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MODULATED STRUCTURES IN ORDERED $(Cu\text{-}Mn)_3Al$ ALLOYS, III-FORMATION OF THE γ PHASE

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ABSTRACT

The alloys along the composition tie-line Cu_3Al-Cu_2MnAl have been studied by electron microscopy. The alloy $Cu_{2.5}Mn_{0.5}Al$ situated near the centre of the miscibility gap decomposes at 300°C into ordered phases rich in Cu_3Al and Cu_2MnAl. During overaging, the Cu_3Al-rich phase transforms to the γ phase of composition near Cu_9Al_4, and plate-like precipitates form in the Cu_2MnAl-rich phase. The latter precipitates resemble those found in the $Cu_{2.2}MnAl_{0.8}$ alloy. Further decomposition within the initially modulated phases suggest a decomposition tie-line close to the Cu_9Al_4-$Cu_{2.2}MnAl_{0.8}$ line for the as-quenched symmetrical alloy. This is in agreement with the observed volume fraction of the observed phases. The various microstructures of the aged asymmetrical alloys studied suggest a rotation of the decomposition tie-line with composition along Cu_3Al-Cu_2MnAl.

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1. INTRODUCTION

In the previous papers,[1] it was shown that the alloys along the line Cu_3Al-Cu_2MnAl order during the quench to an ordered solid solution based on the DO_3 structure of Cu_3Al and the closely related $L2_1$ structure of Cu_2MnAl. During isothermal aging at temperatures below 350°C, the single phase decomposes into a Cu_3Al-rich phase and a Cu_2MnAl-rich phase. The microstructures of the decomposition possess all the metallographic characteristics of a spinodal decomposition.[2,3,4] After prolonged aging at 300°C of the alloy $Cu_{2.5}Mn_{0.5}Al$ having a composition half way between Cu_3Al and Cu_2MnAl, the microstructures clearly show an equal proportion of the two phases. However, the proportion of the Cu_3Al-rich phase to the Cu_2MnAl-rich phase estimated using the lever rule along the composition line of study is closer to 2 to 1 for this alloy. This discrepency between the expected and the observed volume fraction of phases can be explained by the rotation of the decomposition tie-line with respect to the line of study. This is supported by the fact that within a ternary miscibility gap, the decomposition tie-line is not restricted by stoichiometry whereas inside a binary miscibility gap, the decomposition tie-line corresponds to the binary side of the Gibbs triangle.[5]

The purpose of this work was to study the continued transformations that occur in the modulated microstructures of $(Cu\text{-}Mn)_3Al$ alloys using electron microscopy in order to estimate the decomposition tie-lines of the alloys studied, and to check on the discrepancy discussed above.

2. EXPERIMENTAL

The experimental procedure has been described previously.[1] The atomic compositions of the $Cu_{3-x}Mn_xAl$ alloys studied are summarized in Table I of paper I.

3. RESULTS

3.1. The γ Phase

It was found that prolonged aging of alloys rich in manganese ($x > 0.5$) inside and/or outside the miscibility gap results in the heterogeneous precipitation of a γ-type phase. The γ phase is similar to that first discovered in Cu-Al alloys by Bradley.[6] In the Cu-Al binary system and the Cu-Ni-Al ternary system, the γ phase has a composition near Cu_9Al_4.[6,7] In the Cu-Mn-Al system, the composition of the γ phase is also expected to be centered around Cu_9Al_4.

A (001) diffraction pattern of the Cu_2MnAl-rich matrix and the γ precipitates is shown in Fig. 1a. It was found that the first order reflections of the γ-precipitates are located near the 1/3 distances of only the reflections inherited during the B2 ordering of the matrix. This results from the simple cubic symmetry of both the B2 structure and the γ structure.

The diffraction patterns have been indexed according to this simple cubic structure. The lattice parameter of the γ phase estimated from diffraction patterns of mixed microstructures of the γ and Cu_2MnAl

phases is 8.72 ± 0.05Å. This value is in agreement with that reported by Bradley et al.[8] for the Cu_9Al_4 γ phase.

The volume of the γ unit cell is composed of twenty-seven bcc unit cells.[6] In the Cu-Mn-Al alloys, we have found that planes of the γ phase are parallel to those of similar indices in the $L2_1$ matrix (see Fig. 1a). The precipitate reflections just outside some matrix reflections reveal a misfit of about 2%.

The diffraction pattern in Fig. 1a was obtained from large γ particles and shows only one reflection at each γ position whereas that in Fig. 1b was obtained from smaller γ particles after lower temperature of aging. This pattern shows satellite spots near all γ positions. The diffraction patterns in Fig. 1a and b are schematically reproduced in Fig. 2b and c respectively and the presence of the satellites is interpreted in terms of double diffraction.[9] Figure 2b shows the schematic diffraction pattern of both the γ phase and the $L2_1$ matrix without double diffraction.

The diagram in Fig. 2c results from double diffraction by the γ phase of the eight fundamental reflections of the $L2_1$ matrix (large filled circles in Fig. 2a). This diagram corresponds to the $L2_1$ + γ diffraction pattern shown in Fig. 1b. In Fig. 2d, the doubly diffracted spots (in parenthesis) are indexed according to the fundamental $L2_1$ reflections in a) that cause double diffraction.

Precipitation of γ was observed in the three alloys 0.5, 0.8 and 0.9. In the asymmetrical alloys 0.8 and 0.9, the γ phase formed during isothermal aging inside and/or outside the miscibility gap.

