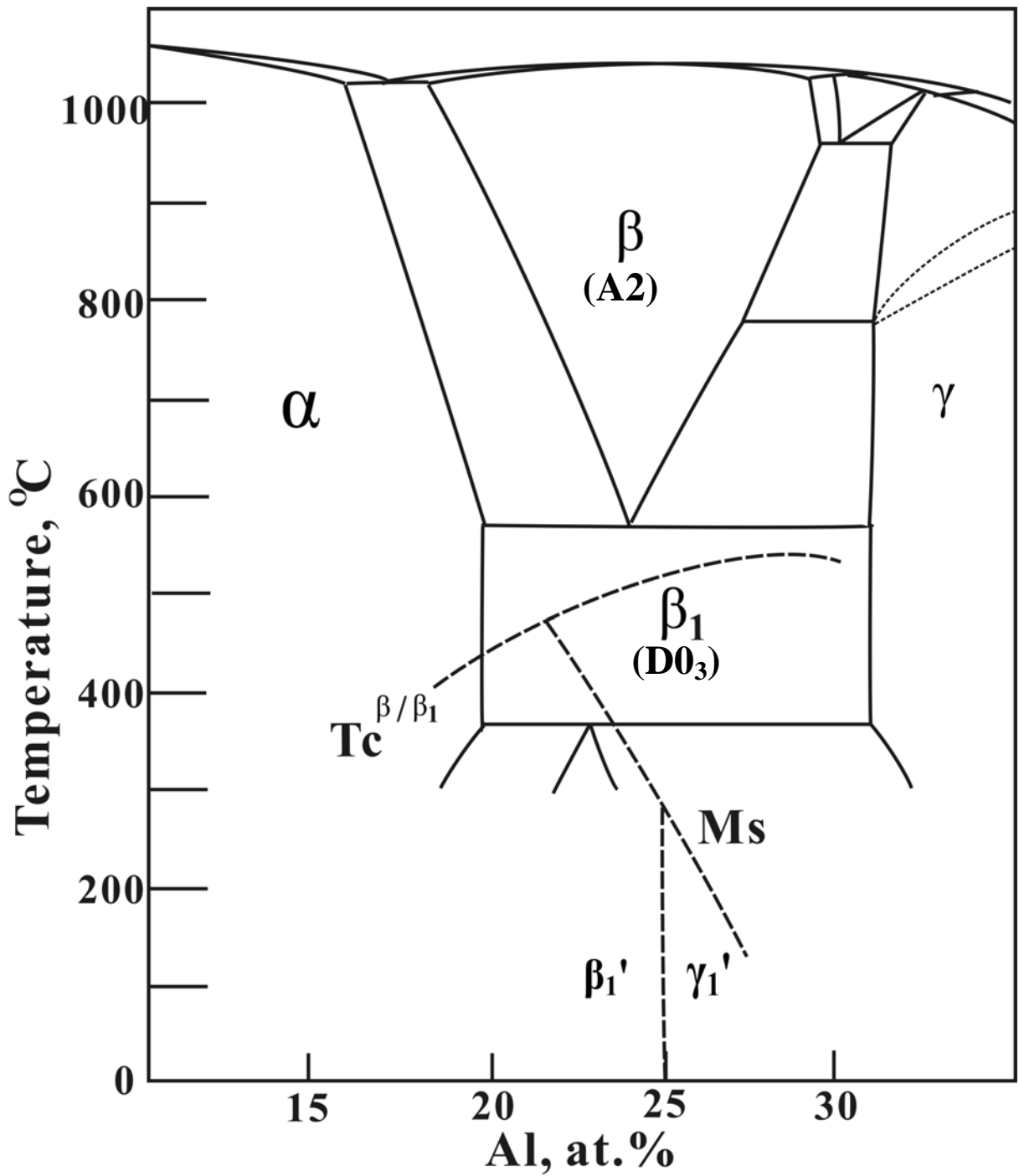


Figure 1.1 A schematic drawing of the phase diagram of the Cu-Al alloy system with A2 \rightarrow B2 and B2 \rightarrow D0₃ order-disorder transition temperatures and martensitic transformation temperatures (Ms) [6-7].

