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Decomposition of the Heusler alloy Cu_2MnAl at 360°C

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During thermomagnetic studies, the as-quenched Heusler alloy $Cu_{2.00}Mn_{1.00}Al_{1.01}$ exhibits two Curie temperatures θ_{C_I} and $\theta_{C_{II}}$. After 98 h at 360° C, above the Curie point, X-ray diffraction patterns indicate two ferromagnetic phases: Cu_2MnAl (I) with $a_I = 5.8707$ Å and $\theta_{C_I} = 151 \pm 10°$ C; Cu_2MnAl (II) with $a_{II} = 5.9656$ Å and $\theta_{C_{II}} = 332 \pm 4°$ C, whereas the 850° C as-quenched alloy exhibits $a = 5.9612$ Å and $\theta_C = 341 \pm 5°$ C.

The results are discussed in terms of the early stages of the decomposition of the Heusler phase. A mechanism, involving mainly the atomic migration of manganese, is suggested in order to reach the equilibrium phases of the ternary Cu–Mn–Al diagram. The kinetics of the decomposition should be ruled by the nucleation and the growth of the Cu_3Mn_2Al intermetallic compound.

1. Introduction

Several alloys with the approximate composition Cu_2MnAl (β-phase) have been prepared and studied in our research group [1, 2]. The β-phase of the Cu–Mn–Al equilibrium diagram does not exist at room temperature and the process of decomposition is not well known. No decomposition was found after 14 days at 200° C of the as-cast Cu_2MnAl alloys. A thermal treatment of 257 h at 350° C leads to the intermetallic compound Cu_3Mn_2Al, and the solid solutions Mnβ and Cu_9Al_4 (γ_2-phase). It is possible to restore the β-phase by reactions between these products [3, 4].

On the other hand, the as-quenched β-phase exhibits two ordering reactions. In the case of the compositions $Cu_{2.00}Mn_{0.93}Al_{0.92}$ and $Cu_{2.00}Mn_{1.00}Al_{1.01}$, we obtained the temperatures of the following transitions [3, 5]:

$T_1 = 620 \pm 20°$ C corresponding to the $L_{2_1} \rightarrow B_2$ transition

$T_2 = 785 \pm 5°$ C corresponding to the $B_2 \rightarrow A_2$ transition.

These results are in agreement with those of other authors [6–10]. In fact, it is established that quenched alloys from 800 to 850° C (A_2 structure) are already partially ordered [5, 6, 9, 11]. The size of the antiphase domain is about 500 Å [5]. After quenching from 850° C, we found an ordering process at about 200° C preceding the β-phase decomposition [5, 12].

In this paper, the decomposition of a 850° C as-quenched β-phase during annealing at 360° C is studied; at this temperature, the kinetics are not too rapid. The evolution of the Curie point during thermomagnetic measurements is particularly emphasized.

2. Experimental procedure

The alloys were prepared by direct melting and casting of pure copper (99.96%), aluminum (99.99%) and manganese (99.9%). The melting was carried out in a sintered alumina crucible heated at about 1400° C, in a high frequency furnace under a pure argon atmosphere. The composition was obtained by classical methods [1]. The results, corresponding to the alloy mainly studied in this work, are given in Table I. The manganese loss is less than 2% and the formula $Cu_{2.00}Mn_{1.00}Al_{1.01}$ was adopted.

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TABLE I Chemical analysis of the Heusler alloy studied in this work

Element	Before melting		After melting	
	wt%	at%	wt%	at%
Cu	59.64	48.77	61.1	49.9
Mn	27.06	25.69	26.5	24.9
Al	13.30	25.63	13.2	25.2

Structural changes were recorded by X-ray diffraction and optical microscopy for bulk specimens, after mechanical polishing and etching by a nitric solution of the chromium oxide CrO_3. Using different X-ray methods, and after corrections [2, 4], the lattice parameters of different Heusler alloys were determined on a 25 μm powder, after quenching from 850° C and tempering for 5 h at 200° C to achieve the most perfect ordering. We obtained the following:

$a = 5.9615 \pm 0.0003$ Å for $Cu_{2.00}Al_{0.93}Al_{0.98}$

$a = 5.9612$ Å for $Cu_{2.00}Mn_{1.00}Al_{1.0}$

The Curie temperatures were recorded on a thermomagnetic balance, while the powder was heated up to 400° C at a rate of about 100° C h^{-1}. We measured:

$\theta_C = 340 \pm 5°$ C for $Cu_{2.00}Mn_{1.00}Al_{1.07}$ quenched from 800° C

$\theta_C = 341 \pm 5°$ C for $Cu_{2.00}Mn_{1.00}Al_{1.01}$ quenched from 850° C.

