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TEM study of the decomposition of the Heusler alloy Cu_2MnAl

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Investigation of the equilibrium phase precipitation in the alloy $Cu_{2.00}Mn_{1.00}Al_{1.00}$ performed previously by X-ray diffraction, magnetometry, SEM and resistometry was continued by means of TEM. It was found that the γ and β-Mn precipitation mechanism was cellular in most cases. No T-phase precipitates were detected. The new results were compared with the previous ones and the temperature dependence of the β-phase decomposition mechanism was explained in terms of the classical phase diagram of the Cu–Mn–Al system.

1. Introduction

The Heusler β phase in the ternary system Cu–Mn–Al is stable over a wide compositional range at high temperatures close to the liquidus surface. However, isothermal sections of the system corresponding to temperatures lower than 1123 K show gradual expansion of (β + β-Mn) and (β + γ) two-phase equilibrium regions reducing the β-phase area, which disappears below 773 K [1, 2].

The decomposition of the stoichiometric β-Cu_2MnAl phase into the γ, β-Mn and T-Cu_3Mn_2Al has been studied by X-ray diffraction, magnetometry, SEM and resistometry [3–7]. It was shown that between 400 and 1000 K heterogeneous precipitation of the equilibrium phases proceeded on grain boundaries. At temperatures above 800 K, Mn-rich particles inside grains were also detected.

Generally, the previous results indicated that there was a change in the mechanism of β-phase decomposition at a temperature close to 700 K. The goal of the present work was thus to investigate these differences by means of TEM and to determine the crystallographic relationships between the parent and the precipitating phases.

2. Experimental details

The preparation procedure of an alloy of the stoichiometric composition $Cu_{2.00}Mn_{1.00}Al_{1.00}$ has been described previously [3]. The 3 mm diameter discs were spark eroded from the ingot and sealed under vacuum in quartz ampoules. Each of them was first homogenized for 20 h at 1123 K and quenched in RT water. In order to repeat the previous thermal treatment leading to the characteristic stages of β-phase decomposition [3–7], the samples were then annealed for 1 week at 633 K, for 1 and 4 h at 733 K and for 10 min at 833 K. Each annealing was followed by RT water quenching. Thin foils were obtained by disc electropolishing in HNO_3 and CH_3OH in the ratio of 1 : 2 at 253 K. TEM examination was carried out using a "Philips EM 301" fitted with goniometer stage and operating at 100 kV.

3. Results

All the electron diffraction patterns taken from the β matrix after quenching the samples from the annealing temperatures showed $L2_1$-type superstructural reflections. The micrographs indicated very large $L2_1$-type ordered antiphase domains.

A transmission electron bright-field image of a grain-boundary region in the sample quenched after annealing for 1 week at 633 K is shown in Fig. 1a (the grain boundary is marked by arrows). Heterogeneously grown cells containing lamallae of γ-phase are clearly visible. As follows from the electron diffraction pattern (Fig. 1b) the γ precipitates were oriented in the following way in relation to the β-matrix:

$$[1\,0\,0]_\gamma \parallel [1\,0\,0]_\beta \qquad (1\,0\,0)_\gamma \parallel (1\,0\,0)_\beta$$

Lamellar heterogeneously growing and similarly oriented γ regions were also observed after ageing the alloy at 733 K (Fig. 2). The latter annealing also caused the β-Mn precipitation. Fig. 3a shows a transmission electron micrograph taken after 4 h at 733 K of a colony of irregularly shaped β-Mn precipitates (indicated by arrows) with the following orientation in relation to the β matrix:

$$[0\,1\,3]_\beta \parallel [0\,1\,1]_{\beta\text{-Mn}} \qquad (1\,0\,0)_\beta \parallel (1\,0\,0)_{\beta\text{-Mn}} \qquad \text{(Fig. 3b)}$$

The morphology of the growing β-Mn regions was quite different after quenching the alloy from 833 K. The well-marked reaction front visible in Fig. 4a and the lamellar shape of the developing β-Mn regions suggest a cellular mechanism of the precipitation process. The orientation of the β-Mn regions precipitating at 833 K in relation to the β matrix was different than at 733 K:

$$[0\,0\,1]_\beta \parallel [0\,0\,1]_{\beta\text{-Mn}} \qquad (1\,0\,0)_\beta \parallel (2\,1\,0)_{\beta\text{-Mn}} \qquad \text{(Fig. 4b)}$$

