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Precipitation from metastable ß-phase in the Heusler alloy $Cu_{2.00}Mn_{1.00}Al_{1.00}$

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The constitution and magnetic properties of the Heusler alloy $Cu_{2.00}Mn_{1.00}Al_{1.00}$ were studied in the temperature range between 423 and 973 K. Polycrystalline specimens of the alloy were annealed isochronally for 24 h at various temperatures. They were examined by means of X-ray diffraction and magnetometry. It was observed that the mechanism of the decomposition of β-phase was quite different below and above 673 K. On the basis of the presented and previously published results it was concluded that the decomposition was controlled by the process of the precipitation of manganese.

1. Introduction

The structure and properties of the β-phase of the system Cu–Mn–Al have been described in many papers [1–6]. This ferromagnetic phase has a cubic structure of the type $L2_1$ and at temperatures below about 923 K decomposes into three phases: β-Mn, γ-Cu_9Al_4 and the Laves' phase T-Cu_3Mn_2Al (their structures are all cubic of the types A13, $D8_3$ and C15, respectively.

The decomposition of β-phase in the alloys Cu–Mn–Al of various compositions has been investigated by many authors. The case of the stoichiometric alloy $Cu_{2.00}Mn_{1.00}Al_{1.00}$ was the subject of our previous papers [7, 8]. The X-ray diffraction phase analysis and the magnetometric measurements of the samples aged isothermally indicated that the decomposition at 633 K proceeded quite differently from that at 733 and 833 K. At 733 and 833 K rapid precipitation of β-Mn was accompanied by the formation of regions of solute depleted β-phase (the phases β_{II}, β_{III} and β_{IV} [7]) the lattice constant and the Curie point of which were reduced. Subsequently, the modified β-phase decomposed slowly. At 633 K the decomposition of the alloy proceeded without variation of the properties of β-phase. The latter results may be compared with those published earlier by Kimura *et al.* [9] and by Yamane *et al.* [10] suggesting that the character of the process of the decomposition of β-phase changed when the annealing temperature went above about 700 K. Thus, it seemed to be advisable to investigate systematically the whole temperature range of the metastability of the β-phase. In this paper we present the results of the X-ray diffraction and magnetometric measurements of the samples of the alloy $Cu_{2.00}Mn_{1.00}Al_{1.00}$ annealed isochronally for 24 h at 50 degree temperature intervals between 423 and 973 K. As none of the ageing treatment carried out caused complete decomposition of the alloy, each specimen contained the β-phase. Its properties were investigated primarily because they depended on the character of the process of its decomposition.

2. Experimental technique

The preparation of the ingots of the alloy and the verification of its composition were described in the previous paper [7]. The composition of the alloy was $Cu_{2.00}Mn_{1.00}Al_{1.00}$. The ingots were reduced into powder and the pressed tablets sealed in vacuum in quartz ampoules were treated thermally. Each specimen was homogenized for 24 h at 1123 K, quenched in water and then tested by X-ray diffraction for homogeneity. Subsequently, the tablets were again sealed in vacuum, annealed for 24 h at the desired temperatures and quenched in water.

The phase analysis of the samples were performed by means of the X-ray diffractometer "Dron-2" at room temperature, using Fe$K\alpha$ radiation. The magnetometric investigations were made by means of the Sucksmith type magnetometer in a magnetic field of 7 kOe (5.6×10^5 A

TABLE I The constitution of the alloy $Cu_{2.00}Mn_{1.00}Al_{1.00}$ annealed isochronally for 24 h. "X" denotes the presence of given phase in the aged specimen, b denotes the broadening of X-ray lines of β-phase, t denotes the solute depletion of β-phase

Annealing temperature (K)	Phases present			
	β	β-Mn	γ	T
423	X^b			
473	X^b			
523	X^b			
573	X			
623	X		X	X
673	X	X	X	X
723	X^t	X	X	
773	X^t	X	X	
823	X^t	X	X	
873	X^t	X		
923	X^t	X		
973	X^t			

m^{-1}). The specimens were heated and cooled at the rate of about 100 deg h^{-1}.