Changes in the Curie point were found if the alloys were kept at higher temperatures [2, 3], but tempering before measurements also influenced the position of the Curie point. For example, in the case of the $Cu_{2.00}Mn_{1.00}Al_{1.01}$ alloy, the Curie point was $\theta_C = 341 \pm 5°$ C, after quenching from 850° C as measured while being heated to 400° C and cooled. If the alloy was tempered 24 h at 185° C before measurements, the Curie point was $\theta_C = 344 \pm 2°$ C; no important variations of the Curie point were detected when the tempering temperature was less than 360° C. After tempering at 370° C, two Curie points clearly appeared while heating up to 400° C and cooling:

$$\theta_{C_I} = 281 \pm 3° \text{ C}$$

$$\theta_{C_{II}} = 343 \pm 2° \text{ C}.$$

In the present study, the evolution of the Curie temperature, as a function of the tempering time at 360° C, is demonstrated and an interpretation of this phenomenon is given with respect to the structural evolution.

3. Results

After being held 30 min at 850° C, the powder was quenched in brine water. The appearance and the evolution of the two Curie points were recorded as a function of the tempering time at 360° C. Using X-ray diffraction, the structural modification of the alloy was recorded to explain the magnetic phenomena.

3.1. Thermomagnetic experiments

After tempering at 360 ± 3° C, the Curie points were recorded while heating (H) up to 400° C and cooling (C). The results shown in Fig. 1 are summarized in Table II.

Two ferromagnetic phases were considered to exist at 360° C when the tempering time was sufficient to obtain the beginning of the β-phase decomposition (between 48 and 72 h at 360° C). If the tempering time was more than 200 h, no Curie points between room temperature and 400° C were detected.

The room temperature equilibrium phases of the Heusler phase Cu_2MnAl are not ferromagnetic, so it is suggested that the two ferromagnetic phases, separated with the aid of a magnet, were transitional phases in the partial decomposition of Cu_2MnAl. X-ray diffraction experiments were carried out to determine the nature of these transitional phases.

3.2. X-ray diffraction results

After tempering at 360° C for 98 h, a precise X-ray study of the powder was undertaken. A transmission device with internal silicon reference in a

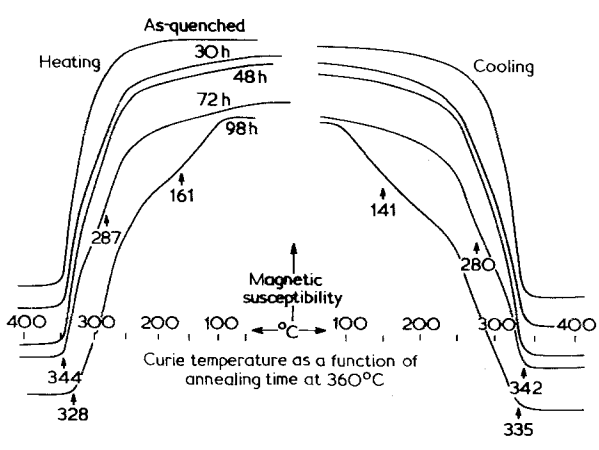

Figure 1 Results of thermomagnetic measurements.

TABLE II Curie temperatures of $Cu_{2.00}Mn_{1.00}Al_{1.01}$ aged at 360° C

Tempering time at 360° C (h)	Curie temperature (° C)
30	$\theta_C = 346$
48	$\theta_C = 342 \pm 2$
72	$\theta_{C_I} = 343 \pm 1$ $\theta_{C_{II}} = 287$ (H) and 280 (C)
98	$\theta_{C_I} = 332 \pm 4$ $\theta_{C_{II}} = 161$ (H) and 141 (C)

focusing camera was used. The precision was between 5×10^{-4} and 10^{-3} Å and errors were minimized. The results are shown in Table III.

