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Ordering and stabilization in quenched CuAlNiMnB alloys

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The ordering and stabilization behaviour of a set of CuAlNi alloys with manganese and boron additions have been studied. Specimens were subjected to different thermal treatments, mostly consisting of a direct quench into martensite from different temperatures. The transformation was studied by differential scanning calorimetry, and X-ray diffraction was also used to check the martensite and parent phase structures. According to the results, the first reverse transformation after quenching into martensite stems from two competitive processes, namely the stabilization of the martensite and a decrease of the transformation temperatures due to quenched disorder. The temperature from which the quench is performed is the critical parameter determining whether stabilization or disorder suppression predominates. The degree of stabilization increases with the manganese content.

1. Introduction

CuAlNi alloys are more stable at high temperatures than CuZnAl alloys, raising the upper limit of operation for shape-memory devices to about 200 °C [1]. However, they are difficult to process because of grain coarsening and precipitation of the brittle γ_2 phase. In the recent years, research work has been carried out to improve the mechanical properties of CuAlNi shape-memory alloys. In this sense, reducing the aluminium content to below 14 at % results in remarkable improvement of the deformation capability, owing to the supression of the γ_2 precipitation; the transformation temperatures are largely raised upon reduction of the aluminium content, and they can be lowered by increasing the nickel content or adding other components such as manganese, which increases the stability of the β-phase [1]. The mechanical properties can be further improved as a result of grain refinement achieved through titanium or boron additions [1, 2]. In this way, several four- or five-component CuAlNi-based alloys have been developed, which show not only improved ductility but also a very good thermal stability at temperatures as high as 200 °C.

As usual for copper-based alloys, the characteristics of the martensitic transformation undergone by such alloys are strongly dependent on the previous thermal treatment. In fact, several alloys belonging to the CuAlNi system (such as CuAlNiTi or CuAlNiMnTi) show an anomalous first reverse transformation after a direct quench into martensite from the β-stability region [3, 4]. It is well known that a quench into martensite and/or ageing in the martensitic condition can stabilize the martensite with respect to the parent phase raising appreciably the reverse transformation temperatures. Martensite stabilization is claimed to be related to a thermally activated process which is enhanced by the presence of any quenched-in vacancies [5]. The interpretations given in the literature of this phenomenon can be broadly divided into two groups [6]: one in which configurational changes occurring in the martensite during ageing are held responsible [7, 8], and the other in which strain energy changes near martensite/parent and martensite/martensite interfaces and defects (commonly referred to as "pinning") are considered to be the cause of stabilization [9]. Nevertheless, the CuAlNi system has been found to be less prone to stabilization than CuZnAl [1].

In this work the first and following reverse martensitic transformations after different thermal treatments have been investigated for a series of CuAlNiMnB alloys, and the characteristics and origin of the anomalous first reverse transformation are discussed.

2. Experimental procedure

Commercially hot-extruded bars with the composition given in Table I were used. All the alloys studied have nominal transformation temperatures around 100 °C and are fully in the martensitic phase at room temperature. Most of the performed thermal treatments consisted of a quench from 800 °C, where the samples are kept for 30 min, into water at room temperature, followed by 5 min ageing in a melted salt bath maintained at different T_q temperatures ranging between 300 and 700 °C and another water quench. Other heat treatments, such as air-cooling from 800 °C and step-quenching from 800 °C to 100 °C followed either by air cooling or by water quenching to room temperature, were also performed in order to obtain additional information.

The martensitic transformation was followed by means of differential scanning calorimetry (DSC) in

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TABLE I Composition (at %) of the studied alloys

Alloy	Cu	Al	Ni	Mn	B
1	70.2	24.9	2.9	2.0	0.15
2	70.0	23.9	2.9	3.1	0.15
3	69.7	26.0	4.1	0	0.20

a Perkin–Elmer DSC-4. The experiments were performed using disc-shaped samples of 6 mm diameter and about 2 mm thickness cut from the original bars. At least two thermal cycles performed between 40 and 200 °C at a temperature rate of 10 K min^{-1} were recorded after each thermal treatment.

The structures of both the martensite and the β phase were analysed by X-ray diffraction performed in a Siemens D-5000 powder diffractometer equipped with high temperature chamber. Usually the 2θ range from 20°–80 ° was scanned. The same technique was used to investigate the ordered structures and critical ordering temperatures for the different alloys. The samples used for X-ray experiments were cut to a prismatic shape of about 6 × 15 mm^2 and 1 mm thickness.