3. Experimental results
3.1. Results of phase analysis
All specimens quenched in water from 1123 K were homogeneous and contained entirely β-phase of lattice parameter equal to 0.5962 ± 0.0001 nm.

The constitution of the samples quenched in water after the isochronal annealing is presented in Table I. Although the samples aged at 973 K and at temperatures below 623 K contained only β-phase, the X-ray lines were considerably broadened in the cases of the specimens annealed at 423, 473 and 523 K. Small amounts of the phases γ-Cu_9Al_4 and T-Cu_3Mn_2Al precipitated in the alloy at 623 K while the annealing at 673 K caused almost complete decomposition of β-phase and the precipitation of γ-Cu_9Al_4, T-Cu_3Mn_2Al and β-Mn. In all the above cases the lattice parameters of β-phase were the same and equal to 0.5962 nm. Another situation was found in the specimens annealed at temperatures between 723 and 923 K. They all contained β-Mn and the β-phase the lattice parameter of which was reduced. The phase γ-Cu_9Al_4 was contained in the samples aged at 723, 773 and 823 K. The dependence of the lattice parameter a of β-phase on the temperature T of the isochronal annealing is presented in Fig. 1. The degree of the decomposition of β-phase may be expressed by the ratio of the integral intensity of its structural X-ray line (2 2 0) and the sum of the integral intensities of the structural X-ray lines (2 2 1) of β-Mn, (4 1 1) of γ-Cu_9Al_4 and (3 1 1) of T-Cu_3Mn_2Al. The temperature dependence of the above quantity is presented also in Fig. 1 and denoted as "$I_{(220)}$".

3.2. The magnetic properties of the alloy
The alloy quenched in water from 1123 K was a ferromagnet of Curie point 590 ± 4 K and saturation magnetization 3.25 ± .01 μ_B/Mn. The magnetic saturation of all the specimens was measured at 123 K in a magnetic field of 7 kOe (5.6×10^5 A m^{-1}). The measurement of each sample consisted of the following stages:

I. Heating from 123 K up to the decay of ferromagnetic properties.
II. Cooling down to room temperature.
III. Repeated heating from 123 up to 173 K in order to evaluate the saturation magnetization of the sample after the heating and cooling cycle.

The difficulties of interpretation of the reported results lie in the fact that they concern the properties of a phase which was metastable in the conditions of the experiment.

The temperature dependence of the magnetization (M) of the specimens is presented in Fig. 2. In almost all cases the anomalous increase of M was observed during the heating (stage I) between 373 and 573 K. The only exceptions were the samples annealed at 573 and 623 K. As was indicated in our previous papers [7, 8] the origin of the anomalous increase of the magnetization was the precipitation of a ferromagnetic phase in partially decomposed alloys occurring during the magnetometric measurements at about 473 K which was ascertained by X-ray diffraction. The phenomenon made it impossible to estimate the value of the Curie point of β-phase with the aid of the usually applied linear extrapolation of the square of magnetization to zero. Thus, the Curie points $\uparrow T_{c,\text{fit}}$ of β-phase (Fig. 1) were evaluated through the fitting of Brillouin functions $B_J(M, T/T_c)$ to the experimental values of the magnetization M below the temperature range of the anomalous increase of M. ($\uparrow$ refers to heating and $\downarrow$ refers to cooling.) The linear extrapolation of M^2 at temperatures above its maximum was the method for the estimation of Curie points $\uparrow T_c$ of the phase whose precipitation caused the increase of M. It is obvious that the ferromagnetic properties observed when

