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Decomposition of β-phase in the Heusler alloy $Cu_{2.00}Mn_{1.00}Al_{1.00}$

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Polycrystalline homogenized specimens of the alloy $Cu_{2.00}Mn_{1.00}Al_{1.00}$ were annealed at temperatures of 360° C, 460° C and 560° C, quenched in water and investigated by means of X-ray diffraction and magnetometry. It was indicated that the process of the decomposition of the β-phase of the system Cu–Mn–Al is different at each of the above temperatures. The investigations showed the occurrence of the additional precipitation in the partially decomposed alloy when it was annealed at 200° C.

1. Introduction

The ternary alloys Cu–Mn–Al were investigated extensively due to their structural and magnetic properties. It was indicated that the ferromagnetism of these alloys is connected with the β-phase of the Cu–Mn–Al system [1–4]. The β-phase has a cubic structure of the type $L2_1$ and exists over a wide compositional range at temperatures higher than 650° C [1, 5]. The "order–disorder" phase transitions occurring in that phase lead to structures of types B2 and A1, of a lower degree of order of atoms [6–8]. At temperatures lower than about 650° C the β-phase is metastable and decomposes. Up to the present, a number of papers dealing with the process of the decomposition of the Cu–Mn–Al alloys have been published, but the compositions of the investigated specimens were not stoichiometric and rather accidental. It is thus very difficult to systematize the results of the researches of the process, the progress of which depends considerably on the chemical composition of the investigated specimens. However, it has been shown that the following phases are the products of the decomposition of the β-phase: γ-Cu_9Al_4 with structure of the type $D8_3$, β-Mn with structure of the type A13 and the intermetallic compound Cu_3Mn_2Al (the T-phase) with structure of the type C15 [1, 5, 9–18]. Our aim was to research systematically the process of the decomposition of the β-phase in the alloy of stoichiometric composition $Cu_{2.00}Mn_{1.00}Al_{1.00}$.

2. Preparation of the specimens

The components, Cu, Mn and Al, all of purities 99.999 %, were melted in appropriate proportions in an induction furnace in a helium atmosphere. The chemical analysis of the alloy produced indicated a loss of copper in relation to the stoichiometric composition. After the addition of Cu the alloy was melted again with the same conditions. The chemical composition of the final product was $Cu_{2.00}Mn_{1.00}Al_{1.00}$. The ingots were then powdered and the separated fraction of grain size 0.06 mm to 0.12 mm was pressed into tablets. The tablets, sealed in vacuum in quartz ampoules, were homogenized for 20 h at a temperature of 850° C and quenched in water. The homogeneity of each specimen was tested by means of X-ray diffraction. The powder was then pressed again into tablets, sealed in vacuum, annealed at the desired temperatures and quenched in water.

3. Experimental technique

The specimens were investigated by means of X-ray diffraction and magnetometry.

The X-ray diffraction experiments were performed at room temperature, and FeKα and FeKβ radiation was used. The lattice constants of the phases were calculated with the aid of extrapolation. The lattice constant of β-Mn was always determined on the basis of the X-ray line (2 2 1), due to the absence of the lines at angles 2θ higher than 60°.

The magnetometric measurements were per-

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formed by means of the thermomagnetic balance of the Sucksmith type. The magnetic field strength was equal to $8.8 \times 10^5 A m^{-1}$. The samples were heated at a rate of about $100^\circ C h^{-1}$ from the temperature of liquid nitrogen up to 300° C and then cooled to room temperature.

4. Results

The alloy quenched from 850° C was homogeneous. Its structure consisted entirely of β-phase and was of the type $L2_1$. The lattice parameter was equal to 0.5961 ± 0.0001 nm. It was a ferromagnet of Curie point 320 ± 5° C and its magnetization at − 150° C was equal to $2.8 \mu_B$/Mn.