It is interesting to compare the lattice parameters of Cu_9Al_4 (γ_2-phase), Cu_3Mn_2Al and Mnβ with those obtained from the complete decomposition of $Cu_{2.00}Mn_{1.00}Al_{1.01}$ by a thermal treatment of the cast alloy during 257 h at 350° C. From previous work [2, 4], the values are the following:

$a = 8.729$ Å for Cu_9Al_4 (γ_2 phase)

$a = 6.918$ Å for Cu_3Mn_2Al

$a = 6.47$ Å for Mnβ.

After 98 h at 360° C, the lattice parameters of Cu_9Al_4 (γ_2-phase) and Cu_3Mn_2Al were very near to those after complete decomposition at 350° C. The lattice parameter of the Mnβ-phase was very different in the two experiments; it was higher than the value $a = 6.316$ Å usually recognized.

The lattice parameters of the two ferromagnetic phases were very different but we noticed that the Cu_2MnAl (II) parameter was not far from the initial value of the as-quenched alloy ($a = 5.9612$ Å).

There was some doubt on 4 lines of the X-ray diagram of the powder tempered 98 h at 360° C; it could be manganese oxide or some other product.

Another set of experiments dealt with the more precise influence of the tempering time on the appearance of the new phases. The same alloy was quenched in brine water after 2 h at 850° C. After 1 h at 360° C and quenching from this temperature, a weak splitting of the (4 0 0), (4 3 2) (4 4 0) lines led to two possible parameters $a_I = 5.96$ Å and $a_{II} = 5.97$ Å. The splitting is very marked after 44 h at 360° C: $a_I = 5.88$ Å and $a_{II} = 5.96$ Å. Two different Curie temperatures appeared clearly after 72 h (Table II). It is possible to detect the two ferromagnetic products after 98 and 141 h but not after 382 h at 360° C.

The beginning of the appearance of the Mnβ and Cu_9Al_4 (γ_2) phases are difficult to detect. The interaction of the precipitation with the ordering process at low temperature has been already observed [12, 24]. It seems that the quenching process must be carefully controlled. The presence of these two phases after an hour at 360° C is not certain but they are clearly detected after 44 h at 360° C. We are not absolutely sure of the simultaneous appearance of these two phases; on a $Cu_{2.00}Mn_{0.90}Al_{0.7}$ alloy, the Mnβ-phase was detected after an hour at 345° C and the Cu_9Al_4 (γ_2) phase only after an hour at 420° C on the same bulk sample [12]. However the kinetics of the formation of the γ_2-phase is supposed faster than those of the Mnβ-phase [2]. We assumed that these two phases were appearing after 44 h at 360° C, at the same time that the two ferromagnetic phases were clearly detected.

The intermetallic compound Cu_3Mn_2Al was obtained after 98 h at 360° C but it may be possible to find it after 72 h at 360° C. At this time, the two Curie points were clearly recorded. As the annealing time increases, it seems that the lattice parameter of Cu_3Mn_2Al becomes higher. We found $a = 6.93$ Å after 141 h at 360° C and $a = 6.94$ Å after 382 h in the second set of experiments.

The optical micrography of a 850° C as-quenched bulk sample, with the approximate composition Cu_2MnAl, showed the beginning of the precipitation between 350° C and 400° C

TABLE III Lattice parameters of the phases obtained after 98 h at 360° C

Ferromagnetic phases
Cu_2MnAl (I) $a_I = 5.8707 \pm 0.0026$ Å associated with $\theta_{C_I} = 151 \pm 10$° C
Cu_2MnAl (II) $a_{II} = 5.9656 \pm 0.0012$ Å associated with $\theta_{C_{II}} = 332 \pm 4$° C

Other phases	Present results	[9, 13–15]
Cu_9Al_4 (γ_2 phase)	$a = 8.7166 \pm 0.0008$ Å	$a = 8.7052 \pm 0.0011$ Å $a = 8.7068 \pm 0.0003$ Å
Cu_3Mn_2Al	$a = 6.9108 \pm 0.0012$ Å	$a = 6.9046$ Å
Mnβ	$a = 6.3964 \pm 0.0007$ Å	$a = 6.260$–6.316 Å