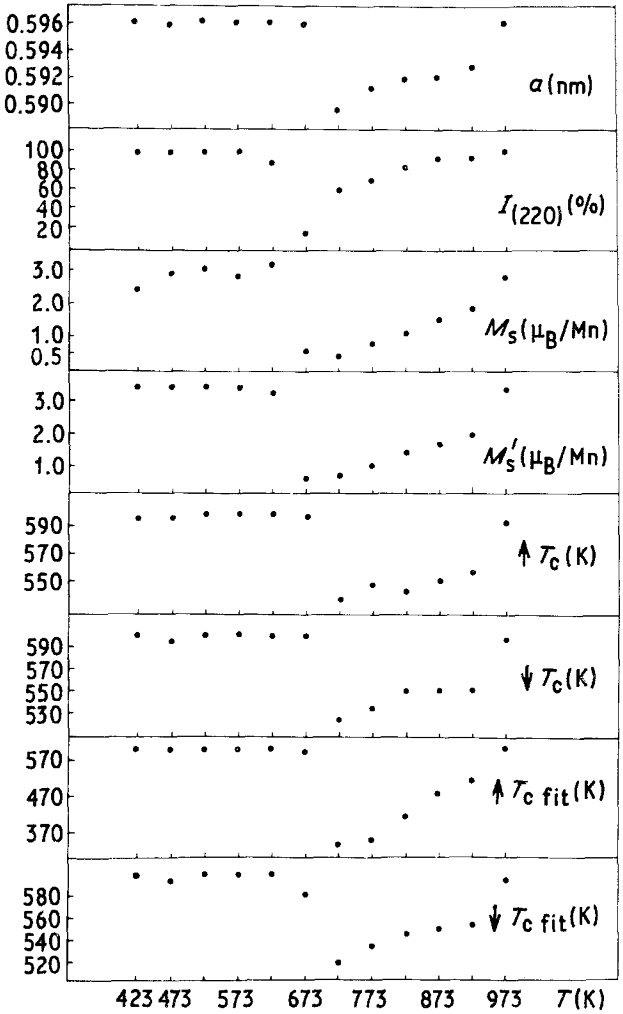


Figure 1 The dependence of structural and magnetic parameters of β-phase of the alloy $Cu_{2.00}Mn_{1.00}Al_{1.00}$ on the temperature T of the isochronal annealing: a denotes lattice parameter, $I_{(220)}$ expresses the contribution of the intensity of the X-ray line (2 2 0) of β-phase to the sum of the intensities of selected structural Bragg reflections of all phases contained in the alloy, M_s and M'_s denote the saturation magnetization before and after the heating, respectively, $\uparrow T_c$, $\downarrow T_c$, $\uparrow T_{c,fit}$ and $\downarrow T_{c,fit}$ denote the values of Curie points of the heated and cooled specimens estimated by linear extrapolation of M^2 and by fitting the Brillouin functions, respectively.

cooling the samples were connected with the latter phase. The Curie points $\downarrow T_{c,fit}$ and $\downarrow T_c$ (Fig. 1) were estimated for the cooled samples, respectively, with the aid of both methods described above. The low temperature values of the magnetization of the samples measured during the stages I and III of the experiment allowed the evaluation of the magnitudes of the saturation magnetization M_s and M'_s respectively. Although M_s concerns β-phase and M'_s is connected with the phase precipitated during the experiment, it should be noted that the interpretation of the latter parameters is difficult because they depended not only on the properties of the ferromagnetic phases themselves but also on their content in the alloy.

4. Discussion

On the basis of the investigations of the alloy $Cu_{2.00}Mn_{1.00}Al_{1.00}$ aged isothermally [7] and isochronally the following conclusions may be drawn:

(a) The upper limit of the metastability of β-phase is probably higher than 973 K. No other phases except the β-phase were detected by X-ray phase analysis of the alloy aged at that temperature but the temperature dependence of its magnetization was modified in relation to that of the alloy quenched from 1123 K (Fig. 2).

(b) The phenomena observed in the samples aged at temperatures between 673 and 973 K show that the decomposition of β-phase proceeded in two stages.

The results of X-ray diffraction and magnetometry may suggest the discontinuous precipitation of manganese during the first stage and the formation of cells containing β-Mn and transient, solute depleted β-phase. Fig. 3 shows the microstructure of the alloy aged for 1 h at 733 K. The heterogeneous precipitation on grain boundaries,