3. Results

3.1. Calorimetric results

After water quenching from 800 °C, alloys 1 and 2 show a first reverse transformation peak with different characteristics from the second and subsequent ones, as can be seen in Fig. 1, which shows the DSC curves obtained for a sample of alloy 1 during two thermal cycles performed between 40 and 200 °C. The first reverse transformation peak occurs at higher temperatures and it spreads over a broader temperature range than the following ones, which are almost coincident with each other, as also happens for the forward transformation peaks (therefore, we consider them to be "stable"). As mentioned above, the same behaviour is found for alloy 2, although in that case the shift and broadness of the first reverse transformation peak are more pronounced. In Fig. 1 the temperatures corresponding to the maximum (minimum) of the reverse (forward) transformation peaks are labelled with the names that will be used hereafter.

Fig. 2a and b show the calorimetric response of alloys 1 and 2, respectively, submitted to a series of thermal treatments consisting of water quenching from 800 °C followed by 5 min ageing at different T_q, and another water quench. It can be seen there that for decreasing T_q the first reverse transformation peak approaches, both in position and shape, the following reverse transformation peaks, and below a certain temperature it appears at lower temperatures than subsequent reverse transformation peaks, remaining for alloy 1 as sharp as they were initially, while for alloy 2 the first reverse transformation remains broader even for $T_q = 300$ °C. This evolution of the relative position of the heating peaks is accompanied by changes in the transformation temperatures of the "stable" forward and reverse transformations. The evolution with T_q of the shift of the first reverse transformation, evaluated as the difference between the peak temperatures of the first and second heating runs ($A_1 - A_2$), and the "stable" transformation temperatures as represented by the second heating and the cooling peak temperatures (A_2 and M, respectively) are shown in Fig. 3 for alloys 1(a) and 2(b).

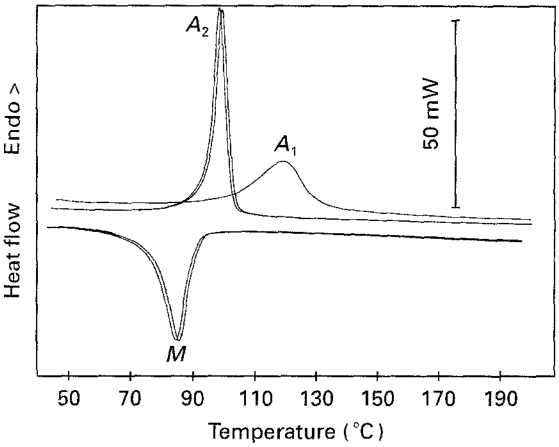

Figure 1 DSC curves obtained for alloy 1 during two thermal cycles performed between 40 and 200 °C. The temperatures corresponding to the maximum (minimum) of the reverse (forward) transformation peaks are labelled A_1, A_2 for the first and second reverse transformations, respectively, and M for the forward transformation.

After air cooling alloys 1 and 2 from 800 °C to room temperature, no differences between the first and following reverse transformation peaks measured by means of DSC are observed. Similarly, no peak shift occurs for alloy 1 step-quenched from 800 °C to 100 °C followed by air cooling to room temperature. However, if step-quenching is followed by water quenching to room temperature, a positive or no shift of the first reverse transformation peak with respect to the following ones takes place depending on the time spent at 100 °C: a positive shift occurs for very short times (up to 30 s) while no shift is observed for longer times. These results suggest that the observed changes from the first to the following reverse transformation peaks could be due to ageing above A_f. To elucidate this point, the calorimetric measurements were repeated for some T_q temperatures, but the first heating run was stopped as soon as the reverse transformation was completed, and subsequent cooling was performed at a faster rate of 40 K min^{-1} in order to reduce as much as possible the ageing time in the β condition. The second heating run (as well as further cycling) was performed at the usual rate of 10 K min^{-1} until 200 °C, where the samples were kept for 5 min. The corresponding DSC curves for alloy 1 and several T_q are plotted in Fig. 4, showing that, except for the lowest T_q, the shift of the first reverse transformation peak as shown in Figs 1–3 is actually composed of two opposite shifts: a temperature decrease which occurs for very short ageing times and a temperature increase which takes place for longer ageing time in the β condition. Alloy 2 shows the same qualitative behaviour for the same T_q temperatures.