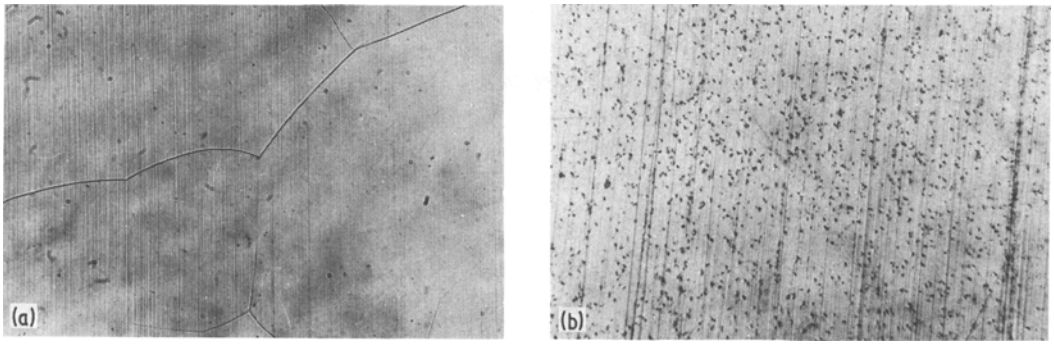

Figure 2 Bulk sample of 850° C as-quenched $Cu_2Mn_{0.9}Al_{0.81}$ (a) tempered 1 h at 350° C (× 290); (b) tempered 1 h at 400° C (× 290).

(Figs. 2a and b). On this sample, an X-ray diffraction pattern indicated the presence of the Mn β-phase after annealing an hour at 400° C.

Finally, on a 850° C as-quenched $Cu_{2.00}Mn_{1.00}Al_{1.01}$ alloy, we found: (i) two ferromagnetic phases Cu_2MnAl (I) and (II) and the non-ferromagnetic phases Mn β and Cu_9Al_4 (γ_2) after 44 h at 360° C; (ii) the intermetallic compound Cu_3Mn_2Al after 72 h at 360° C; (iii) the disappearance of the two ferromagnetic phases between 141 and 382 h at 360° C. In fact these phases were not detected after 257 h at 350° C [2].

4. Discussion

The equilibrium products of the decomposition of the Heusler phase (β-Cu_2MnAl phase) are approximatively the same at room temperature and at 400 to 410° C [16, 17]. We have selected the 410° C isothermal section [17] for comparison with the results obtained at 360° C (Fig. 3). This annealing temperature was chosen to avoid too rapid or too low decomposition kinetics, but it is difficult to predict the time necessary to reach the thermodynamic equilibrium.

We have assumed the following model for the tempering of the as-quenched Cu_2MnAl alloy. Up to 250° C, an ordering process occurs [5]. At 290° C, an increasing of the antiphase domain size and a decrease in the interaction between magnetic domain walls and antiphase boundaries was detected [18]. After 10 h at between 300 and 350° C, there was no precipitation [19] but the numerous dislocations and the point contrast at antiphase boundaries were related to vacancies [20]. It was thought that the low temperature phase decomposition was more difficult than in a non-stoichiometric alloy [21]. Theoretical work in this field is in progress in relation to our experiments [35]. It would be interesting also to compare the ageing of a stoichiometric alloy exactly at the Curie temperature and just below, as studied in the case of Fe–Si alloys [22].

In this study, we have assumed only a migration of manganese atoms occurring at 360° C. This agrees with the fact that the as-quenched alloy presents a partial disorder involving 20% of manganese atoms [9]. X-ray diffraction analysis has shown that the lattice parameter of the Cu_2

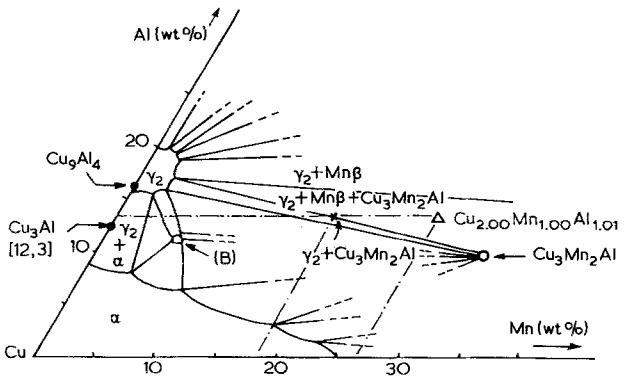

Figure 3 Isothermal section of the Cu–Mn–Al equilibrium diagram at 410° C [17]. B is the composition of the β Heusler phase just before disappearance during cooling.

