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On the peritectoid transition of the quasi-crystalline and crystalline T_2 phases in rapidly solidified Al–Cu–Mn alloys

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Abstract

The solid phase transformations on heating a rapidly solidified $Al_{57}Cu_{32.5}Mn_{10.5}$ alloy have been investigated in a hot-stage electron microscope in order to elucidate the nature of the phases which participate in the formation of the crystalline equilibrium T_2 phase. The sample was initially formed of a mixture of decagonal quasi-crystalline T_1 and a bcc ordered Al–Cu–Mn solid solution. The transformation of the d quasi-crystalline phase into crystalline T_1 was observed directly and in situ before the formation of the T_2 phase between 650 and 680°C following the reaction $\beta + T_1 \rightarrow T_2$. Finally, T_2 was reversibly transformed into β and T_1 between 685 and 720°C according to the equilibrium phase diagram.

INTRODUCTION

The T_2 phase in the Al–Cu–Mn system was first reported by Guertler and Rassmann [1] and was described as $Mn_3Cu_5Al_{11}$ (or $Al_{58}Cu_{26}Mn_{16}$ where the subscripts represent nominal atomic percentages of the respective components). Later on, the unit cell of T_2 was determined by Köster and Gödecke (oP380; $a = 1.210$, $b = 2.408$, $c = 1.921$ nm) and a small range of homogeneity around the $Al_{57}Cu_{32.5}Mn_{10.5}$ composition was found [2].

The evidence of the peritectoid formation of T_2 ($\beta + T_1 \rightarrow T_2$) between two crystalline phases β and T_1 on slow cooling below 700°C was first described in ref. 2. β is a bcc ordered ternary solid solution (cI2 [3], $a = 0.297$ nm [4]) and T_1 a ternary intermetallic phase with an orthorhombic structure (oC156, $a = 2.420$, $b = 1.250$ and $c = 0.772$ nm around the mean composition $Al_{72}Cu_{10}Mn_{18}$ [5]). The respective positions of the T_1, T_2 and β phases in the phase diagram at room temperature (up to 50 at.% Mn and

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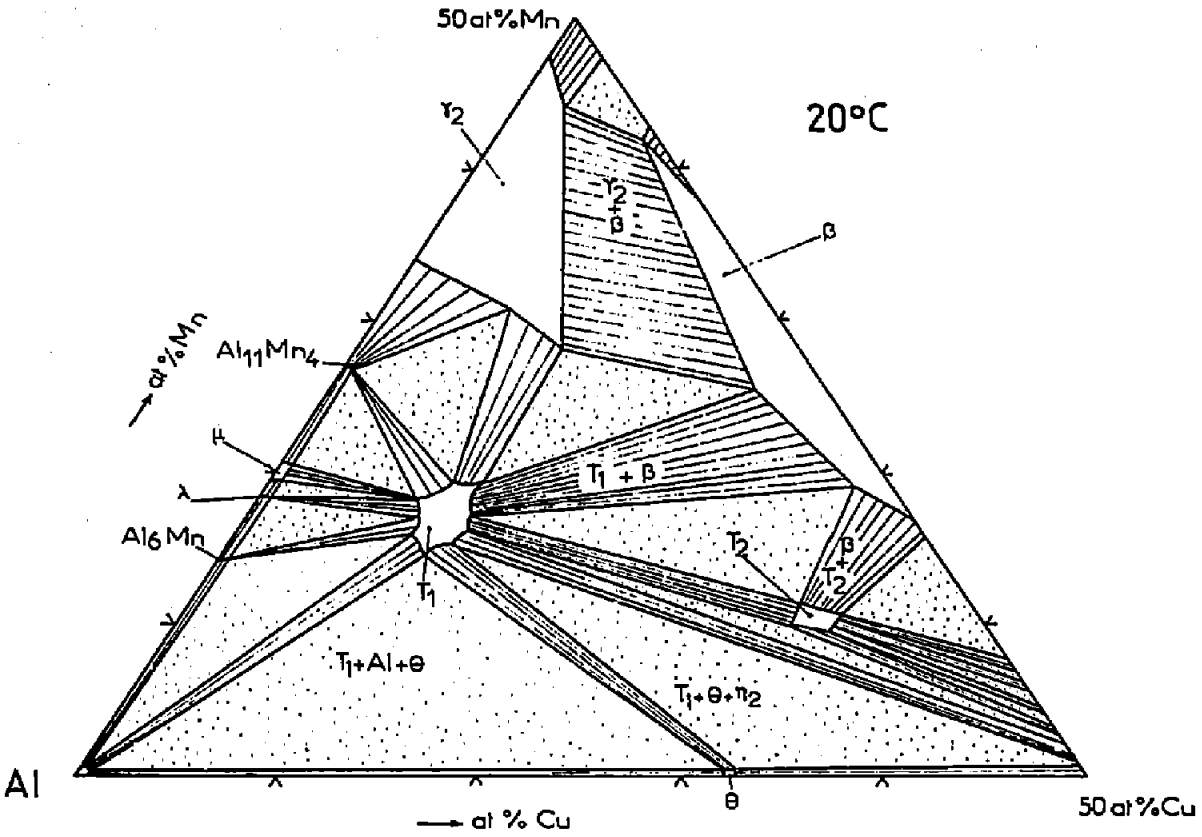