Inside it, the precipitation of γ occurs concurrently with the formation of the Cu_3Al-rich minor phase. The microstructures of the asymmetrical alloys are therefore partially determined by the relative growth kinetics of the two competing processes. A typical example of a microstructure obtained from the alloy 0.8 aged inside the miscibility gap is shown in the bright field micrograph of Fig. 3. The micrograph shows a large density of γ particles at the grain boundary surrounded by a zone free of Cu_3Al-rich platelets. The density of γ particles is lower inside the grain than at the grain boundary. Inside the grains, both the γ particles and the Cu_3Al-rich platelets are imbedded in the Cu_2MnAl-rich matrix. The Cu_3Al-rich phase is identified by the lighter contrast and by the presence of interfacial dislocations.[1]

Inside the grains, rows of equiaxed γ particles have precipitated on cube planes and which seem to have coalesced to form needles and plates of the γ phase. This is illustrated in the micrograph obtained from the alloy 0.8 aged at 315°C for 1,100 minutes shown in Fig. 4. A comparison of the regions labelled A and B in Fig. 4 showed the presence of a zone free of Cu_3Al-rich platelets around the γ particles.

The coexistance of four phases was observed in the alloy 0.9 aged at 300°C for 18,000 minutes. This is illustrated in Fig. 5 showing the Cu_3Al-rich phase, the γ phase and the $L1_o$ phase[1] imbedded in the Cu_2MnAl-rich matrix. The circled area marked B contains γ particles and is the selected area used to form the diffraction pattern in B. The $L1_o$ diffraction pattern in C was obtained from the $L1_o$ particle in the selected area marked C. This was confirmed by selected dark field microscopy. The Cu_3Al-rich platelets were identified by the characteristic diffraction patterns and the interfacial dislocation network. According to the phase rule, the coexistance of four phases in a three component system is possible only along an horizontal or vertical line through the ternary composition vs temperature diagram.[10]

In contrast to the asymmetrical alloys, no γ precipitation was observed in the symmetrical alloy 0.5 prior to loss of coherency at the Cu_3Al-Cu_2MnAl interfaces. In the fully decomposed symmetrical alloy, further precipitation of the γ phase occurred within the Cu_3Al-rich phase characterized by a "tweed like" texture.[1] This is illustrated in the microstructure in Fig. 6. This micrograph reveals that the γ phase grows from a local region and gradually consumes the Cu_3Al-rich component. It is believed that the growth of γ occurs by the gradual transformation of the Cu_3Al-rich phase from local embryos through the highly interconnected Cu_3Al-rich particles until the Cu_3Al-rich phase is fully transformed.

3.2. Precipitation Within the Cu_2MnAl Phase

After prolonged aging of the symmetrical alloy x=0.5, plate-like precipitates form in the Cu_2MnAl-rich phase. This is illustrated in Fig. 12 of paper I where the precipitates marked P are observed exclusively in the Cu_2MnAl-rich component marked A. The precipitates were never observed to extend in the Cu_3Al particles (marked B) characterized by the "tweed-like" texture. The micrograph also reveals that the precipitates are located near the surface of impingment of two Cu_2MnAl-rich particles. The plate-like morphology and diffraction patterns of the precipitates resemble very closely those of the precipitates found in the alloy $Cu_{2.2}MnAl_{0.8}$.[11] For comparison, the micrograph in Fig. 7 shows plate-like precipitates in the $Cu_{2.2}MnAl_{0.8}$ aged at 225°C for 18,000 minutes.

4. DISCUSSION

The decomposition of $Cu_{3-x}Mn_xAl$ alloys has been studied by transmission electron microscopy. A total of five phases were found to occur sequentially upon quenching and aging of the alloys. The schematic diagram in Fig. 8 illustrates the sequence of transformations that occurs in the symmetrical alloy 0.5.

Upon prolonged aging of the symmetrical alloy, the Cu_3Al-rich phase transforms to the γ structure based on the Cu_9Al_4 binary composition and the Cu_2MnAl-rich phase contains plate-like precipitates resembling those found in the $Cu_{2.2}MnAl_{0.8}$ alloy. These further transformations of the two Cu_3Al-rich and Cu_2MnAl-rich phases suggest that the decomposition tie-line of the as-quenched symmetrical alloy x=0.5 lies near the compositions tie-line Cu_9Al_4-$Cu_{2.2}MnAl_{0.8}$ rather than along Cu_3Al-Cu_2MnAl. This estimated decomposition tie-line is shown in Fig. 9 and it represents a slight clockwise rotation with respect to the Cu_3Al-Cu_2MnAl line of alloys studied. If the symmetrical alloy 0.5 was to decompose along the Cu_3Al-Cu_2MnAl tie-line, it is expected that the Cu_3Al-rich phase would easily transform to martensite.[12] In agreement with this interpretation the martensite transformation was observed in the Cu_3Al-rich phase of the asymmetrical alloy x=0.2 decomposed at 240°C. Furthermore, no plate-like precipitates would be expected to form in the Cu_2MnAl-rich phase.[11-13]

The estimated limit of the miscibility gap shown in Fig. 9 was obtained by electron microscopic observations of the four alloys 0.2, 0.5, 0.8 and 0.9 aged at 300°C. According to the isothermal section in Fig. 9 and the lever rule, it is expected that the decomposition of the symmetrical alloy (x=0.5) at 300°C produces a volume fraction of the two phases (Cu_3Al-rich and Cu_2MnAl-rich) close to 2:1 along Cu_9Al_4-$Cu_{2.2}MnAl_{0.8}$ and close to 1:1 along Cu_3Al-Cu_2MnAl. The observation of a ratio close to 1:1 (see Fig. 12 of paper I) is in agreement with the estimated decomposition tie-line in Fig. 9.