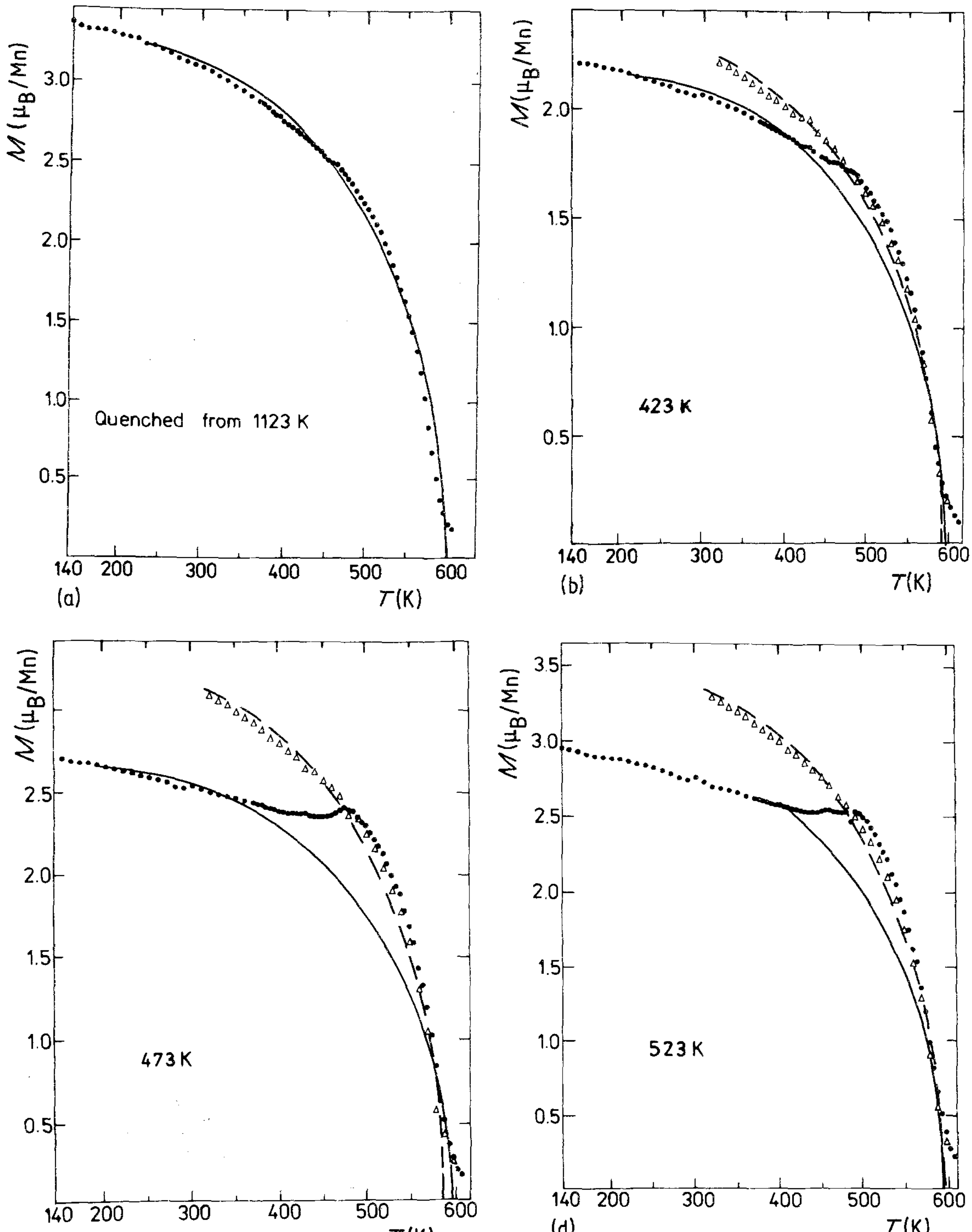


Figure 2 Temperature dependence of the magnetization of the alloy $Cu_{2.00}Mn_{1.00}Al_{1.00}$ aged isochronally at marked temperatures: • and △ denote the points obtained during the heating and cooling respectively; full and dashed lines represent the fitted Brillouin functions.