Observation of the samples quenched after anneal-

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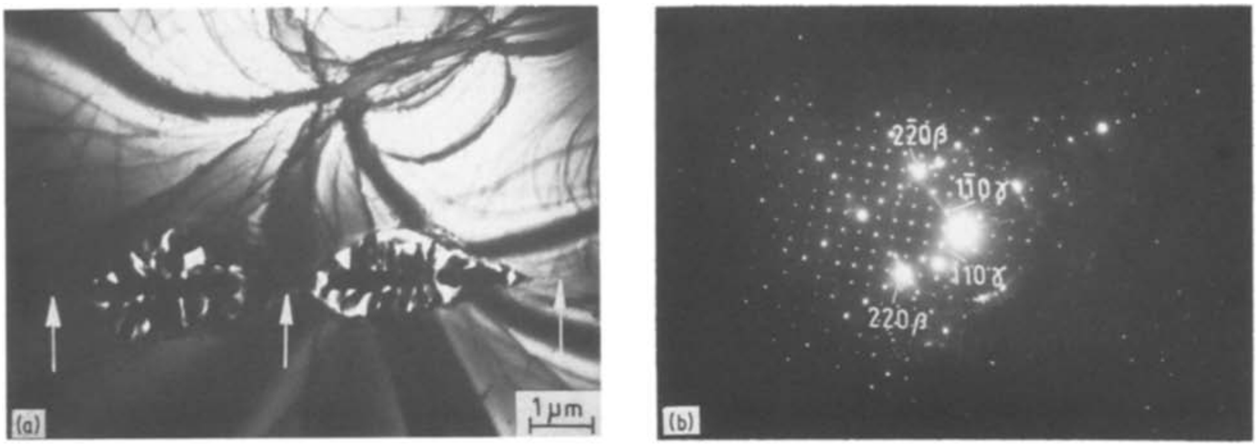

Figure 1 Cellular γ precipitation on a grain boundary (marked by arrows) in $Cu_{2.00}Mn_{1.00}Al_{1.00}$ after 1 week at 633 K. (a) Bright-field micrograph, (b) electron diffraction pattern, zone axis $[0\,0\,1]_\beta \parallel [0\,0\,1]_\gamma$.

ing both at 733 and 833 K indicated the presence of an additional phase, denoted X, a single precipitate of which is visible in Fig. 5a. On the basis of the electron diffraction pattern (Fig. 5b) the X-phase was found to be cubic and the reflections were indexed in terms of an ordered fcc-type structure with the lattice parameter equal to 0.386 nm, oriented in relation to the β matrix as follows:

$$[1\,0\,0]_\beta \parallel [1\,0\,0]_X \qquad (0\,0\,1)_\beta \parallel (0\,0\,1)_X$$

4. Discussion

The experimental results described in the previous section provide some new information concerning the mechanism of the precipitation processes occurring in the Cu_2MnAl alloy in the temperature region of the β-phase metastability. Using SEM, it has been shown previously that the γ precipitation always started at grain boundaries (see Figs 1 and 2 of [6]).

The TEM results presented above indicated that the mechanism of the process was cellular. In fact, micrographs taken after annealing the alloy both below and above 700 K (Figs 1a and 2a) show no marked difference in the morphology of γ precipitates, which in both cases were of lamellar shape and developed in cells growing at grain boundaries. Such a result gives rise to the question why the splitting of the β-phase X-ray lines, typical for a cellular decomposition and reported previously [3], was observed only after quenching the samples from above 700 K. The explanation is given by the detailed β decomposition analysis performed by West and Thomas [2]. They indicated the occurrence of peritectoidal reaction

$$\beta + \beta\text{-Mn} \rightarrow \text{T-}Cu_3Mn_2Al$$

in a certain compositional range of Cu–Mn–Al alloys, which comprised the stoichiometric composition Cu_2MnAl at temperatures below 700 K. The lack of TEM evidence of T-phase formation at 633 K might be due to the thin-foil preparation procedure being extremely difficult because of a considerable difference in the electrochemical properties of the precipitating phases. Probably, the T-phase has always been etched out during the electropolishing process. However, it seems to be highly probable that the β lamellae precipitating together with the γ lamellae in the cells growing below 700 K immediately reacted peritectoidally with β-Mn to form the T-phase. The β-Mn precipitation at 633 K detected by means of X-ray diffraction [3] supports this supposition.