At variance with the results obtained for alloys 1 and 2, alloy 3 (which does not contain manganese)

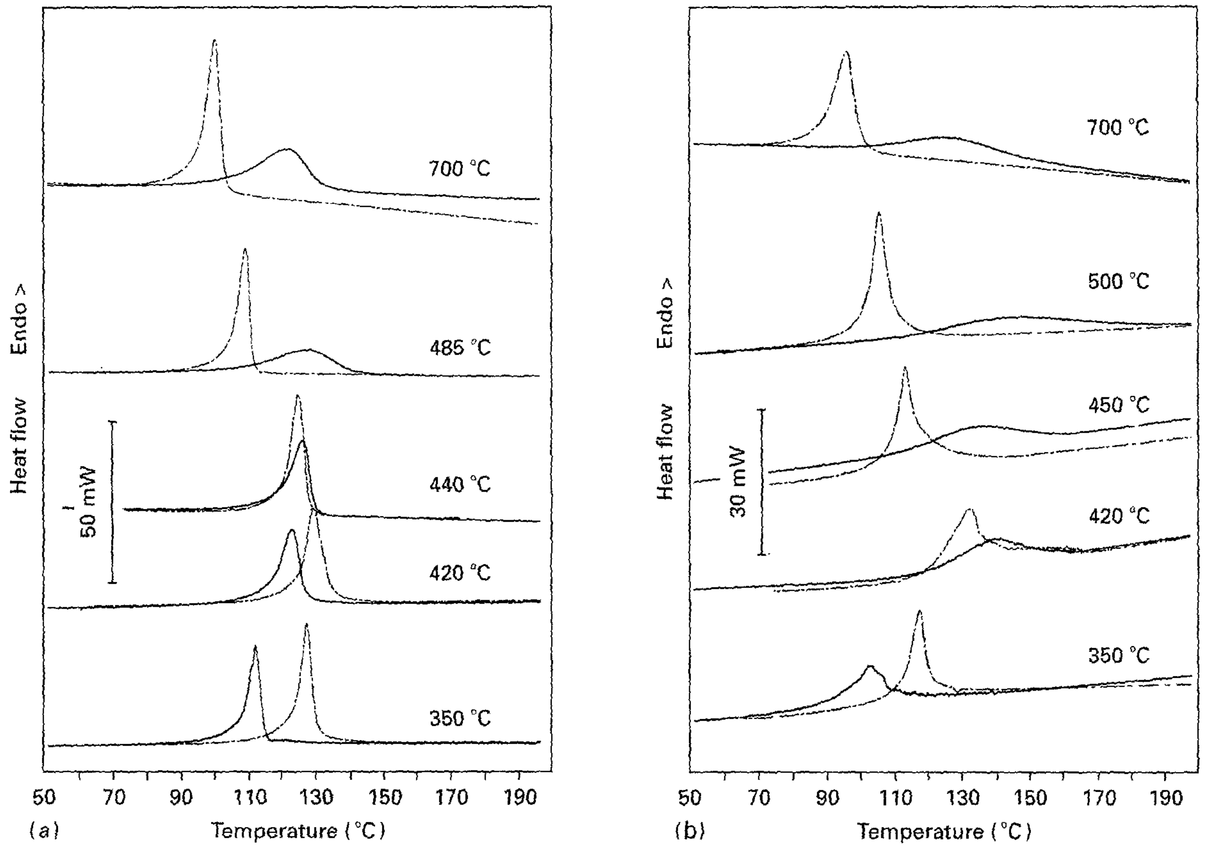

Figure 2 DSC curves measured during (——) the first and (- - -) second reverse transformations undergone by alloys 1(a) and 2(b) after water quenching from 800 °C followed by 5 min ageing at different T_q and another water quench (T_q is indicated over the corresponding curves).

does not show, at any instance, the mentioned characteristics of the first reverse transformation peak. This can be seen in Fig. 5 where the DSC curves obtained for samples of alloy 3, either water quenched from 800 °C or submitted to water quenching from 800 °C, followed by another water quench after 5 min ageing at 500 and 350 °C, are shown. Fig. 6 shows the evolution with T_q of the peak temperature difference ($A_1 - A_2$) and the "stable" transformation temperatures represented by A_2 and M. Similar experiments to those explained above to show the role of ageing above A_f were performed, always resulting in a monotonic increase of the peak temperatures with increasing ageing time, regardless of T_q.