Contrary to binary system, the decomposition inside a ternary miscibility gap is not restricted by stoichiometry.[5] Instead, the decomposition tie-line can rotate within the dome-shaped miscibility gap in composition-temperature space. This decomposition tie-line is determined by joining the composition of the non-decomposed alloy situated inside the dome and the compositions of the two components of the decomposed alloy situated on the surface of the dome.

The compositions of the non-symmetrical alloys studied x=0.2, 0.8 and 0.9 do not lie on the decomposition tie-line of the symmetrical alloys x=0.5. This suggests that the decomposition tie-lines of the non-symmetrical alloys studied do not coincide with that of the symmetrical alloy. This is in agreement with the observation of heterogenous precipitates of the γ phase inside and outside the miscibility gap in alloys near the ternary-rich end (Fig. 3, 4 and 5) and the absence of γ precipitates in an alloy near the binary-rich end.

In the symmetrical alloy x=0.5, the $L1_o$ phase forms during decomposition[1] whereas its formation is heterogenous in the asymmetrical alloy x=0.9 (see Fig. 5). These different modes of formation of the $L1_o$ phase can also be interpreted by a rotation of the decomposition tie-line of alloys situated along Cu_3Al-Cu_2MnAl and additionally support the Cu_9Al_4-$Cu_{2.2}MnAl_{0.8}$ decomposition tie-line.

SUMMARY

1. At 300°C, the alloy near the center of the ternary miscibility gap $Cu_{2.5}Mn_{0.5}Al$ decomposes into composition modulations rich in Cu_3Al and Cu_2MnAl. During further aging, the DO_3 structure of the Cu_3Al-rich phase further transforms to the γ-type structure. The composition of the γ phase is believed to be close to Cu_9Al_4.
2. The transformation of the DO_3 structure to the γ structure is accompanied by precipitation of plate-like particles within the Cu_2MnAl-rich phase. The structure and morphology of the precipitates resemble those of the precipitates found in the $Cu_{2.2}MnAl_{0.8}$ alloy.
3. The formation of the γ phase and plate-like precipitates in the matrix suggests a decomposition tie-line close to Cu_9Al_4-$Cu_{2.2}MnAl_{0.8}$ for the as-quenched symmetrical alloy aged inside the miscibility gap.
4. In the symmetrical alloy $Cu_{2.5}Mn_{0.5}Al$, the volume fraction of the Cu_3Al-rich and Cu_2MnAl-rich composition modulations is close to unity. This observation is in agreement with the above estimated decomposition tie-line.
5. In the ternary-rich asymmetrical alloys studied, the γ phase rapidly forms heterogenously whereas in the binary rich asymmetrical alloy studied, the γ precipitation does not occur. The change in the mode of precipitation of the γ phase in alloys along Cu_3Al-Cu_2MnAl suggests a rotation of the decomposition tie-line with the composition of the alloys.

ACKNOWLEDGEMENTS

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REFERENCES

1. M. Bouchard and G. Thomas - see papers I, and II.

2. E. P. Butler and G. Thomas, Acta Met. 18, 347, (1970).

3. J. E. Hilliard, Phase Transformations, ASM, Metals park, 1970, p.497.

4. D. de Fontaine, Ultra Fine Grain Metals, Syracuse University Press, 93, 1970.

5. J. E. Morral and J. W. Cahn, Acta Met. 19, 1037, (1971).

6. A. J. Bradley, Phil. Mag., 6, 878, (1928).

7. P. R. Swann, Phil. Mag. 14, 461, (1966).

8. A. J. Bradley, H. J. Goldsmidt and H. Lipson, J. Inst. Metals, 63 149, (1938).

9. P. B. Hirsh, A. Howie, R. B. Nicholson, D. W. Pashley and M. J. Whelan, Electron Microscopy of Thin Crystals, London Butterworths, (1965).

10. P. G. Shermon, Physical Metallurgy, R. W. Cahn ed., Amsterdam, North Holland Publishing Company, (1965).

11. M. Bouchard and P. R. Swann, Seventh Int. Congress of Electron Microscopy, Grenoble, 475, (1970).

12. P. R. Swann and H. Warlimont, Acta Met. 11, 511, 1963.

13. G. B. Johnston and E. O. Hall, J. Phys. Chem. Solids 29, 195, (1968).

FIGURE CAPTIONS

Fig. 1. 001 diffraction pattern of the γ phase and $L2_1$ phase obtained from the alloy $Cu_{2.2}Mn_{0.8}$ (x=0.8) aged a) at 375°C for 450 min. and b) at 315°C for 1100 min. b). Note the double diffracted satellites near all γ positions in b).

Fig. 2. Schematic diagrams of the 001 diffraction pattern of a) the $L2_1$ phase b) the $L2_1$ and γ phase and c) the $L2_1$ phase, the γ phase and the double diffracted satellites. In d), the satellite spots (in parenthesis) are indexed according to the fundamental $L2_1$ reflections in a) giving rise to double diffraction.

Fig. 3. Heterogenous precipitation of the γ phase dark contrast at grain boundaries and inside the grains in the alloy $Cu_{2.2}Mn_{0.8}Al$ (x=0.8) aged at 300°C for 18,000 min. The formation of Cu_3Al-rich platelets light contrast is also observed inside the grains. Note the presence of a zone free of Cu_3Al-rich platelets near the grain boundaries.

Fig. 4. Precipitation of the γ phase in a microstructure consisting of Cu_3Al-rich platelets and a Cu_2MnAl-rich matrix. Alloy $Cu_{2.2}Mn_{0.8}$ (x=0.8) aged at 315°C for 1,100 min. Note the zone free of Cu_3Al-rich platelets around the γ particles.