Fig. 1. Isothermal section at room temperature of the Al-rich side of the Al–Cu–Mn system (0–50 at.% Cu, 0–50 at.% Mn).

50 at.% Cu) are shown in Fig. 1. In this figure, the composition ranges of the other various phases have been redrawn by combining the recently assessed binary diagrams Al–Mn [6] and Al–Cu [7] with the isothermal section proposed in ref. 2 for the ternary system. The formation of T_2 on cooling is illustrated at 700°C (Fig. 2) and 680°C (Fig. 3). At 700°C (Fig. 2), the T_2 phase begins to nucleate by reaction between T_1 (composition t_1) and β (composition β_1) along the corresponding tie line $t_1-\beta_1$. Just below 700°C, this reaction generates a three-phase field ($T_1 + \beta + T_2$) between the T_1, β and T_2 phases (Fig. 3). This three-phase field ($T_1 + \beta + T_2$) allows T_2 to grow at the expense of T_1 and β when enough time is allowed for solid state diffusion in the 650–680°C range. The equilibrium vertical section through the T_2 range composition (Fig. 4) shows the respective fields of the various phases versus composition and temperature [2].

In a previous paper, we have observed that the formation of the crystalline T_2 phase is avoided by quenching the alloys from the liquid state [8]: quasi-crystalline phases (icosahedral (i) and decagonal (d) which is a two-dimensional quasi-crystal with translational periodicity along the ten-fold axis) in coexistence with the β phase are the only phases to be detected in the as-quenched alloys. On heating, the i phase disappears and