3.2. X-ray diffraction results

Two main tests were performed on samples of the studied alloys.

1. The structure of the martensite was analysed at room temperature after a water quench from 800 °C (in the state previous to the first reverse transformation) and after one heating and cooling run (that is, in the state previous to the second reverse transformation). The heating and cooling runs were performed *in situ* in the X-ray chamber. For the three studied alloys, the martensite had M18R structure, and no differences could be observed in peak positions when the as-treated and cycled martensites were compared. As a consequence, neither the lattice parameters of the monoclinic cell, nor other parameters, such as the splitting parameter, or the deviation from the regular hexagonal arrangement of the basal plane, were found to vary from one to the other state. The structure of the martensite was also analysed after some thermal cycles, and did not show any change.

The structure of the β phase was checked at 200 °C during the same experiments, the peaks of the ordered $L2_1$ structure [10] being observed for the three alloys. No diffraction peaks corresponding to other phases such as α or γ were observed in any of the samples.

2. The ordering behaviour of the alloys was also investigated by analysing the diffraction peaks which appear on cooling from 850 °C to 200 °C. The results indicated that the manganese-containing alloys 1 and 2 undergo well-separated B2 and $L2_1$ transitions, while in the case of alloy 3 the peaks corresponding to B2 and $L2_1$ order appear almost simultaneously. The critical ordering temperatures for the studied alloys are given in Table II within an uncertainty of ± 10 °C. It is interesting to point out that the $L2_1$ transition was also checked by means of DSC, the results being in complete agreement with those obtained by X-ray diffraction.

4. Discussion

4.1. Shift of the first reverse transformation

From the results presented above, it can be established that for the manganese-bearing alloys directly quenched into martensite from a range of T_q, a competition between two processes giving rise to opposite temperature shifts takes place. Both effects decay during ageing in the β condition, but at different time