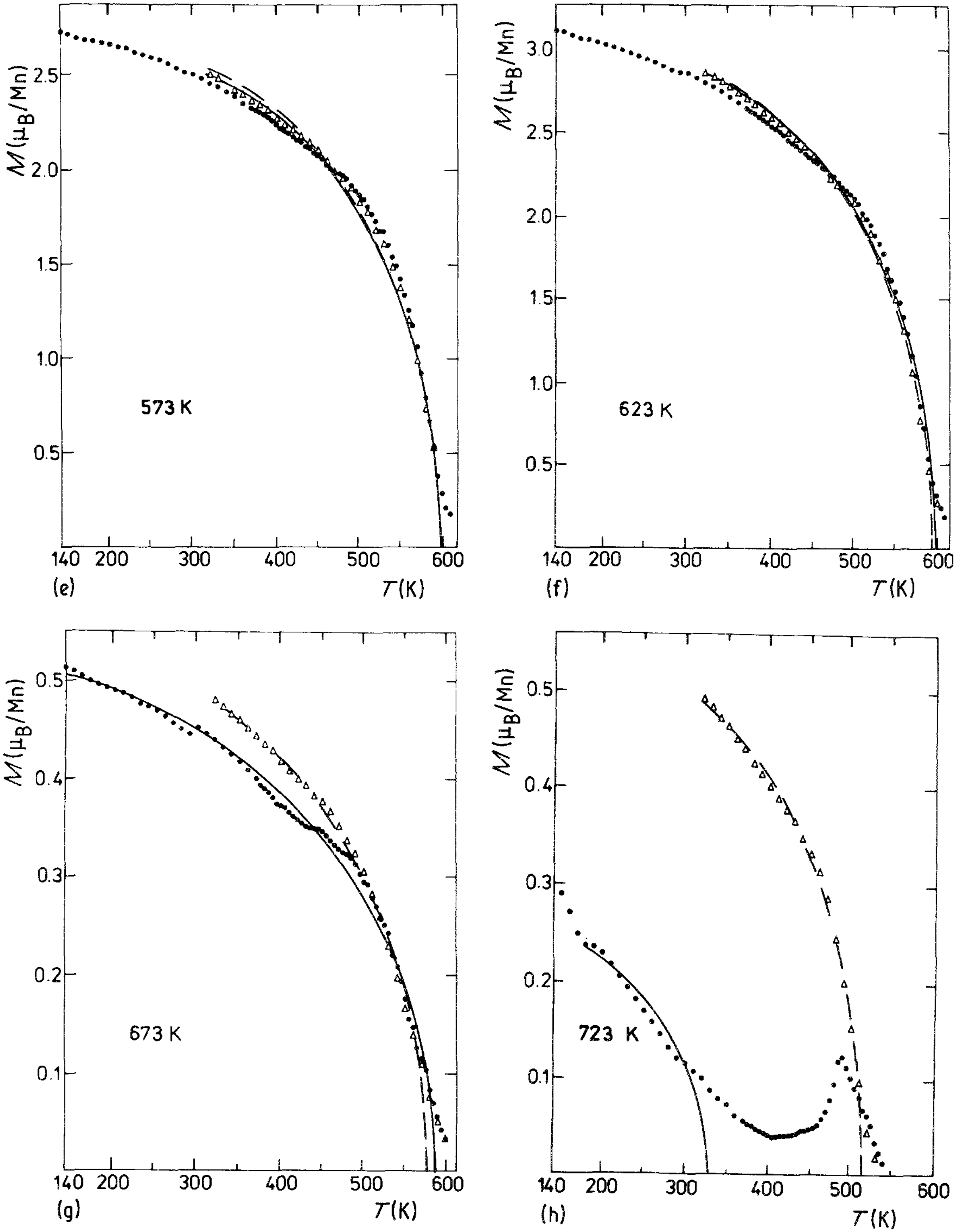


Figure 2 Continued.

such as visible in the photograph, is often observed in cases when cellular precipitation occurs. This problem, however, requires further investigation.