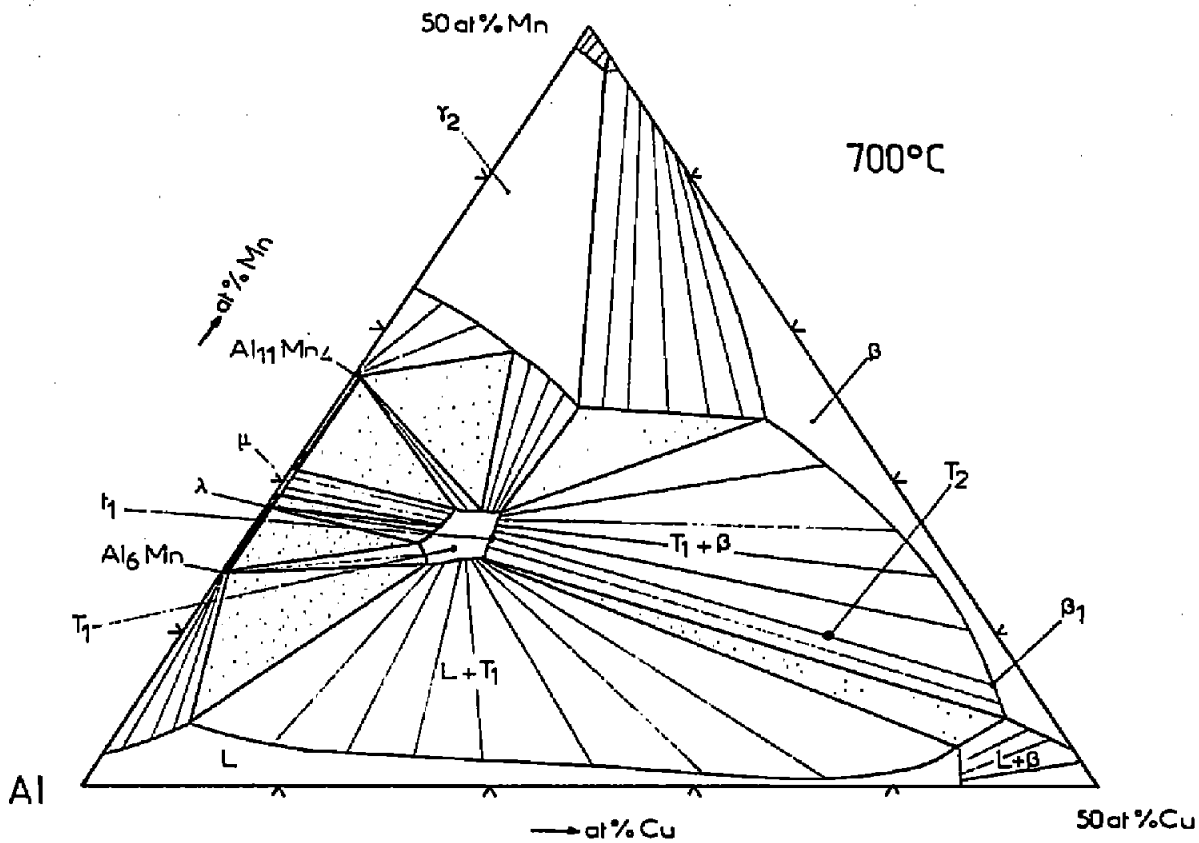

Fig. 2. Isothermal section at 700°C of the Al–Cu–Mn system.

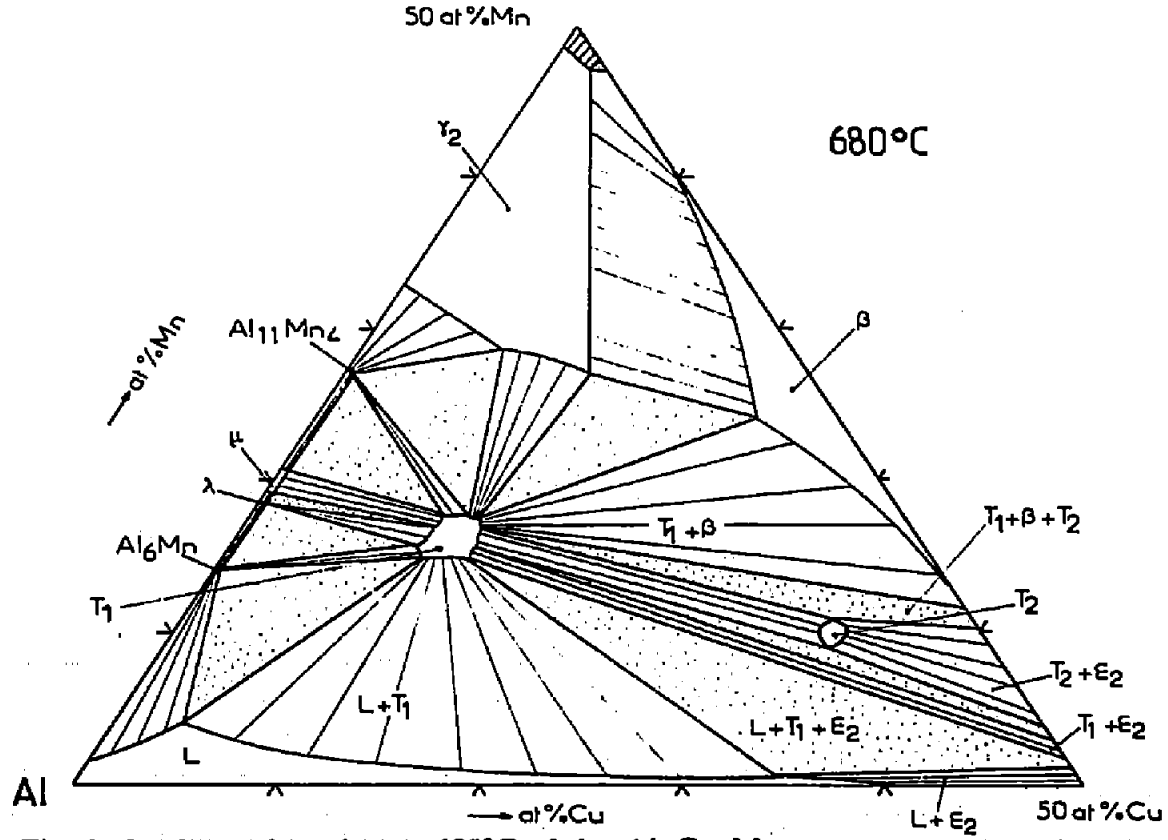

Fig. 3. Isothermal section at 680°C of the Al–Cu–Mn system.