4.1. The properties of the alloy aged at 360° C

Very weak X-ray lines of γ-Cu_9Al_4 and T-Cu_3Mn_2Al were only registered after 12 h of ageing while the precipitation of β-Mn was detected after 40 h. The X-ray lines of the β-phase disappeared after 220 h of ageing. The lattice parameter of the β-phase was constant during the whole process of its decomposition and was equal to 0.5961 ± 0.0001 nm. The lattice constants of γ-Cu_9Al_4, T-Cu_3Mn_2Al and β-Mn were equal to 0.8715 ± 0.0002 nm, 0.6903 ± 0.001 nm and 0.641 nm, respectively. The magnetometry indicated that during the process of the decomposition of the alloy its ferromagnetic properties and the Curie points were preserved. Only the magnitude of the magnetization was decreased, due to the loss of β-phase.

4.2. The properties of the alloy aged at 460° C

After 30 min of annealing the simultaneous precipitation of β-Mn and γ-Cu_9Al_4 was detected. The X-ray lines of the β-phase were considerably broadened. The magnetic properties of the alloy were also changed (see Fig. 1). On heating, the specimen showed an increase of the magnetization in the range of temperature from about 100° C up to 200° C. The anomaly was not observed when the sample was cooled. The Curie point recorded during the heating of the specimen was equal to 290 ± 5° C.

Further annealing caused an increase in the intensities of the X-ray lines of the β-Mn and γ-Cu_9Al_4 phases, the lattice parameters of which were equal to 0.640 nm and 0.8691 ± 0.0002 nm, respectively. Simultaneously, a new phase precipitated. Its structure was of the type $L2_1$ while the lattice parameter was smaller than the one of the initial β-phase and was equal to 0.5889 ± 0.0001 nm.

The X-ray lines of the new phase, referred to in this paper as the β_{II}-phase, were rapidly increased and at the same time, the Bragg reflections of the initial β-phase were decreased and disappeared after 4 h of annealing.

During the decomposition of the β-phase the magnetic properties of the alloy continued to change. The value of the Curie temperature and the magnetization were decreased. In the case of the magnetization the decrease was rapid (see Table I). The temperature dependence of the magnetization of the alloy after the decay of the initial β-phase is presented in Fig. 1c and d. It can be seen that the magnetization measured during the cooling was higher than that measured during the heating and its temperature dependence was typical of that for a ferromagnet. During further ageing the β-phase decomposed slowly and, after

TABLE I Magnetic properties of the alloy $Cu_{2.00}Mn_{1.00}Al_{1.00}$ aged isothermally at temperatures of 460° C and 560° C: T_c denotes the Curie temperature, M denotes the magnetization at temperature − 150° C. The errors of the values of T_c and M do not exceed 5° C and 0.1 μ_B/Mn, respectively

Annealing at 460° C			Annealing at 560° C		
Period of annealing	M (μ_B/Mn)	T_c (° C)	Period of annealing	M (μ_B/Mn)	T_c (° C)
30 min	2.1	283	5 min	1.7	295
1 h	1.5	288	10 min	1.1	277
1.5 h	1.2	269	15 min	0.9	269
2 h	0.7	263	30 min	0.8	274
4 h	0.6	261	8 h	0.7	271
16 h	0.4	260	240 h	0.8	272
40 h	0.4	260	1400 h	0.9	262
200 h	0.3	258			
700 h	0.1	250			