The highly compatible crystallographic orientation of γ precipitates in the β matrix has also been reported by Zalutskii *et al.* [8] and their remarks about the possibility of an easy rearrangement of atoms transforming from β to γ structure explain the high rate of γ-phase formation. As follows from Figs 3a and 4a, there was a considerable difference between the morphologies of β-Mn precipitates in the samples quenched from 733 and 833 K. This, in turn, was highly likely to result from the interaction of γ and β-Mn precipitation processes. At 733 K rapid precipitation of γ-phase was stimulated by manganese-depletion of grain boundaries [6]. This reaction proceeded apparently by a similar vacancy mechanism as described by Nesterenko and Osipenko [9] who observed a discontinuous γ precipitation on antiphase boundaries in the long-range ordered β matrix. In our case, the manganese atoms migrating out of the region of grain (not antiphase) boundaries formed clusters, which then developed into irregularly shaped particles (Fig. 3).

On the other hand, at higher temperatures (e.g. at 833 K) the β-Mn precipitation became an independent

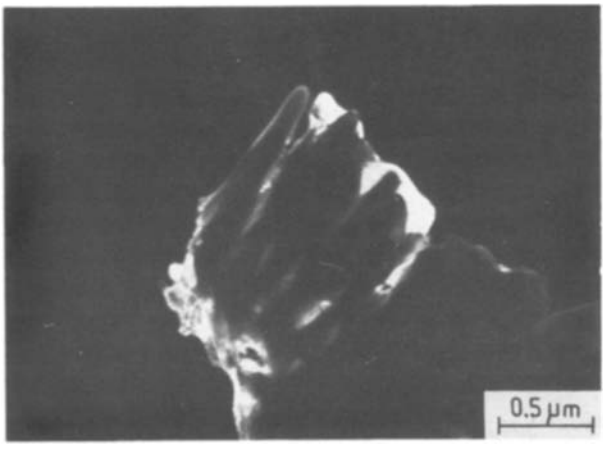

Figure 2 γ precipitates in $Cu_{2.00}Mn_{1.00}Al_{1.00}$ after 1 h at 733 K, bright-field micrograph.

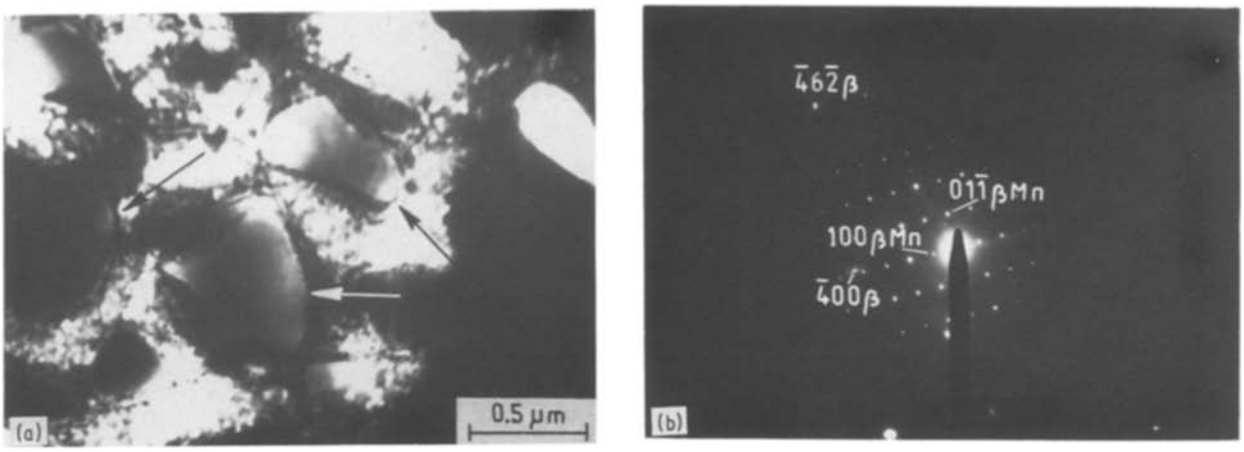

Figure 3 β-Mn precipitates in $Cu_{2.00}Mn_{1.00}Al_{1.00}$ after 4 h at 733 K. (a) Bright-field micrograph, (b) electron diffraction pattern, zone axis $[0\,1\,3]_\beta \parallel [0\,1\,1]_{\beta\text{-Mn}}$.