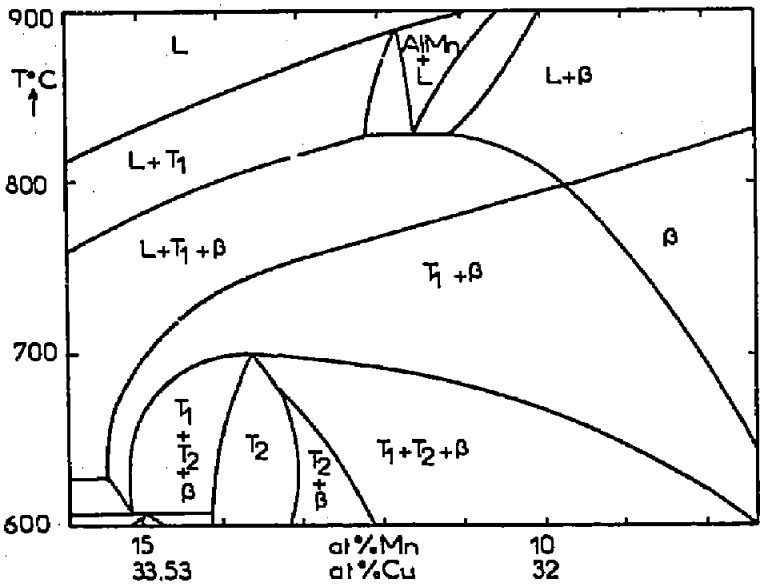

Fig. 4. The vertical section through the T_2 phase, after Köster et al. [2]. (Note that this section is slightly shifted with respect to the T_2 composition used in this work.)

after 2 h at 425°C the alloy consists essentially of a mixture of d and β phases with only some traces of T_2. After annealing for 2 h at 650°C, the crystalline phase T_2 is obtained. From these results, it was not clear whether the T_2 phase was formed by reaction between the decagonal quasi-crystalline or the equilibrium T_1 phase with β. The aim of the present paper is to clarify this question. For this purpose, an electron microscope equipped with an in situ hot-stage has been used.

EXPERIMENTAL PROCEDURE

The alloy composition used for T_2 was $Al_{57}Cu_{32.5}Mn_{10.5}$ obtained by rapid quenching from the melt and then annealed for 2 hours at 425°C. The preparation of the master ingot, the quenching of the alloy and the identification of the various phases has been described elsewhere [6, 9]. A Setaram micro differential thermal analyser (DTA) was used to reveal the successive transformations on heating the as-quenched or annealed samples. The specimens (typically 20 mg) were put inside alumina crucibles and heated at 10°C min^{-1} in flowing pure argon up to 1100°C. X-ray diffraction (XRD) transmission was used to establish the structures of the various phases. Samples for transmission electron microscopy (TEM) were thinned by jet electropolishing with an acid solution of 1.5% HNO_3 and 5% $HClO_4$ in methanol at −40°C. The observations were carried out on a 120 CXII Jeol electron microscope equipped with a Jeol EM-SHH4 hot stage. The samples were placed directly on a copper grid.