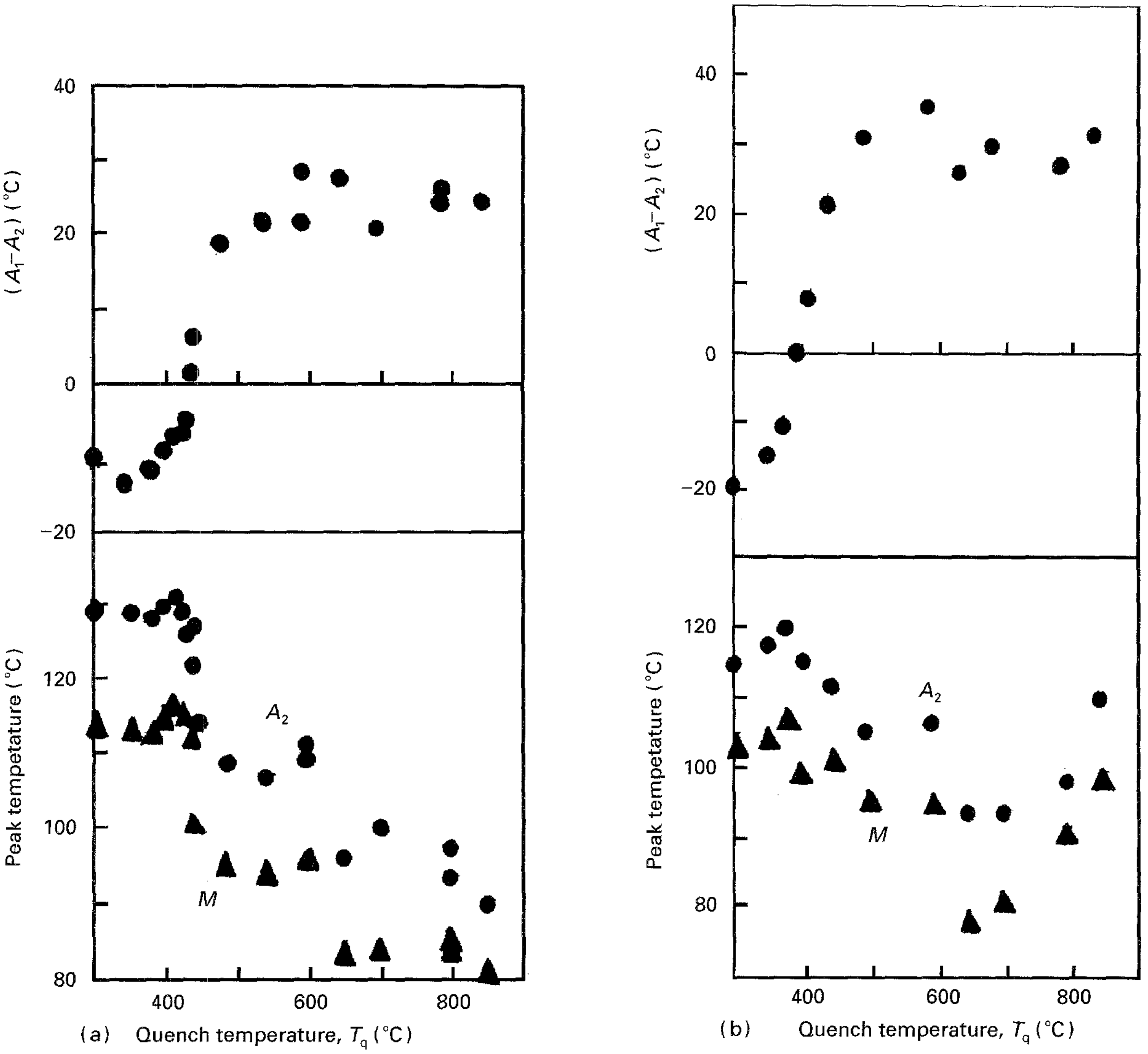

Figure 3 Evolution with T_q of the difference between peak temperatures of the first and second heating runs ($A_1 - A_2$) and the "stable" transformation temperatures as represented by the second heating and the cooling peak temperatures (A_2 and M, respectively) for alloys 1(a) and 2(b).

scales: decrease of the transformation temperatures occurs for short and further increase for longer ageing time. Although the ordering behaviour of CuAlNiMn alloys is not yet known in detail, it can be established that $L2_1$ disorder causes the transformation temperatures to decrease [11], as also happens for CuAlNi alloys [12]. Therefore, the increasing transformation temperature stage can be attributed to progressive $L2_1$ ordering, while the former decrease remains to be clarified. Concerning this aspect, it was speculated whether a certain degree of quenched B2 disorder could cause a positive shift of the first reverse transformation, but comparison between the peak temperature shifts shown in Fig. 3 and the B2 ordering temperatures given in Table II shows that quenching from above the critical B2 ordering temperature does not produce a higher ($A_1 - A_2$) difference. Therefore, quenched-in first neighbours disorder cannot be held directly responsible for the increase of the first reverse transformation, and stabilization of the martensite is considered to be the cause.

The position of the first reverse transformation peak has to be considered as a result of both an increase of the reverse transformation temperatures due to the stabilization of the martensite and a suppression of the transformation temperatures due to quenched-in $L2_1$ disorder. If A_1 is the peak temperature of the first reverse transformation and A_2 the "stable" reverse transformation peak temperature (as measured after 5 min at 200 °C), then

$$A_1 = A_2 + \Delta A - \delta A \qquad (1)$$

where ΔA and δA ($\Delta A > 0$ and $\delta A > 0$) are the stabilization and the suppression temperature shifts, respectively. It is desirable to have quantitative knowledge of ΔA and δA, but this becomes a difficult task considering that ΔA depends on T_q (as it can be concluded from Fig. 3) as also does δA, because the state of order inherited by the martensite after the quench depends on this temperature. Owing to the lack of knowledge about the ageing behaviour of the studied alloys, only a rough estimation of δA, based on experiments such as those presented in Fig. 4, can be made, leading to values of 10–15K for the investigated T_q. According to this, the degree of stabilization, ΔA, can be approached by raising 10–15 K the difference ($A_1 - A_2$) shown in Fig. 3a and b.