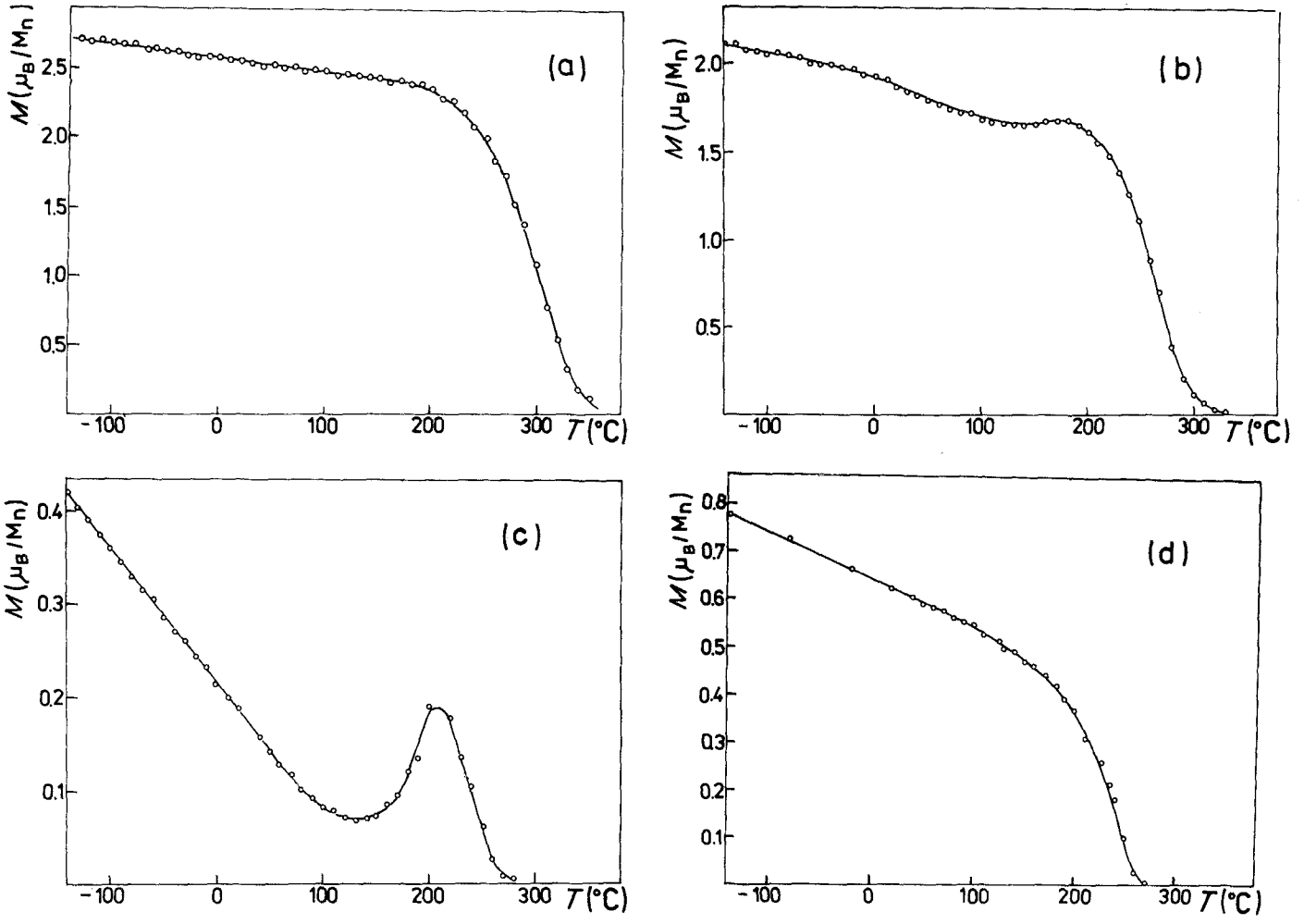

Figure 1 The temperature, T, dependence of the magnetization, M, of the alloy $Cu_{2.00}Mn_{1.00}Al_{1.00}$: (a) homogenized at 850° C, heated from — 150° C; (b) homogenized at 850° C and aged for 30 min at 460° C, heated from — 150° C; (c) homogenized at 850° C and aged for 40 h at 460° C, heated from — 150° C; (d) homogenized at 850° C and aged for 40 h at 460° C, cooled from 300° C.

ageing for 200 h, weak X-ray lines of the T-Cu_3Mn_2Al phase were detected. The magnetization and the Curie point were still slowly decreased. After two months of ageing the alloy contained only γ-Cu_9Al_4 phase, T-Cu_3Mn_2Al phases having a lattice parameter of 0.6903 ± 0.0002 nm, and β-Mn.