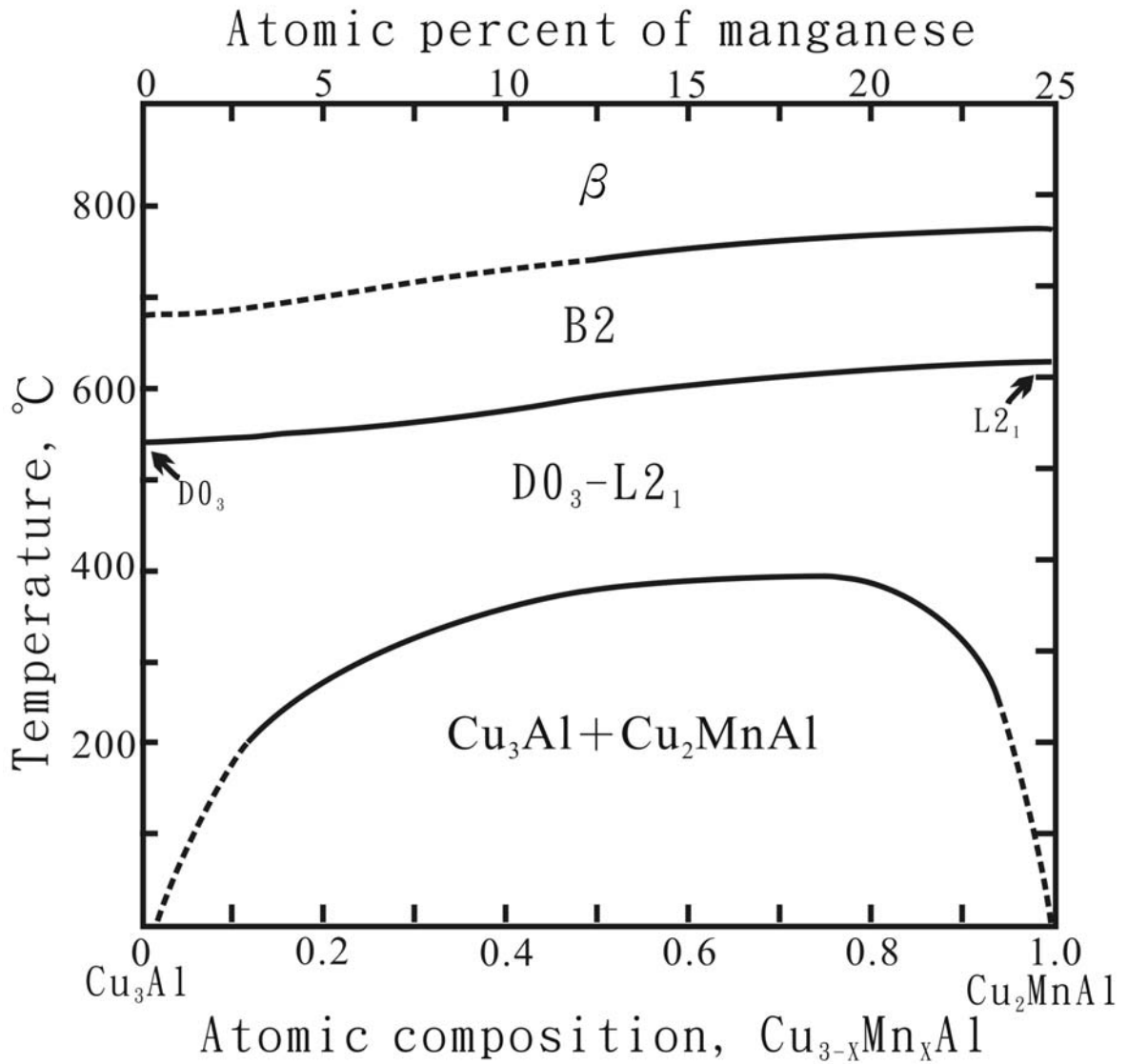


Figure 1.2 A schematic drawing of the ordering temperatures T_c (B2) and T_c ($\text{D0}_3 + \text{L2}_1$) and the miscibility gap of the $(\text{Cu-Mn})_3\text{Al}$ alloy [25].