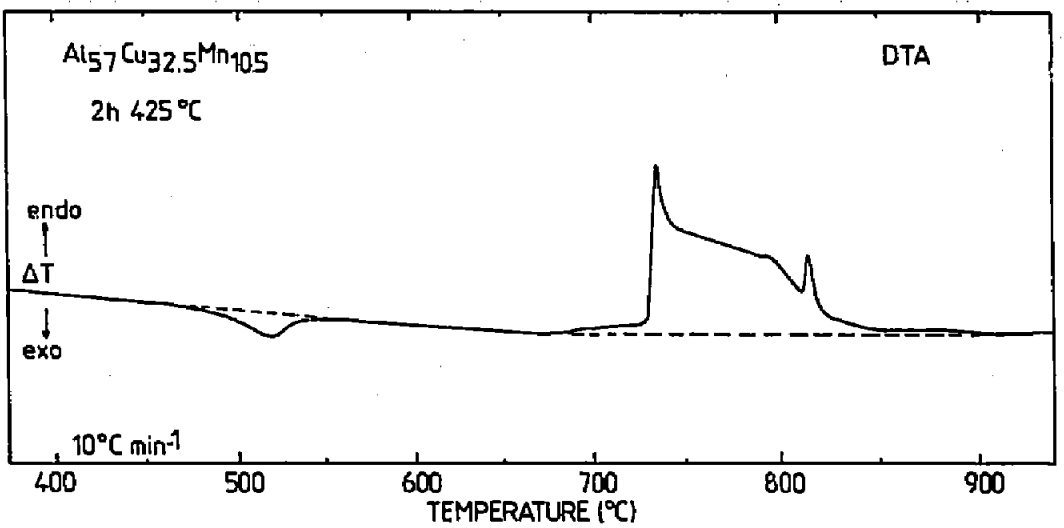

Fig. 5. DTA curve obtained with the sample used in this work, $Al_{57}Cu_{32.5}Mn_{10.5}$ annealed for 2 hours at 425°C.

RESULTS AND INTERPRETATION

DTA

The formation of the crystalline T_2 phase on heating the sample described above is revealed on the DTA curves by a broad exothermic effect between 450 and 550°C (Fig. 5). Below 450°C, the d and β phases are present. Above 550°C, the crystalline T_2 phase is obtained and above 700°C, the endothermic peaks are in good agreement with the vertical section shown in Fig. 4. The first endothermic effect beginning at ≈680°C corresponds to the transitory formation of $T_1 + T_2 + \beta$. The non-congruent invariant transformation $T_2 \rightarrow T_1 + \beta$ is then revealed as the sharp and intense endothermic peak at ≈720°C. The two-phase field $T_1 + \beta$ is crossed before the formation of the liquid phase ($L + T_1 + \beta$). Both fields are observed in the range 730–800°C. The second invariant transformation at ≈810°C ($L + T_1 + \beta \rightarrow L + T_1 + AlMn$) is finally detected as the small and sharp endothermic effect before complete melting of the sample at ≈880°C.

TEM

Previous study of X-ray diffraction patterns indicated the coexistence of d and β phases as the major components, with some traces of periodic T_2 phase in the specimen annealed for 2 h at 425°C [8, 9].

The typical TEM microstructure obtained at room temperature with such a specimen was formed of a very fine mixture of d and β phases with a mean size of about 200 nm. The presence of both phases was confirmed by selected area diffractions (SAD) (Figs. 6 and 7). The β phase is identified in

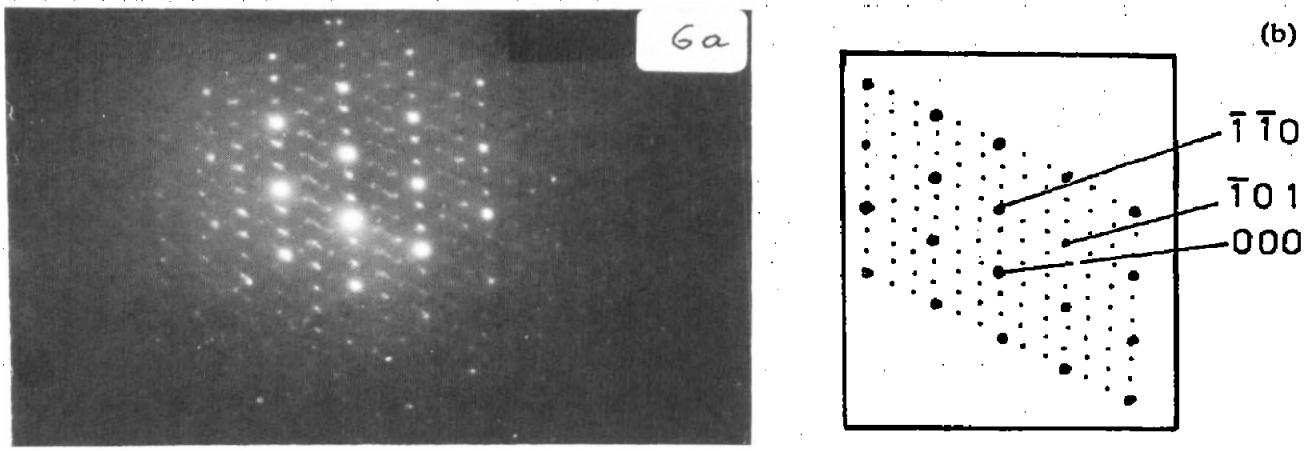

Fig. 6. (a) Selected area diffraction (SAD) showing the presence of the β phase in the sample at room temperature. (b) The corresponding indexation of the β phase.