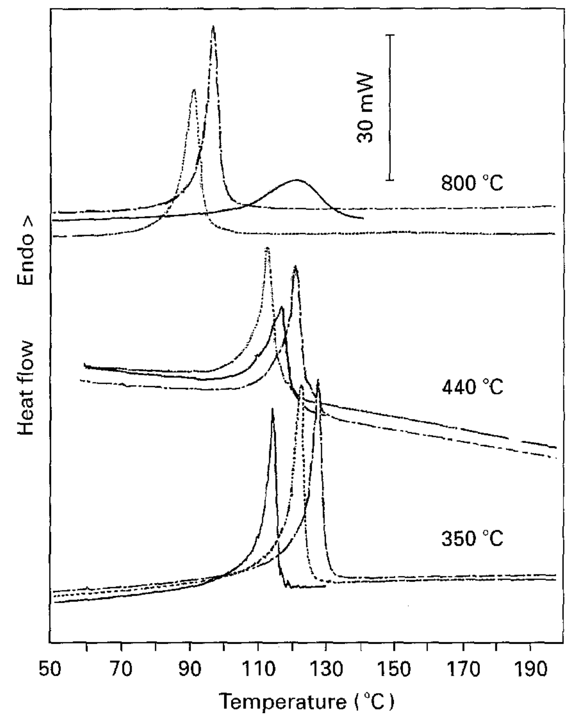

Figure 4 DSC curves measured during (——) the first, (···) second and (- - -) third reverse transformations undergone by alloy 1 after water quenching from the indicated T_q. The first heating run corresponds to zero ageing time, the second to short and the third to longer ageing times in β. See text for details.

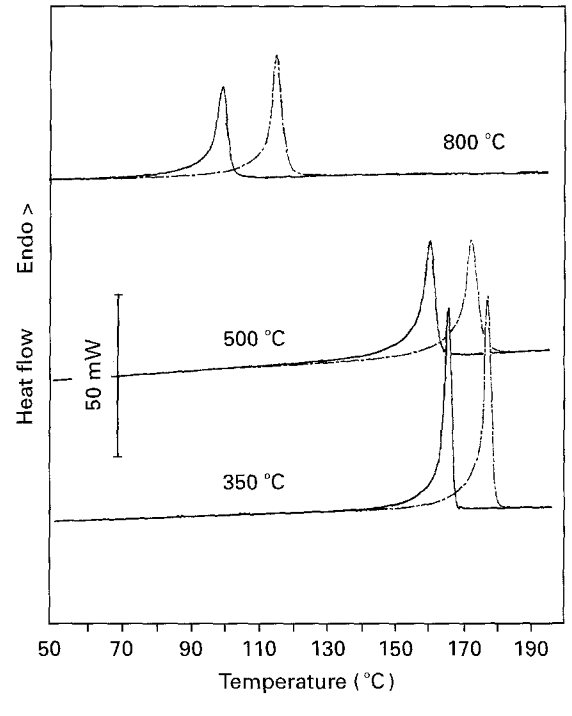

Figure 5 DSC curves measured during (——) the first and (- - -) second reverse transformations undergone by alloy 3 water quenched from 800 °C and submitted to water quenching from 800 °C followed by another water quench after 5 min ageing at T_q = 500 and 350 °C.

4.2. Origin of the stabilization

To help in understanding the origin of the observed stabilization, some of its characteristics must be taken into account. First, the stabilization seems to be due to the quench itself, and not to ageing in the martensitic condition. In fact, according to the mass of the data, the degree of stabilization, ΔA, does not depend on the time spent in martensite after the quench. It has been also observed that the studied alloys are not prone to stabilization by ageing in martensite, because specimens either air cooled from 800 °C or after removing the stabilization produced by a quench, were maintained for several months in martensite at 60 °C and they hardly showed a 2–3 K stabilization shift.