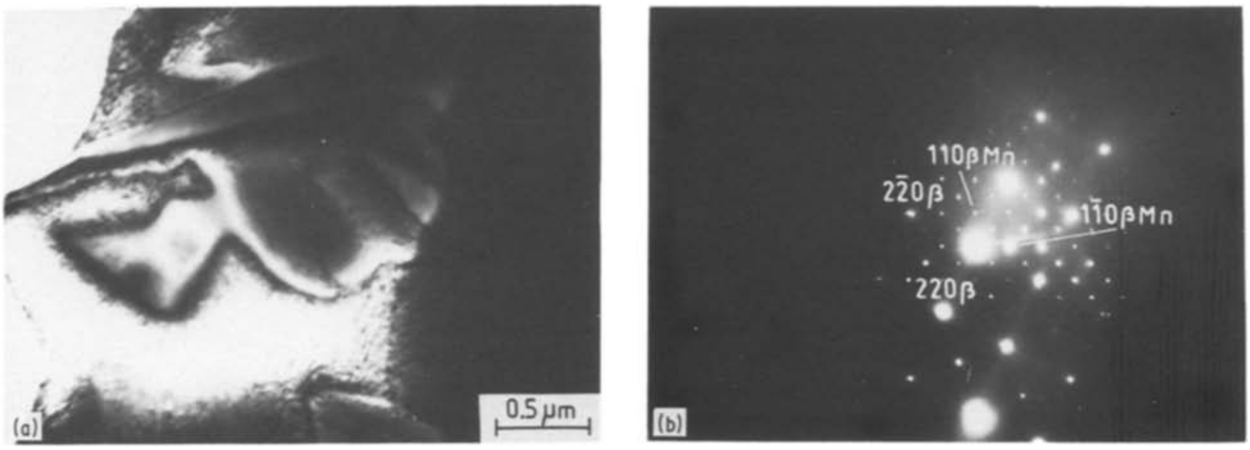

Figure 4 β-Mn precipitation in $Cu_{2.00}Mn_{1.00}Al_{1.00}$ after 10 min. at 833 K. (a) Dark-field micrograph, (b) electron diffraction pattern, zone axis $[0\,0\,1]_\beta \parallel [0\,0\,1]_{\beta\text{-Mn}}$.

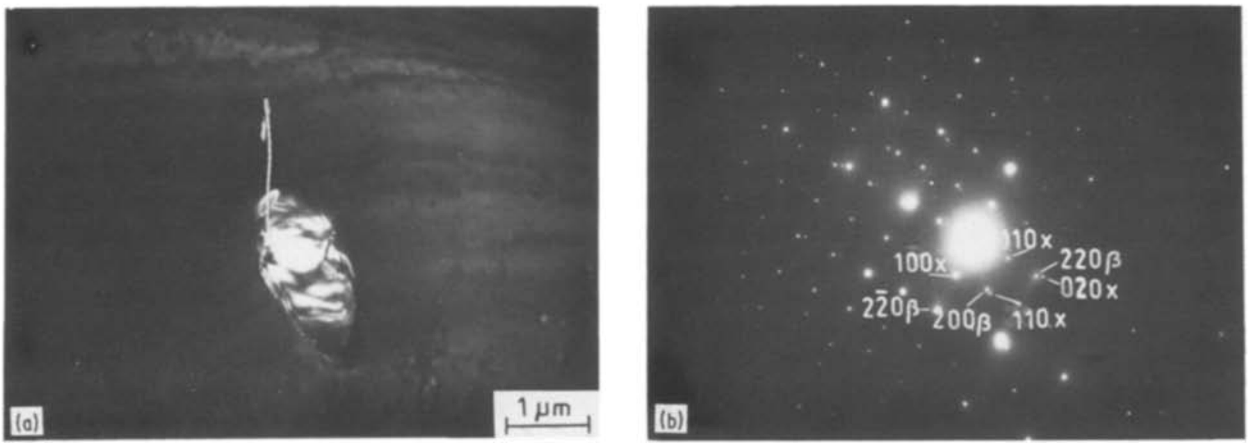

Figure 5 X-phase precipitate in $Cu_{2.00}Mn_{1.00}Al_{1.00}$. (a) Dark-field micrograph, (b) electron diffraction pattern, zone axis $[0\,0\,1]_\beta \parallel [0\,0\,1]_X$.

process occurring without the γ-phase formation. As follows both from TEM (Fig. 4a) and scanning electron micrographs [6], the reaction started at grain boundaries and probably on other structural defects, too. The lamellar morphology of the developing β-Mn regions suggests a cellular mechanism of the process. The main conclusion following from the presented TEM results is that the heterogeneous precipitation processes in the decomposing Cu_2MnAl alloy are of a cellular nature. Unfortunately, for reasons of an apparently technical nature, the mechanism of the peritectoidal reaction:

$$\beta + \beta\text{-Mn} \rightarrow \text{T-}Cu_3Mn_2Al$$

has not been clarified. Instead, a new X-phase was detected, also growing in a discontinuous, though not cellular way. Its structure and the lattice parameter may fit the manganese-rich Cu–Mn solid solution reported by Pearson [10] being probably a transition phase in the process of β-Mn precipitation.

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