Fig. 5. a) Formation of the γ phase, Cu_3Al-rich phase and $L1_o$ phase in the Cu_2MnAl-rich matrix of the alloy $Cu_{2.1}Mn_{0.9}Al$ (x=0.9) aged at 300°C for 18,000 min. The diffraction patterns in b) and c) were obtained from the selected areas indicated in the micrograph a).

Fig. 6. Microstructure obtained from the symmetrical alloy $Cu_{2.5}Mn_{0.5}Al$ (x=0.5) aged at 300°C for 10,000 min. and showing the transformation of the Cu_3Al-rich phase (marked B) to the γ structure. Notice the interfacial dislocations.

Fig. 7. Heterogenous precipitation of plate-like particles in the alloy $Cu_{2.2}MnAl_{0.8}$ aged at 225°C for 18,000 min.

Fig. 8. Schematic diagram showing the ordering reactions upon quenching and the phases resulting from the isothermal decomposition of the symmetrical alloy $Cu_{2.5}Mn_{0.5}Al$ (x=0.5).

Fig. 9. The Cu-rich portion of the Cu-Mn-Al Gibb's triangle showing the limits of the miscibility gap estimated at 300°C and the decomposition tie-line of the symmetrical alloy $Cu_{2.5}Mn_{0.5}Al$ x=0.5 also estimated at 300°C.

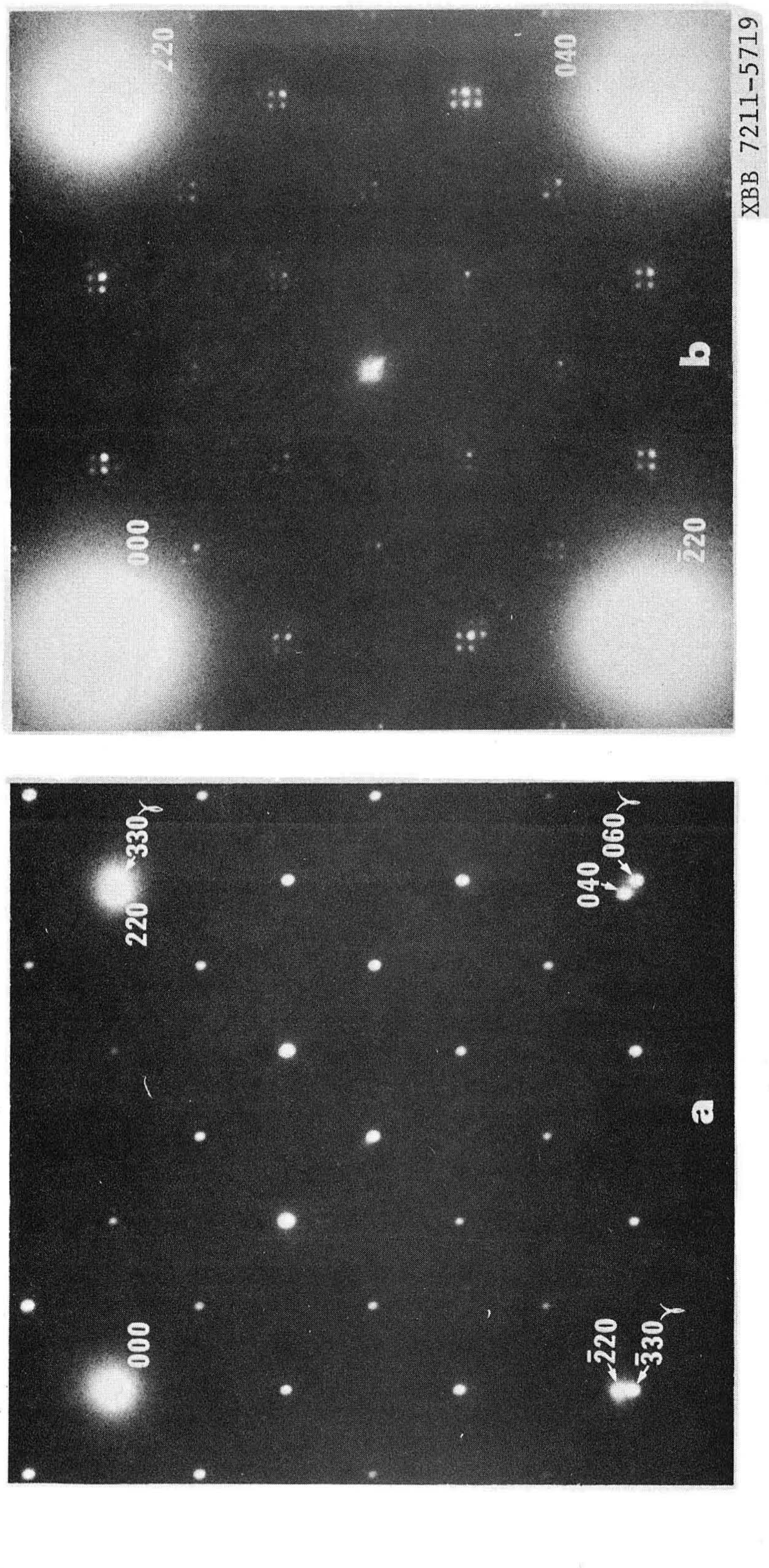
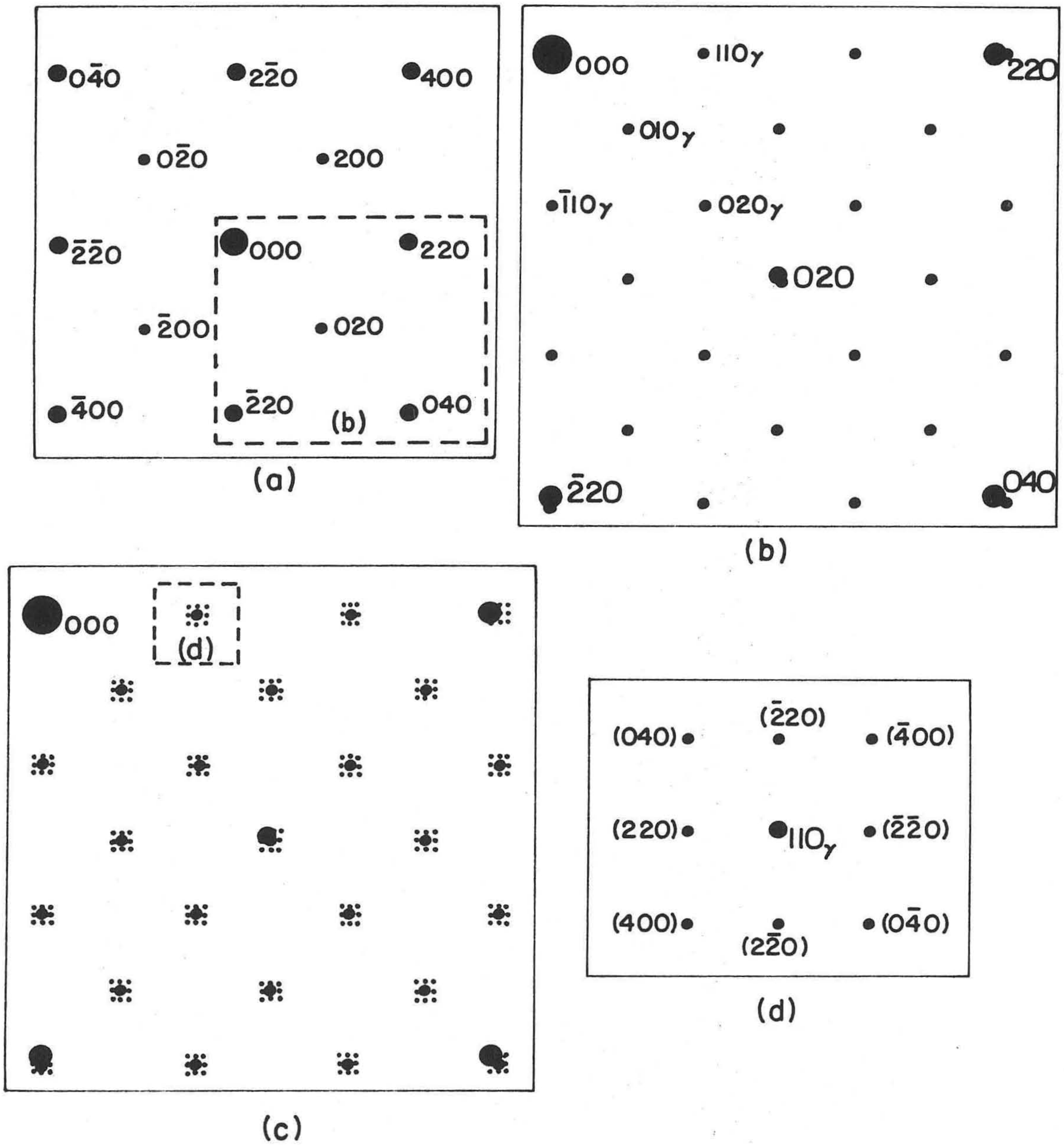