The next stage of the process was the decomposition of the solute depleted β-phase and the nucleation and growth of γ-Cu_9Al_4 and probably of T-Cu_3Mn_2Al. The elevation of the annealing temperature caused the increase of the rate of the precipitation of β-Mn and the decrease of the rate of the further decomposition of β-phase. After

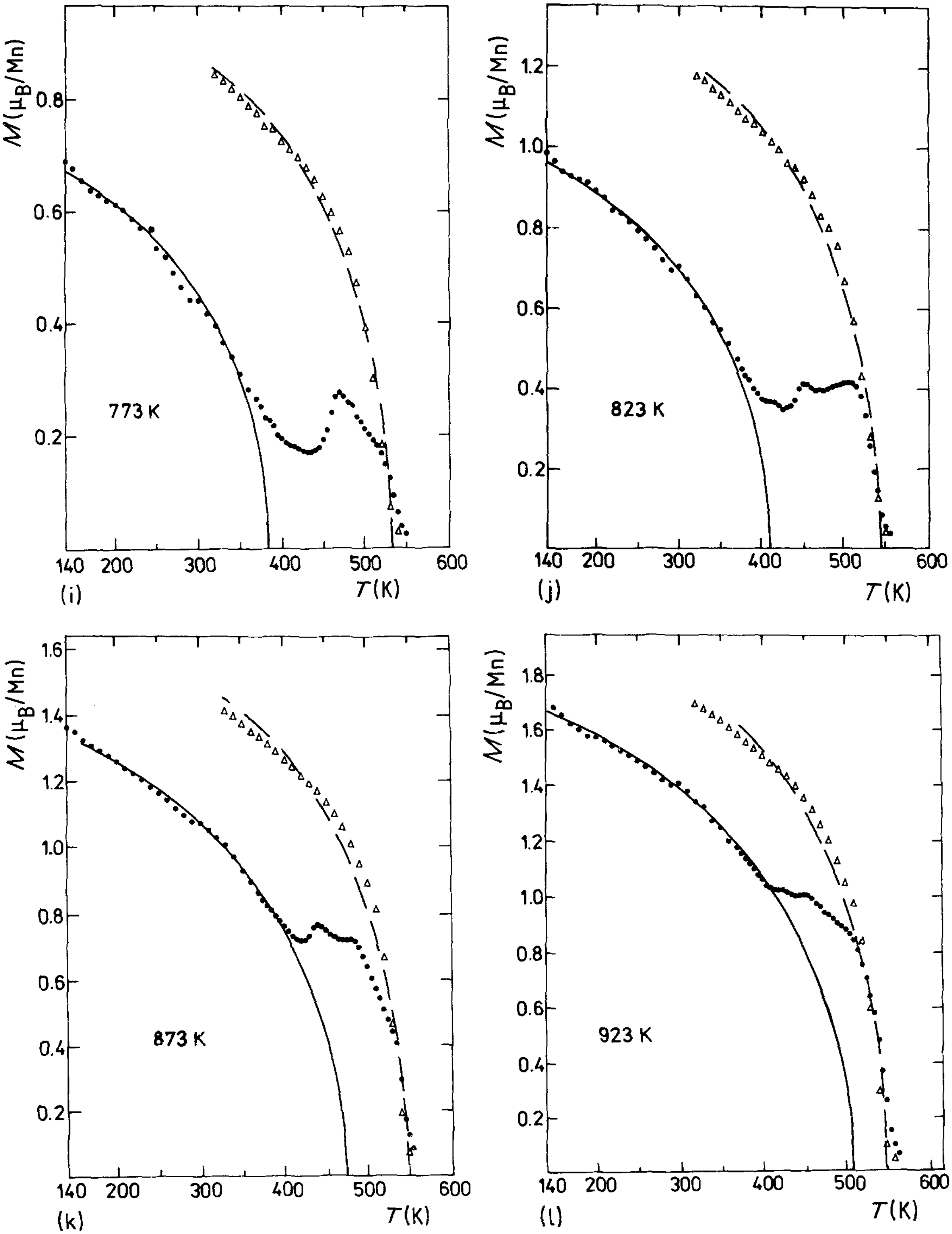
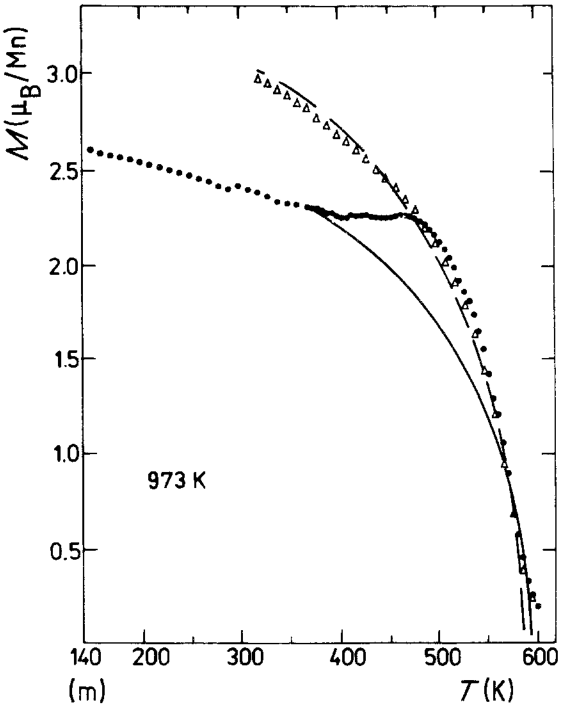