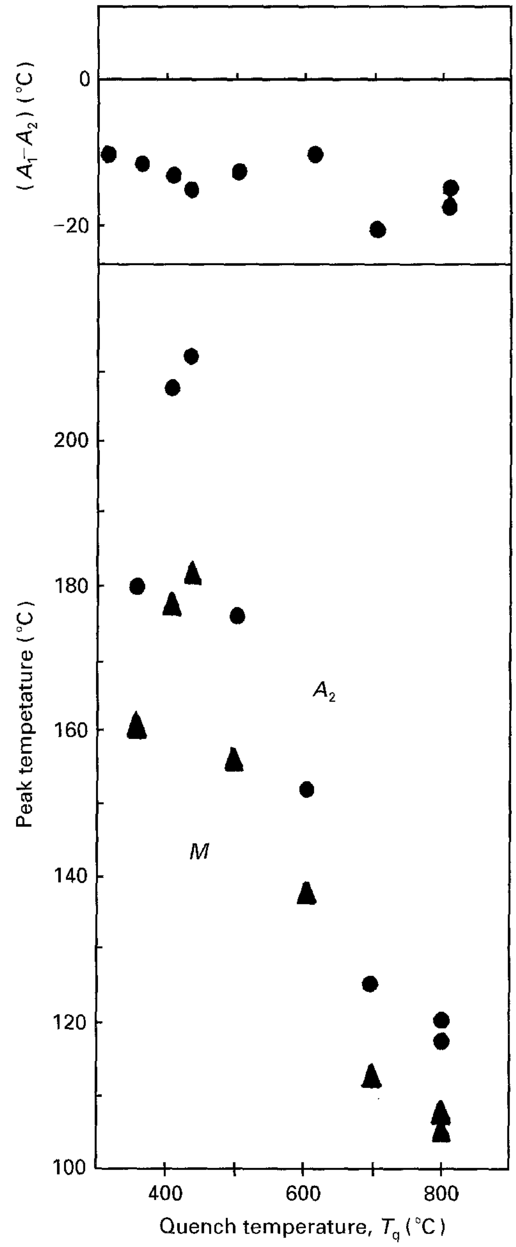

Figure 6 Evolution with T_q of the difference between peak temperatures of the first and second heating runs ($A_1 - A_2$) and the "stable" transformation temperatures A_2 and M for alloy 3.

TABLE II Critical ordering temperatures (°C) for the studied alloys. The uncertainty is estimated to be ± 10 °C

Alloy	T_c(B2)	T_c($L2_1$)
1	800	560
2	700	550
3	600	600

Further supporting this idea, it can be mentioned that other authors have observed that a CuAlNiMnTi alloy aged in martensite requires 2 days ageing at 150 °C to show noticeable stabilization [13]. If, on the contrary, the stabilization is supposed to occur in martensite after the quench, then it has to be accepted that it is completed in a very short time (less than 1 min).

Second, the stabilization temperature shift is accompanied by a shape change of the first reverse transformation peak measured by means of DSC. The first peak is broader and lower in height than the following ones. It should be noticed that although A_f experiences a larger shift than A_S, both temperatures are shifted upwards with respect to the second and following reverse transformations.

Finally, no differences between the structures of the stabilized and non-stabilized martensite were found by means of X-ray diffraction. Structural differences between stabilized and normal martensite, particularly indicating a lowering of the line-splitting parameter, ρ, and an increase of the monoclinic angle, β, approaching 90 ° for the stabilized martensite, have been found for CuZnAl alloys aged in the martensitic form [14, 15], while other authors have reported the lack of differences between the stabilized and normal martensites obtained, respectively, after direct quenching and step-quenching of a CuZnAl alloy [16]. Notwithstanding these contradictory precedents, which prevent our results from being conclusive, the absence of any difference in the presently studied alloys indicates that if structural differences between the stabilized and non-stabilized martensites exist, they do not change the monoclinic unit cell. Of course, eventual atom rearrangement, such as the interchange between copper and zinc atoms found for a CuZnAl alloy using channelling-enhanced microanalysis (ALCHEMI) [17] cannot be ruled out.

Considering the above characteristics, especially the shape change of the first reverse transformation, the observed stabilization would seem to have mechanical causes rather than purely chemical ones, which would shift all the transformation temperatures through a shift of the equilibrium temperature but would not produce any shape change. In fact, the first reverse transformation, being spread over a larger temperature interval than following transformations, can be interpreted as occurring with more impingement to the interface motion. It has been also suggested in the literature [17] that a lower density of stacking faults in the stabilized martensite compared to the normal, non-stabilized one, could lead to a broader reverse transformation, because an extra lattice invariant shear should be introduced to compensate for the decrease in stacking fault density. Transmission electron microscope (TEM) observation is being actively performed on the studied alloys to elucidate this point, but to date such a difference in the stacking fault density has not been observed [18].

According to Fig. 3 a and b and to the evaluation of the stabilization degree, ΔA is approximately constant for the manganese-bearing alloys 1 and 2 in the T_q range from 800–500 °C and decreases for lower T_q until it becomes nil. This indicates a strong influence of the quenching temperature on the stabilization degree, which could arise from (i) the degree of disorder quenched from T_q, (ii) an excess of quenched-in vacancies, and (iii) the quenching rate through (i) and (ii), but also through the elastic or plastic stresses arising from rapid quenching.