a
000
220
330
$\bar{2}20$
$\bar{3}30$
040
060
b
000
220
040
$\bar{2}20$
XBB 7211-5719

Fig. 1.



XBL7211-7266

Fig. 2.

XBB 7211-5734

Fig. 3.

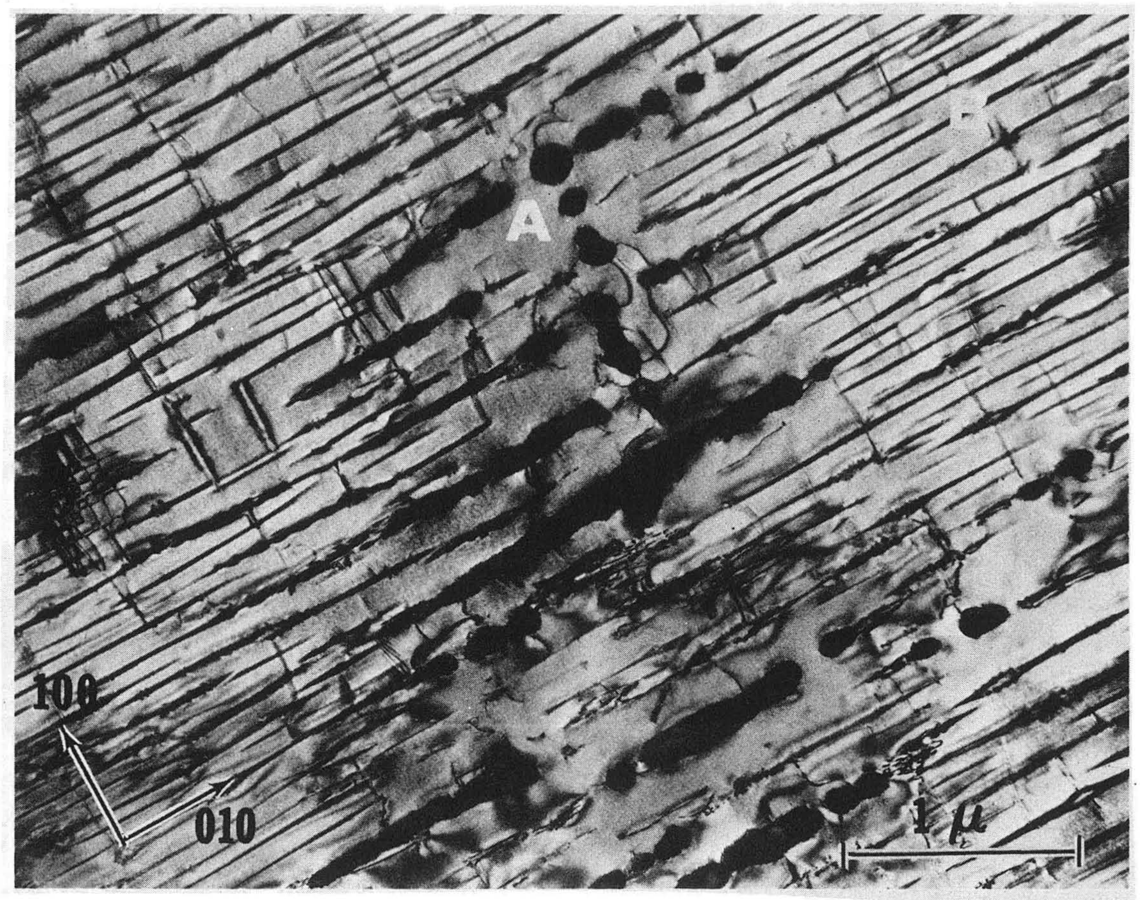


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Fig. 4.

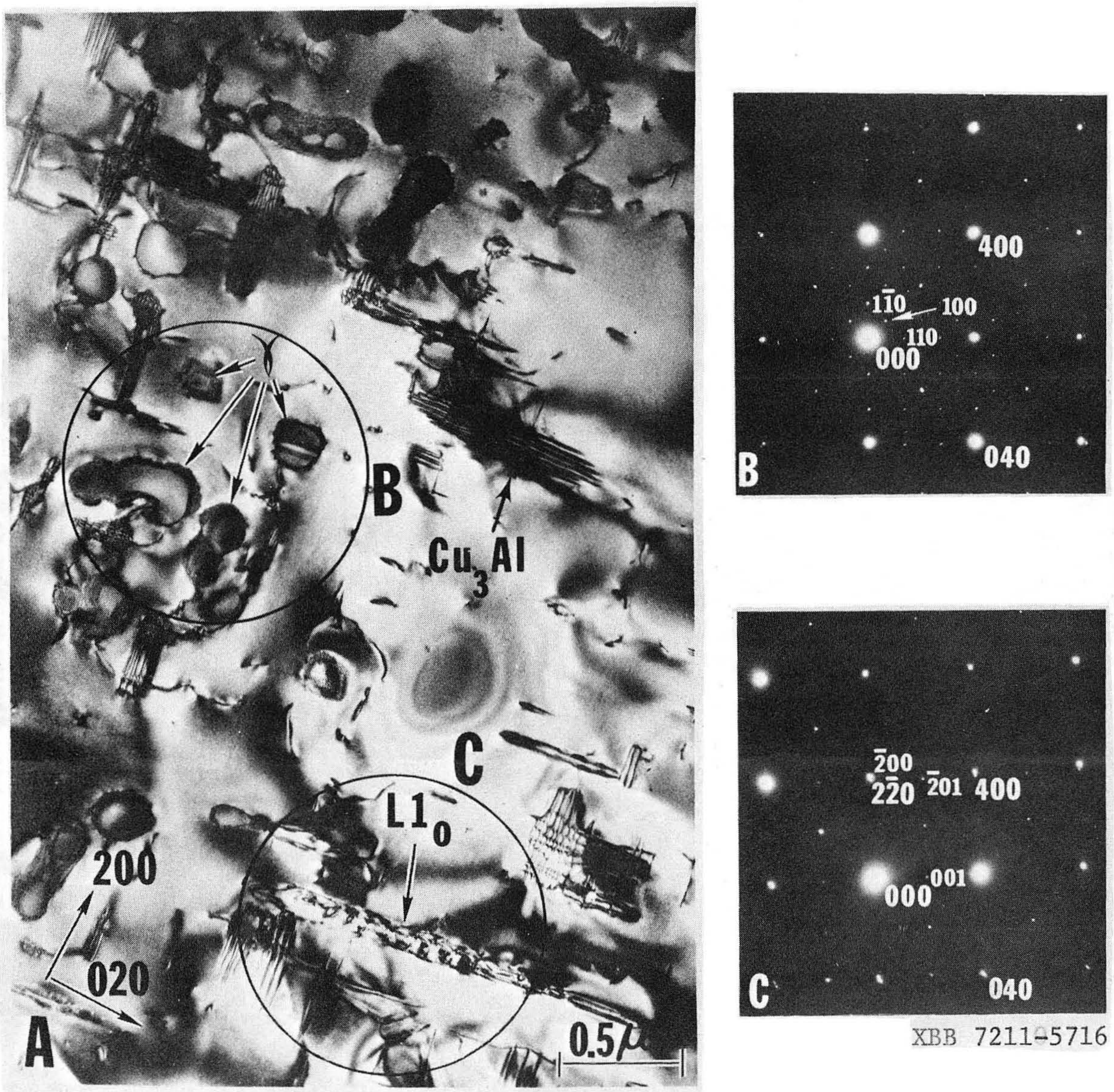

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Fig. 5.

XBB 7211-5889

Fig. 6.