Fig. 6(a). The evidence of a superstructure of β is shown by the two fine spots between two reinforced spots. The indexation of the β phase with the superstructure is shown in Fig. 6(b). A typical SAD obtained with the d phase taken along the ten-fold axis is shown in Fig. 7(a). The presence of the ten reinforced spots characteristic of the d phase is illustrated in Fig. 7(b). Some of the spots are badly revealed on the pattern and others are clear. This is a consequence of the very fine, defective microstructure typical of the sample.

It is worth noting that the same SAD was obtained with a decagonal specimen obtained by quenching an alloy of composition corresponding to the pure T_1 phase ($Al_{75}Cu_{10}Mn_{15}$). An example is given in Figs. 8(a) and 8(b). Thus, whatever the way of obtaining the d phase, (i.e. by quenching alloys corresponding to the respective compositions of T_1 or T_2, the same SAD pattern is obtained. This result agrees with the phase diagram shown

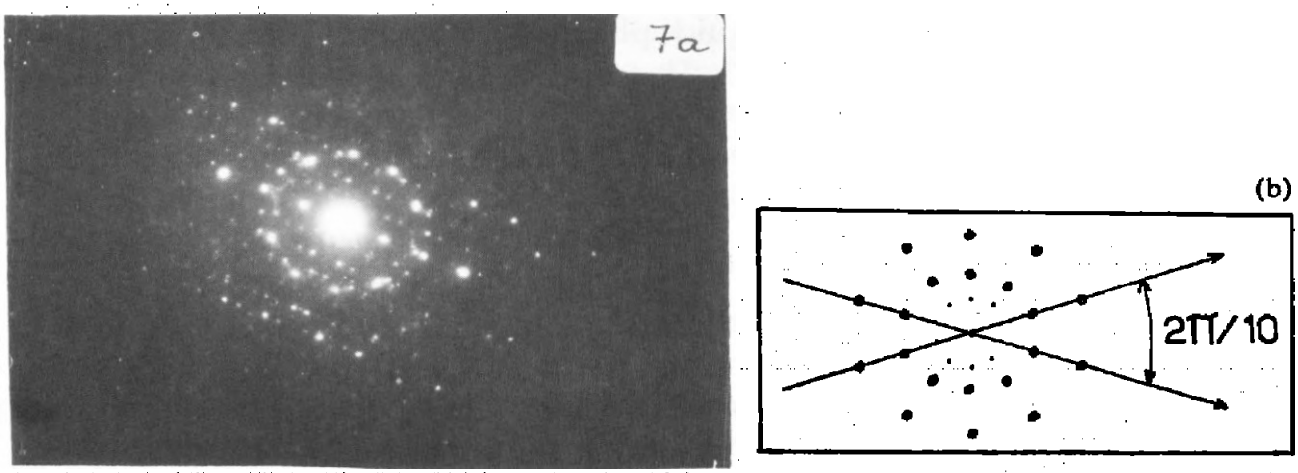

Fig. 7. (a) SAD showing the presence of the d quasicrystalline phase in the sample at room temperature. The electron diffraction pattern of the d phase is taken along the ten-fold axis. (b) The corresponding indexation.