MnAl (I) alloy was decreasing from 5.96 Å to 5.87 Å during annealing at 360° C. This fact can be interpreted as a tendency towards the parameter $a = 5.84$ Å of the ordered β-phase (Cu_3Al) of the Cu–Al equilibrium diagram [15]. A part of the initial Heusler phase (L_{2_1} structure) of the as-quenched $Cu_{2.00}Mn_{1.00}Al_{1.01}$ alloy gives rise to a solid solution of manganese in the β-phase (Cu_3Al) of the Cu–Al diagram with the DO_3 or DO_{22} structure. Almost at the same time, the Mn β-phase (indicating the manganese migration) and the Cu_9Al_4 (γ_2) phase were appearing. The other part of the Heusler alloy kept the L_{2_1} structure. A quantitative study of the X-ray intensities was not carried out but no significant changes were observed in the relative intensities of the split X-ray lines of the Heusler phase. After a long time at 360° C, there was a simultaneous disappearance of all the split lines. We did not detect the L_{10} structure indicated by Bouchard and Thomas [23] due to the fact that the 360° C temperature was just above the miscibility gap that they found.

The assumption of no significant aluminium movement is supported by the thermomagnetic results. A classical reference [25] enables us to estimate the changes in the chemical composition of the Cu_2MnAl (I) phase from the variation of the Curie temperature. After 72 h at 360° C, we determined $\theta_{C_I} = 284 \pm 4°$ C and the Heusler's curve [25] yields the composition $Cu_2Mn_{0.64}Al_{0.86}$ (with about 19% in weight of manganese). After 98 h at 360° C, the Curie point $\theta_{C_I} = 150 \pm 10°$ C and the composition would be $Cu_2Mn_{0.48}Al_{0.82}$ (with about 15% in weight of manganese).

These results are in agreement with the assumption that about 19% of mananese in weight is necessary to obtain good ferromagnetic properties of the Heusler alloy of the approximate composition Cu_2MnAl at room temperature [26, 27].

We have devised a model of the decomposition of the Heusler phase at 360° C. In the first stage (about 44 h at 360° C) the decomposition of the 850° C as-quenched $Cu_{2.00}Mn_{1.00}Al_{1.01}$ alloy gives rise to the following phases: Cu_2MnAl (I) and Cu_2MnAl (II); Mn β and Cu_9Al_4 (γ_2). The decreasing of the parameter and of the Curie point of Cu_2MnAl (I) with the annealing time must be related to the migration of manganese atoms in this part of the alloy. The detection of manganese as the Mn β-phase is easy and has been already reported [17, 31]. However the parameter of this Mn β-phase is difficult to obtain in a reproducible way.

The appearance of Cu_9Al_4 (γ_2) is more difficult to explain (Fig. 3). It is noticeable that the parameter of the γ_2-phase is almost 1.5 times those of Cu_2MnAl (I) after 98 h at 360° C. But, even if the Cu_2MnAl (I) phase has the DO_3 or DO_{22} structure, the superlattice X-ray lines (1 1 1) (3 1 1) are always observed even after 141 h at 360° C. These lines are also detected in the Cu_2MnAl (II) phase. This observation is in agreement with results on Cu–Al–Ni alloys [28]: it is not sure that the B_2 structure aids the nucleation of the γ_2-phase. The γ_2-phase in ternary alloys is certainly a distorted γ-brass structure, always difficult to study [14, 29, 30]. For the appearance of this γ_2-phase, we can only suggest that the reaction already indicated [2]

$$\underset{\text{(as-quenched Heusler phase)}}{Cu_2MnAl} \longrightarrow Cu_9Al_4 + Mn\,\beta \qquad (1)$$

was occurring simultaneously with the formation of Cu_2MnAl (I).

In later stages, when the manganese content reaches 15% (for example in Cu_2MnAl (I) after 98 h at 360° C), Fig. 3 shows the possibility of the reaction

$$Cu_2MnAl\ (I) \longrightarrow Cu_9Al_4\ (\gamma_2) + Cu_3Mn_2Al. \qquad (2)$$

The evolution towards the β-phase (Cu_3Al) of the Cu-Al diagram should be stopped by this reaction.

In the case of the Cu_2MnAl (II) phase, we detected only weak variations of the parameter and a 10° C decreasing of the Curie temperature during annealing at 360° C. The disappearance of the Heusler phase (approximately Cu_2MnAl) has been suggested [17] as a reaction with the Mn β-phase following

$$\underset{\text{(particular composition of the Heusler alloy)}}{Cu_2MnAl + Mn\,\beta} \longrightarrow Cu_9Al_4\ (\gamma_2) + Cu_3Mn_2Al \qquad (3)$$

The intermetallic compound Cu_3Mn_2Al is not far from the stoichiometric composition, the γ_2-phase is a solid solution containing 5% of manganese, and the Mn β-phase is probably a solid solution of 11% aluminum and 1.5% copper [17].