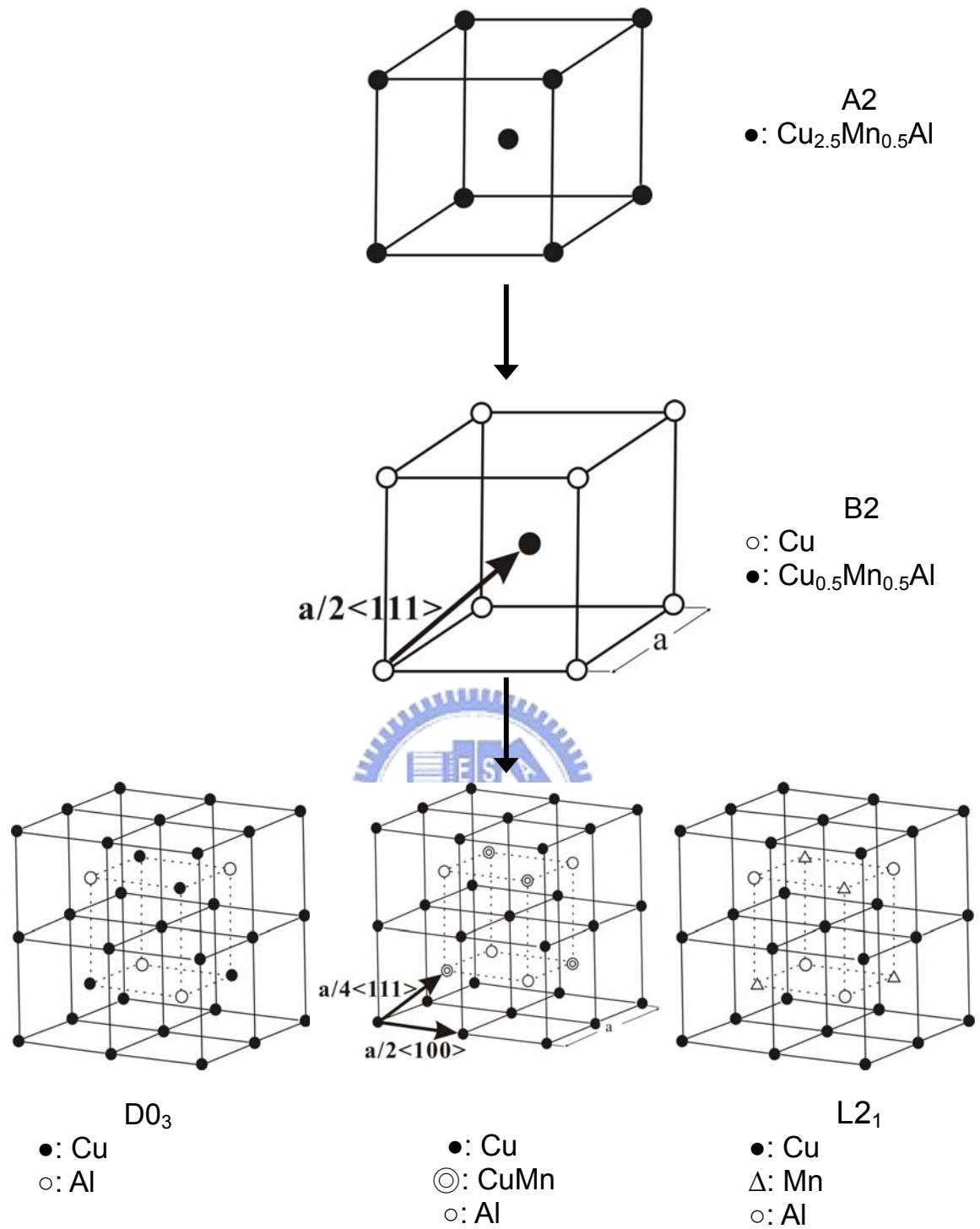


Figure 1.3 Schematic representation of the ordering sequence of the quenched $\text{Cu}_{2.5}\text{Mn}_{0.5}\text{Al}$ alloy (vertically) and its isothermal decomposition (horizontally) [19, 25, 39].