A different degree of order after quenching from each T_q temperature is held responsible for the evolution of the "stable" transformation temperatures represented by A_2 and M in Fig. 3a and b. The first heating up to 200 °C allows substantial reordering, which leads to recovery of the suppression due to the quench, but is not enough to reach the equilibrium state of order at 200 °C, so that the state of order is mainly set by the initial quench from T_q. Taking into account the results given in Section 3.2, it can be observed that the T_q temperatures at which ΔA starts to decrease are in good agreement with the $L2_1$ ordering temperatures, while B2 ordering seems not to have a direct role. However, a direct relationship between $L2_1$ disorder and the stabilization degree is questioned by the fact that for T_q temperatures below the critical value, where the $L2_1$ order is expected to be almost complete, ΔA remains above zero.

Excess of quenched-in vacancies has been widely associated with the martensite stabilization [8, 9]. Indeed, an excess of vacancies is retained at room temperature after a quench from T_q the amount of which depends on the initial concentration at T_q and on their migration during the quenching process. Heating to above A_f allows its annihilation and therefore the disappearance of any vacancy-related effect. If the observed stabilization relies on the quenched-in excess of vacancies, then one would expect that removal of the stabilization would proceed progressively as a thermally activated time-dependent process; but on the contrary, stabilization is removed as soon as the samples reach the parent phase with apparent independence of the maximum temperature achieved in this procedure. It should be considered, however, that annihilation of the excess vacancies is very fast at temperatures where their mobility is high enough, as are the A_f temperatures in the studied alloys (100 °C and above). Furthermore, ordering and vacancy migration are coupled processes. Therefore, the faster kinetics of the stabilization removal compared to ordering and the apparent relationship of stabilization with the degree of order, could be explained in terms of the vacancy concentration frozen in after the quench from T_q. Other experimental results, such as the non-occurrence of stabilization after step quenching at 100 °C, provided that the sample is kept there for a time long enough to ensure vacancy annihilation, are consistent with the vacancy mechanism.

On the other hand, low cooling rates allow both ordering and vacancy concentration to reach values very close to equilibrium, thus minimizing the effects described above. In fact, slow cooling from 800 °C does not lead to martensite stabilization. Apart from this, rapid quenching might have other effects, such as creation of residual quenching stresses which could also have some influence on stabilization; in this sense, quenching stresses are non-homogeneously distributed and could assist a shape change or non-homogeneous shift of the transformation temperatures.

Alloy 3 shows a quite different behaviour from the manganese-containing alloys. Other authors have shown that similar behaviour to that found for alloys 1 and 2 occurs for several alloys belonging to the CuAlNi system, such as CuAlNiTi, CuAlNiMnTi and CuAlNi itself [3, 19], and therefore the presence of manganese does not appear to be essential to the occurrence of stabilization. Nevertheless, as can be observed in Figs 5 and 6, no stabilization takes place on quenching alloy 3, regardless of T_q. Decreasing T_q leads to increasing transformation temperatures and, in all cases, suppression of the first reverse transformation temperatures can be observed. At variance with the manganese-containing alloys 1 and 2, alloy 3 does not undergo well-separated B2 and $L2_1$ order transitions. While this cannot be held responsible for the lack of stabilization, because as already mentioned B2 ordering does not seem to be directly related to stabilization, it can account for the larger change with T_q of the "stable" transformation temperatures A_2 and M.

Considering the non-occurrence of stabilization for alloy 3, together with the comparison of the results obtained for alloys 1 and 2, especially concerning the broadening of the first reverse transformation peak, it can be concluded that manganese has the effect of enhancing the martensite stabilization. The possible roles of manganese consistent with the other aspects influencing stabilization which have been discussed above could be a promotion of high quenched-in vacancy populations due to solute manganese or interaction of manganese atoms with vacancy or vacancy clusters to form barriers which oppose the interface motion.

It does not appear possible to determine, from the present results, whether configurational order changes in the stabilized martensite or interface pinning are the predominant stabilization mechanisms. While configurational changes cannot be ruled out, in the presently studied alloys it appears necessary to consider an interface-pinning component to understand the observed behaviour, and given the relationship between manganese content and stabilization degree, it is suggested that a manganese-vacancy interaction mechanism is at play.

Along with the lack of structural evidence which could help to identify the operating mechanisms, comparison of the observed stabilization with other works in the literature [6, 14, 15, 16] suggests that the stabilized martensite structure, as well as the stabilization mechanisms, could present some differences depending on whether stabilization stems from direct quenching or from ageing in martensite.

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