4.3. The properties of the alloy aged at 560° C

The precipitation of β-Mn was detected even after annealing for only 5 min. Its lattice constant was equal to 0.640 nm and its appearance was accompanied by the precipitation of the phase denoted as β_{III} of structure of the type $L2_1$ and of lattice constant equal to 0.5910 ± 0.0001 nm. The X-ray lines of the initial β-phase disappeared after only 15 min of ageing. The further decomposition of the alloy proceeded much more slowly than at 460° C and only after two months were very weak Bragg reflections of γ-Cu_9Al_4 registered. However, the X-ray lines of the β_{III}-phase were still intense.

The magnetic properties of the samples aged at 560° C were similar to those of the specimens aged at 460° C. Though the magnetization of the alloy was somewhat higher than in the preceeding case (see Table I) its temperature dependence showed the same anomalies as the specimen aged at 460° C.

4.4. The properties of the alloy aged at 460° C and 200° C

In order to explain the origin of the change of the magnetic properties of the alloy caused by the isothermal annealing one of the samples aged previously for 40 h at 460° C was additionally annealed for one week at 200° C. The latter ageing caused the restoration of the ferromagnetic properties of the alloy. No anomaly was observed in the temperature dependence of its magnetization which was considerably increased and finally reached 0.8 μ_B/Mn at − 150° C (before the annealing at 200° C the magnetization at − 150° C was equal to 0.4 μ_B/Mn). The Curie point was recorded at 270 ± 5° C. The X-ray diffraction measurement indicated that the ageing of the partially decomposed alloy at 200° C caused the precipitation of the phase with structure of the $L2_1$ type (see Fig. 2). The X-ray lines of that phase were strongly broadened and the precise measurement of its lattice parameter was impossible. However, its value estimated on the basis of the X-ray line (2 2 0) was about 0.597 nm and seemed to be higher than the value of the lattice parameter of the initial β-phase. The new phase was called the β_{IV}-phase. It always precipitated when the alloy was heated during the magneto-thermal measurements when the temperature reached 200° C. The relatively high magnetization of the β_{IV}-phase was the reson for the occurrence of the maximum of the magnetization of the specimens at that temperature. The fact that no anomaly was observed in the temperature dependence of the magnetization when the alloy was cooled indicated that the β_{IV}-phase was ferromagnetic.

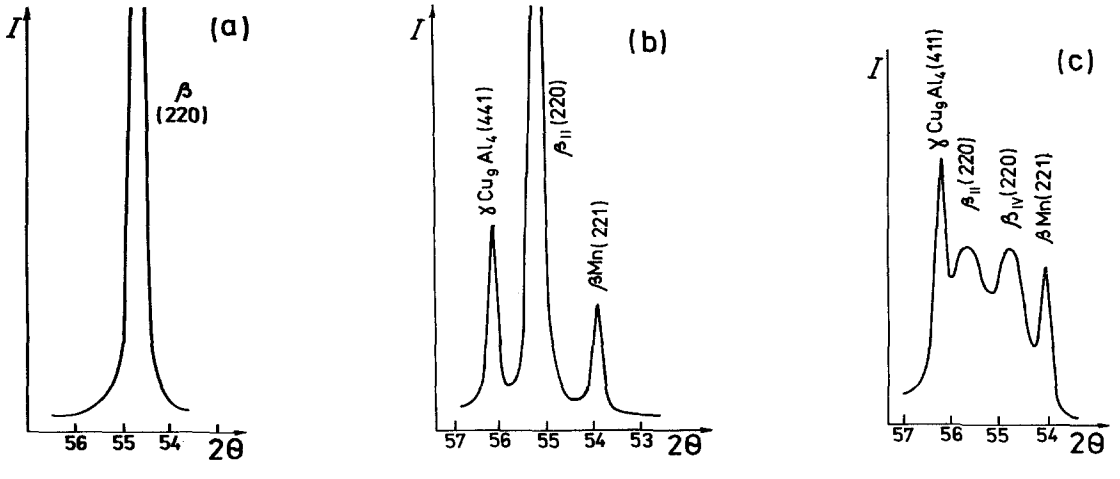

Figure 2 Fragments of the X-ray diffraction patterns of the specimens of the alloy $Cu_{2.00}Mn_{1.00}Al_{1.00}$: (a) homogenized at 850° C; (b) homogenized at 850° C and aged for 40 h at 460° C; (c) homogenized at 850° C, aged for 40 h at 460° C and aged for one week at 200° C. *I* denotes the diffraction intensity (arbitrary units) and 2θ is the diffraction angle.