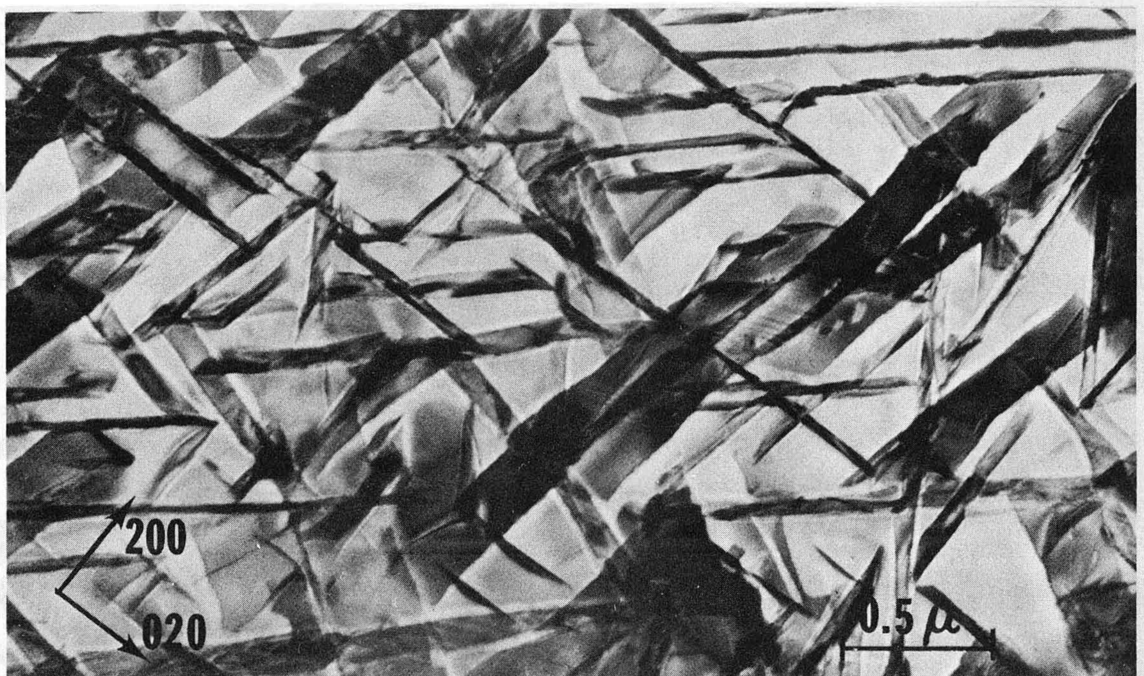

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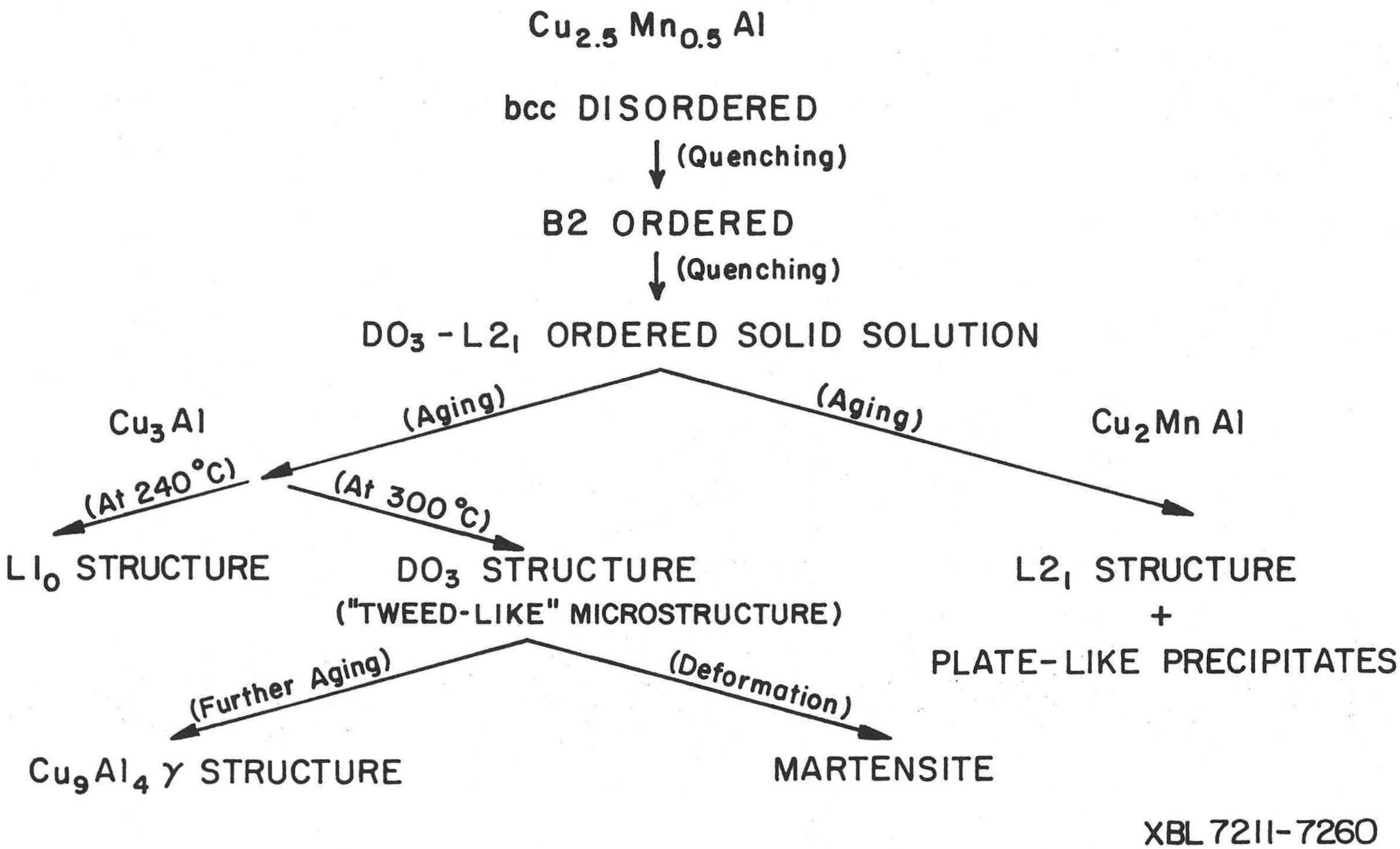
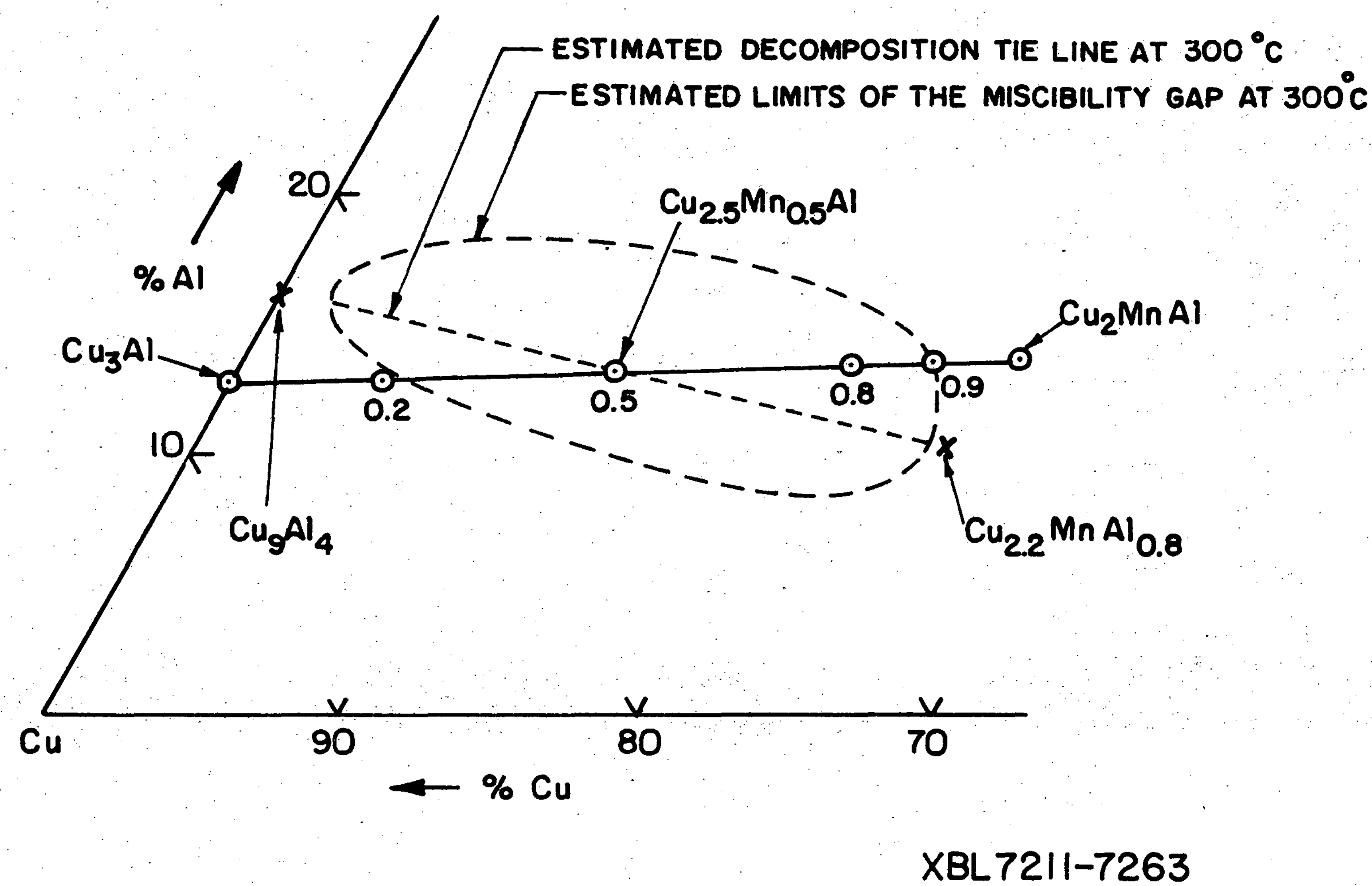
Fig. 7.



$Cu_{2.5}Mn_{0.5}Al$
bcc DISORDERED
(Quenching)
B2 ORDERED
(Quenching)
DO_3 - $L2_1$ ORDERED SOLID SOLUTION
(Aging)
(Aging)
Cu_3Al
Cu_2MnAl
(At 240°C)
(At 300 °C)
$L1_0$ STRUCTURE
DO_3 STRUCTURE
("TWEED-LIKE" MICROSTRUCTURE)
$L2_1$ STRUCTURE
+
PLATE-LIKE PRECIPITATES
(Further Aging)
(Deformation)
Cu_9Al_4 γ STRUCTURE
MARTENSITE
XBL 7211-7260

Fig. 8.



ESTIMATED DECOMPOSITION TIE LINE AT 300 °C
ESTIMATED LIMITS OF THE MISCIBILITY GAP AT 300°C
20
% Al
$Cu_{2.5}Mn_{0.5}Al$
Cu_2MnAl
Cu_3Al
0.2
0.5
0.8
0.9
10
Cu_9Al_4
$Cu_{2.2}MnAl_{0.8}$
Cu
90
80
70
% Cu
XBL7211-7263

Fig. 9.

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