Figure 2 Continued.

24 h of ageing all specimens contained completely transformed β-phase and β-Mn. It is visible that the lower was the ageing temperature the greater was the degree of the solute depletion of β-phase (Fig. 1) reflected by the decrease of the lattice parameter and Curie point. The rate of the further decomposition of β-phase was rapidly decreased at temperatures higher than 773 K [7] and it made it very difficult to determine the equilibrium constitution of the alloy.



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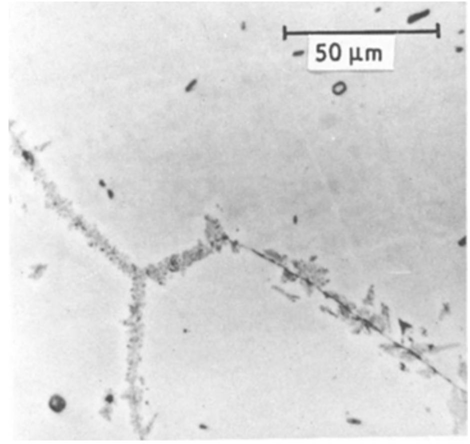

Figure 3 Microstructure of the alloy $Cu_{2.00}Mn_{1.00}Al_{1.00}$ aged for 1 h at 723 K.

(c) At temperatures lower than 723 K no solute depletion of β-phase was observed. It decomposed into γ-Cu_9Al_4, T-Cu_3Mn_2Al and β-Mn without variation of the lattice parameter and Curie point. The rate of its decomposition was decreased by the lowering of the annealing temperature and no stages of it could be distinguished. The phase β-Mn precipitated very slowly and was detected by X-ray diffraction only after the formation of Bragg reflections of both γ- and T-phases.

(d) The precipitation of the ferromagnetic phase occurring during heating the specimens in the magnetometer perturbed the temperature dependence of the magnetization of solute-depleted β-phase especially strongly. Comparing Figs. 1 and 2 one may see that the greater was the depletion the sharper was the anomalous increase of M. The latter leads to the conclusion that the deviation from stoichiometry of the β-phase stimulated the process. It may be confirmed by the recent results of Kokorin and Osipenko [11] and of Wachtel and Winkler [12]. Kokorin and Osipenko observed the anomalies of the temperature dependence of the magnetization of non-stoichiometric alloys Cu–Mn–Al quenched from the temperature of homogenization. The anomalies were similar to those reported in this paper. Wachtel and Winkler investigated a series of the alloys containing 25 at% Al and observed that when aged isothermally at 500 K the non-stoichiometric alloys showed an increase of the magnetization. The origin of that increase was explained on the basis of the work of Johnston and Hall [13] and of Bouchard and Thomas [14] as the precipitation of the stoichiometric β-phase in nonstoichiometric alloys. However, the observed variation of the values $\uparrow T_c$, $\downarrow T_c$ and $\uparrow T_{c,fit}$ (Fig. 1) suggest that the composition of the phase precipitated in our specimens was not constant and depended on the history of the alloy.