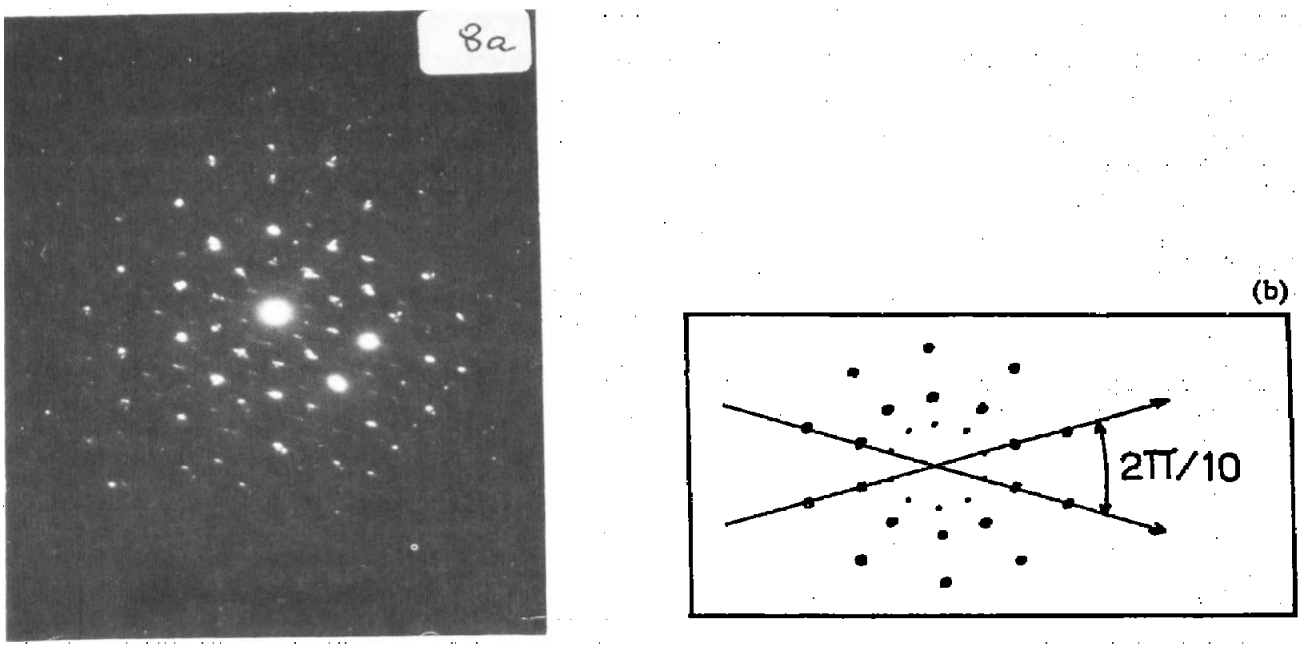

Fig. 8. (a) SAD showing the presence of the d phase in an alloy with composition corresponding to T_1 ($Al_{75}Cu_{10}Mn_{15}$). The electron diffraction pattern is taken along the ten-fold axis. (b) The corresponding indexation.

in Fig. 2 where the composition of T_1 in the alloy corresponding to the T_2 phase is given by the point t_1 at the extremity of the t_1–β_1 tie line passing through the T_2 composition point.

No noticeable change in the TEM patterns was observed on heating from room temperature up to 550°C.

The complete transformation of the d quasi-crystalline phase into crystalline (orthorhombic) T_1 was achieved after 1 minute at 650°C, as shown in Fig. 9(a). In this case, all the spots are clearly visible and arranged

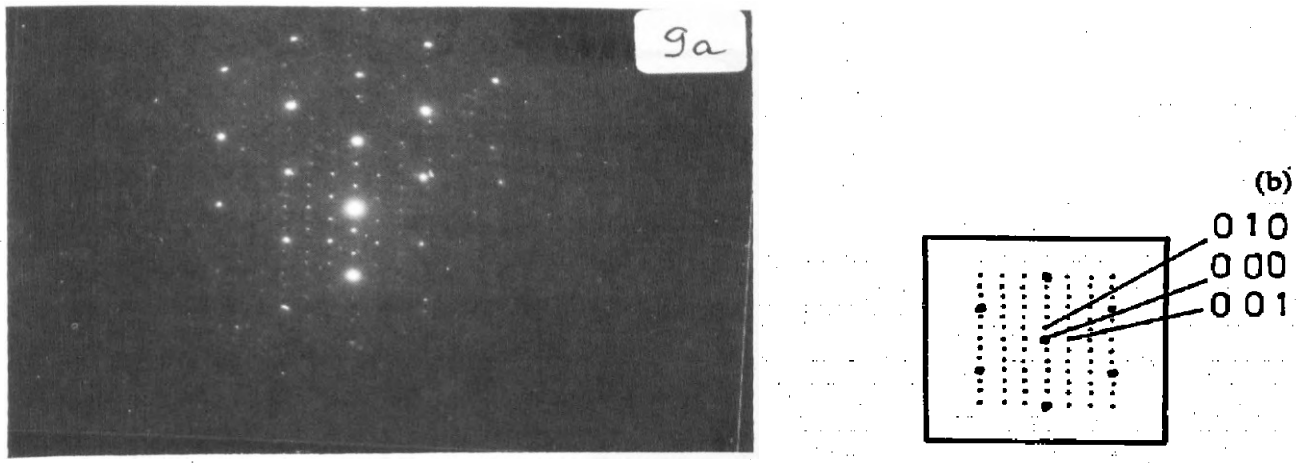

Fig. 9. (a) SAD after 1 min at 650°C showing the disappearance of the d phase, the beginning of the formation of the orthorhombic T_1 phase and the remaining β phase. (b) The corresponding indexation.