It is possible to consider this reaction for the disappearance of Cu_2MnAl (II) between 98 h and 257 h at 360° C.

$$Cu_2MnAl\ (II) + Mn\,\beta \longrightarrow Cu_9Al_4\ (\gamma_2) + Cu_3Mn_2Al. \qquad (4)$$

The Mn β-phase would be provided by the evolution of the Cu_2MnAl (I). Other reactions can be considered, such as Reaction 1, depending on the Heusler phase composition.

However, considering the simplified Reactions 3 to 5 we have thought that the Heusler phase decomposition is controlled by the formation of the intermetallic compound Cu_3Mn_2Al. This phase appears after 72 h at 360° C and the previous reactions are certainly complete between 141 and 382 h at 360° C. According to the equilibrium diagram, there is an excess of the Mn β-phase.

In any case, the possible reactions giving the equilibrium phases of the decomposition of Cu_2MnAl are related to the proportion of Mn β-phase and we were not able to detect the fluctuations of these phases. We have studied the possibilities of other phase transformations. A diffusionless transformation [32] requires a lower manganese content. The transitional μ-phase (approximatively Cu_4Al) with a β manganese structure and a parameter $a = 6.260$ Å [33] is possible. We detected neither this phase, nor the α-phase from the peritectoidal reaction of the Cu–Al equilibrium diagram [34, 36]. In our opinion, it would be interesting to measure the manganese diffusion, using, for example a radioactive tracer, but also to determine perfectly the composition and the structure of the phases which appear at every stage of the decomposition.

5. Conclusions

The decomposition of the 850° C as-quenched Heusler alloy $Cu_{2.00}Mn_{1.00}Al_{1.01}$ was studied at 360° C. The investigations were carried out with X-ray diffraction and thermomagnetic measurements. These methods were found convenient to investigate the stages of the decomposition of the Heusler alloy.

After 44 h at 360° C, two ferromagnetic Heusler phases clearly appeared beside the Mn β and Cu_9Al_4 (γ_2) phases. After 98 h at 360° C, the characteristics of the ferromagnetic phases are:

$$\text{Cu}_2\text{MnAl (I)} \quad \begin{cases} a = 5.8707\ \text{Å}; \\ \theta_{C_I} = 151 + 10^\circ\ \text{C} \end{cases}$$

$$\text{Cu}_2\text{MnAl (II)} \quad \begin{cases} a = 5.9656\ \text{Å}; \\ \theta_{C_{II}} = 332 + 4^\circ\ \text{C}, \end{cases}$$

where θ_C is the Curie point.

The formation of the Cu_2MnAl (I) phase is closely related to the loss of manganese during annealing as indicated by the decrease of the Curie point and of the parameter. The evolution towards the β-phase (Cu_3Al) of the Cu–Al equilibrium diagram was stopped by the nucleation and the growth of the Cu_3Mn_2Al intermetallic compound.

It is noticeable that the detection of Cu_3Mn_2Al phase is simultaneous with two well-separated Curie points corresponding to Cu_2MnAl (I) and Cu_2MnAl (II) phases.

The parameter and the Curie point of the Cu_2MnAl (II) phase are not much modified until the quantity of the Mn β-phase, provided by the formation of Cu_2MnAl (I), was sufficient to give rise to the Cu_3Mn_2Al intermetallic compound by reaction with Cu_2MnAl (I). At this stage the Curie point of Cu_2MnAl (I) is decreasing.

The nucleation, growth and complete formation of Cu_3Mn_2Al are certainly the phenomena controlling the decomposition of the Heusler phase, particularly in the later stages. This is the explanation of the simultaneous disappearance of the Cu_2MnAl (I) and Cu_2MnAl (II) between 141 and 257 h at 360° C.

It is also noticeable that the parameters of the phases which appear during the decomposition are not far from those given in the literature, whereas the lattice parameter of the Mn γ-phase is always difficult to obtain in a reproducible way. Therefore a knowledge of the migration of manganese would be the main factor necessary to explain the decomposition of the Heusler phase at 360° C.

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