5. Discussion

The systematic investigation of the decomposition of the alloy $Cu_{2.00}Mn_{1.00}Al_{1.00}$ showed that the process was quite different at different temperatures. From the study some observations could be made:

(a) The alloy aged at 360° C contained only one ferromagnetic phase while Dubois and Chevereau [17] reported the coexistence of two ferromagnetic phases in the alloy $Cu_2MnAl_{1.01}$ treated thermally in the same way. The products of the decomposition of the alloy researched in our group appeared in a different sequence. The simultaneous precipitation of the γ-Cu_9Al_4 and T-Cu_3Mn_2Al phases preceeded the appearance of β-Mn and the explanation of the process of the decomposition of the alloy Cu_2MnAl proposed by Dubois and Cheverau could not be applied to our results.

(b) The precipitation of β-Mn and γ-Cu_9Al_4 at 460° C and of β-Mn at 560° C did not cause the continuous decrease of the lattice constant of the β-phase, as has been recently suggested by Yamane *et al.* [18]. In fact, the appearance of these phases was accompanied by the precipitation of the β_{II}- and β_{III}-phases, the lattice parameters of which were constant during the whole further process of the decomposition of the alloy.

(c) The character of the decomposition of the alloy at 360° C differed considerably from the character of that process at 460° C and 560° C. It was evident that the presence or absence of the intermetallic compound T-Cu_3Mn_2Al was the most important factor controlling the progress of the process. At 360° C the decomposition of the β-phase led directly to the appearance of the phases of quite different structures. At 460° C and at 560° C, however, the β-phase preserved the structure and only its lattice parameter was varied due to the change of the composition caused by the precipitation of β-Mn and γ-Cu_9Al_4. The change of the composition of the β-phase was determined by the temperature of annealing and it was the origin of the appearance of the β_{II}- and β_{III}-phases. It was surprising that the intermetallic compound T-Cu_3Mn_2Al precipitated in the alloy at 460° C because the results of some experiments seemed to indicate that this phase appeared only at tempertures lowe than about 410° C [5, 18]. The following reaction, corresponding with the process of the decomposition of the alloy at 460° C, may be suggested:

$$\beta \rightarrow \beta_{II} + \gamma\text{-}Cu_9Al_4 + \beta\text{-Mn}. \qquad (1)$$
$$\downarrow$$
$$T\text{-}Cu_3Mn_2Al$$

It is then probable that the composition of the β_{II}-phase approximated Cu_3Mn_2Al. The further investigation of that problem is in progress using the technique of X-ray microanalysis.

(d) The investigation of the decomposition of the alloy at 560° C was made difficult because the process was not finished even after two months of annealing and it was not ascertained whether the β_{III}-phase was stable or unstable at that temperature.

(e) The occurrence of the ordering process in the alloy at temperatures lower than 250° C has been reported in some papers (see, for example, [1, 17]). However, it is interesting that the process was much more intensive in partially-decomposed alloys containing the phases β_{II} and β_{III} where the annealing at 200° C caused the precipitation of the strongly ferromagnetic β_{IV}-phase. The investigation of the character of the β_{IV}-phase may be an interesting problem. It should be emphasized that although the lattice constant of that phase approximated to that of the initial β-phase the difference between the Curie points of both phases was considerable and so there was no basis to identify one phase with another.

The main reason for the discrepancies between the results presented in this paper and those reported by other authors is probably that of the differences of the compositions of the researched specimens. This supposition may be confirmed by our observation; when treated thermally several times, the alloy changed its properties due to the evaporation of its components during the annealing. Even such a small deviation from the initial composition of the alloy influenced the progress of its decomposition.

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