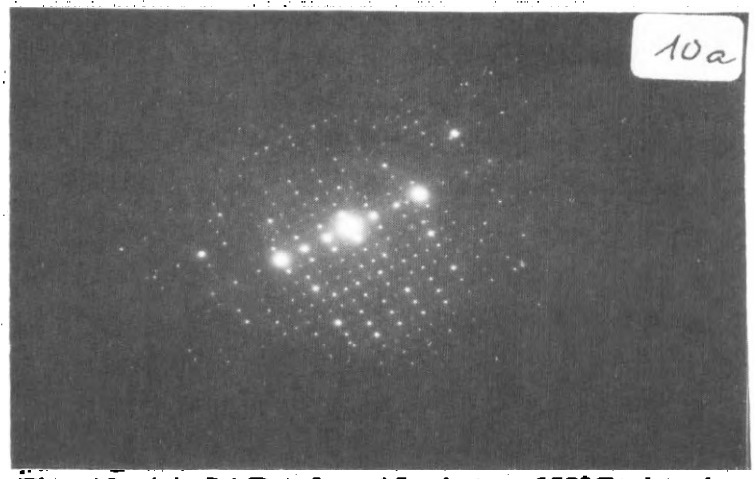

Fig. 10. (a) SAD after 15 min at 650°C showing the orthorhombic T_2 phase. (b) The corresponding indexation.

periodically. Evidence of an orientation relationship with the β phase is given by the superimposed strong spots. The indexation of T_1 is shown in Fig. 9(b).

After 5 min at 650°C, the formation of the orthorhombic T_2 phase was evidenced (Fig. 10(a)) and the corresponding indexation is shown in Fig. 10(b).

This typical pattern remained observable up to 685°C. At 720°C, the T_2 phase disappeared and the T_1 and β phases were again observed (Fig. 11(a)). The indexation of T_1 and β is shown in Fig. 11(b).

CONCLUSION

These results give clear evidence of three successive reactions on heating the alloy $Al_{57}Cu_{32.5}Mn_{10.5}$ prepared by rapid solidification.

(a) Transformation of the quasi-crystalline decagonal phase into the crystalline orthorhombic T_1 phase at around 550°C.

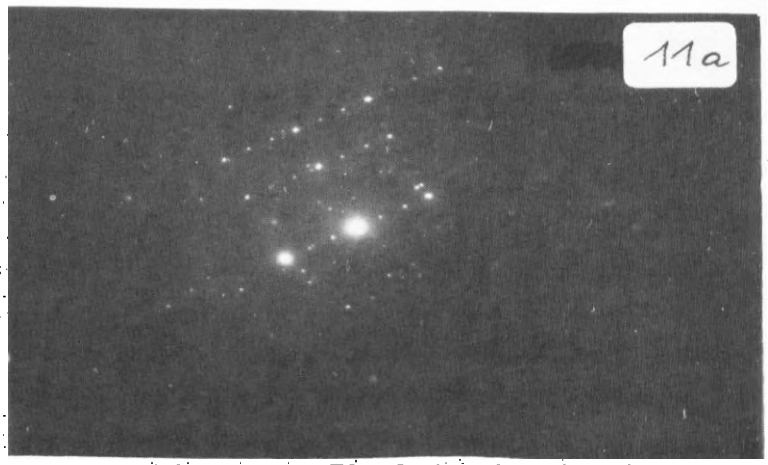

Fig. 11. (a) SAD at 720°C showing the disappearance (absence) of the T_2 phase and the presence of the T_1 and β crystalline phases. (b) The corresponding indexation.

(b) Formation of the crystalline orthorhombic T_2 phase in the range 650–685°C by reaction between β and T_1; it is worth noting that this is the first time that direct evidence is given for the formation of the periodic T_1 phase from the d phase before reaction with β.

(c) Decomposition of the T_2 phase into β and T_1 between 685 and 720°C.

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