The anomalous increase of the magnetization was also observed in cases of specimens aged at temperatures below 723 K except for two samples annealed at 573 and at 623 K. It should be noted that just in the case of the latter specimens no broadening of X-ray lines of the β-phase was observed. Nesterenko and Osipenko [15–17] investigated by TEM (transmission electron microscopy) coherent precipitations in the alloy Cu_2MnAl aged at about 473 K. Such precipitations might generate the defects of the crystalline lattice which would cause the broadening of X-ray lines. It could also be expected that the stoichiometry of the matrix would be slightly perturbed in the regions surrounding the coherent precipitations. At about 473 K the matrix could be thus transformed in the magnetometer but the effect would be much weaker than it was in the case of the alloy containing the solute depleted β-phase.

The above notes may be the basis of the elaboration of the thermodynamics of the decomposition of the β-phase of the system Cu–Mn–Al.

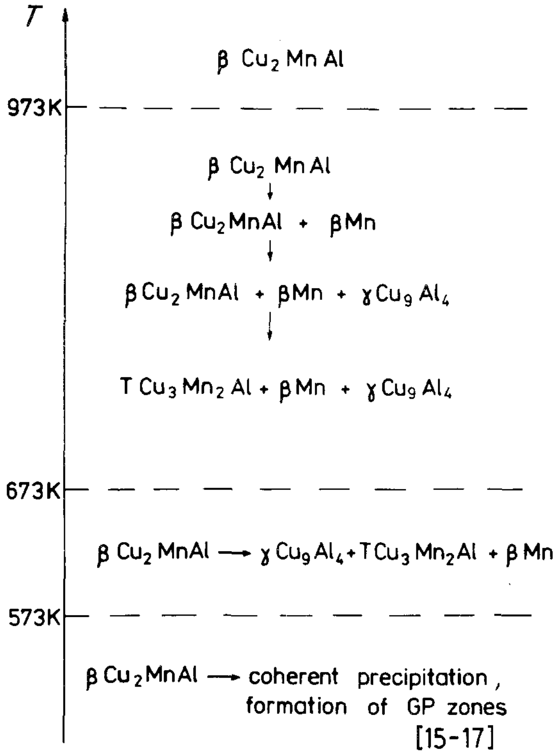

Figure 4 Sequence of precipitation from metastable β-phase at various temperatures below 973 K.

The mobility of the atoms of manganese seems to be the most important factor of the process of precipitation in the alloy. It was high at temperatures above 673 K and led to the rapid precipitation of β-Mn causing the formation of solute depleted β-phase. Below 673 K the mobility of atoms of manganese was considerably lower. The nucleation and growth of γ-Cu_9Al_4 and T-Cu_3Mn_2Al was the origin of the appearance of the Mn-rich regions in the alloy but the structure of β-Mn was formed quite slowly.

Further abatement of the annealing temperature led again to the increase of the mobility of manganese atoms and at about 473 K it was the origin of either the broadening of X-ray lines of the stoichiometric β-phase or the precipitation processes in nonstoichiometric one. The proposed scheme of the phase equilibrium of the alloy Cu_2MnAl is presented in Fig. 4.

The analysis of the isothermal sections of the system Cu–Mn–Al published by Köster and Gödecke [3] and by West and Thomas [2] indicates that the sequence of precipitation from β-phase proposed in this paper is generally in agreement with the considerations of the above authors. The discrepancies concern mainly the temperature limits of the existence of the phases. However, the difficulty of the evaluation of them, noted already by Köster and Gödecke, is connected with the fact that at certain temperatures the stoichiometric Heusler alloy Cu_2MnAl is situated just on the line separating different regions of phase equilibria on the isothermal sections. The above problem concerns mainly the limit of the existence of the phase γ-Cu_9Al_4 (see the 600° C isothermal section of Köster and Gödecke [3]).

The application of long periods of annealing [7] showed that the upper temperature limit of the existence of T-Cu_3Mn_2Al is higher than it was suggested by other authors [2, 3, 10] and that the marked change of the mechanism of the decomposition of β-phase at 673 K was caused rather by the change of the properties of manganese atoms than by the lack of the precipitation of T-Cu_3Mn_2Al.

Further investigations of the phenomenon by means of electron microscopy and of X-ray microanalysis are in progress and the results will be published soon.

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