

Study of precipitate formation in Cu–Al–Ni–Mn–Fe shape memory alloys

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The paper analyses the precipitation of γ_2 phase within the γ'_1 thermally induced martensitic matrix of five Cu–Al–Ni–Fe–Mn shape memory alloys (SMAs), by means of differential scanning calorimetry (DSC) thermograms, optical microscopy (OM) and scanning electron microscopy (SEM). It has been proved that the flat exothermic peaks, occurring during the heating of martensitic specimens, correspond to the formation of γ_2 phase precipitates, which are characterized by two specific morphologies, with dendrite arms at about 90° and 120° , respectively. In spite of the presence of γ_2 phase precipitates, the occurrence of thermal memory has been emphasized, characterized by shape recovery degrees higher than 96 %

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1. Introduction

Cu–Al–Ni shape memory alloys (SMAs) with quaternary modifications, containing Mn, have been developed grain refined with B, Ce, Co, Fe, Ti, V, and Zr [1]. In Cu–Al–Ni-based SMAs three equilibrium phases (α , NiAl and γ_2), an ordered parent phase, also called austenite (β_1) and up to four martensites (α'_1 , β'_1 , β''_1 and γ'_1) can be observed [2].

In previous reports the structure of γ'_1 thermally induced martensite [3], its reversion on heating accompanied by length changes [4], as well as the influence of γ_2 phase formation on shape memory behaviour [5] were analyzed. It has been shown that, within certain limits, the formation and growth of hard γ_2 -phase into a softer matrix, represented by γ'_1 thermally induced martensite (2H orthorhombic) [6] didn't cause major changes in the reversion of martensite to β_1 austenite ($D0_3$) [7] on heating, which was accompanied by shape recovery degrees above 97 % [8].

In fact, it has been revealed that the exothermic formation [9] of small γ phase precipitates [10], besides contributing to hardness increase [11], also causes oriented stress fields [12]. These fields were effective in martensite stabilization [13] allowing the development of a new training method [14] the mechanism [15] of which relies on γ nanoprecipitates in Cu–Zn–Al SMAs [16].

On the other hand, the studies performed by Picornell *et al.* and by Kustov *et al.* on Cu–Al–Ni and on Cu–Al–Be SMA single crystals, respectively, reported the stabilisation of thermally and stress induced martensite. In

Cu–Al–Ni, martensite stabilization was produced by compressive stress [17] being enhanced by the increase of permanent strain [18].

In Cu–Al–Be single crystals, the athermal stabilization of β'_1 martensite was ascribed to the combined action of heat treatment and plastic deformation [19]. The former was found responsible for martensite instantaneous stabilization, of heterogeneous nature [20] while the latter contributed to the occurrence of the second martensite reversion at much higher temperatures [21] emphasizing the two stage reverse transformation of hyperstabilized martensite [22].

The present paper aims to reveal the precipitation of hard γ_2 phase into a soft γ'_1 martensitic matrix and its effect on the reverse transformation of stabilized martensite, in polycrystalline Cu–Al–Ni–Mn–Fe SMAs.

2. Experimental details

Five Cu–Al–Ni–Mn–Fe SMAs were obtained by induction melting using an original grain-refinement procedure [23]. As cast specimens were homogenized (1173 K/ 8·3.6 ksec/ water) and hot forged (60 % thickness reduction) at 973–1023 K before being quenched (973, 1023, 1073 K/ 300 sec/ water) in order to obtain γ'_1 thermally induced martensite.

The final chemical compositions of the alloys under study are listed in Table 1.

Table 1. Chemical compositions of experimental alloys, wt. %.

Chemical element	Alloy number				
	3	4	6	7	12
Cu	Bal.	Bal.	Bal.	Bal.	Bal.
Al	13.67	13.95	14.95	13	12.25
Ni	4.28	3.62	4.63	3.73	3.22
Fe	0.14	0.2	2.95	0.61	0.09
Mn	0.54	0.002	0.006	0.002	0.000
Zn	0.12	0.005	0.005	0.005	0.04
Sn	0.000	0.007	0.023	0.019	0.000
Pb	0.04	0.005	0.002	0.001	0.04
Si	0.02	0.04	0.06	0.07	0.00
Mg	0.003	0.003	0.002	0.003	0.000
Ti	0.007	0.001	0.001	0.001	0.003
Co	0.000	0.01	0.01	0.02	0.004
Cd	0.003	0.003	0.003	0.002	0.002
P	0.01	0.003	0.003	0.003	0.000
S	0.019	0.003	0.003	0.003	0.016

After being etched with 30% HNO₃ aqueous solution, the specimens were analysed by means of: (i) differential scanning calorimetry (DSC); (ii) X-ray diffraction (XRD); (iii) optical microscopy (OM) and (iv) scanning electron microscopy (SEM).

DSC thermograms were recorded by means of a Q600 V8.3 build 101 device using Ar as protective gas and platinum crucibles. The heating rate was 10 deg./ 60 sec.

OM micrographs were recorded by means of a NEOPHOT 32 optical microscope while SEM micrographs were recorded by means of a SEM – VEGA II LSH TESCAN scanning electron microscope, coupled with an EDX – QUANTAX QX2 ROENTEC detector.

Shape recovery degree, $G_{rec} = (f_p - f_{res})/f_p \cdot 100$ was determined by shape memory effect (SME) tests in bending performed by means of a special device. The device allowed measuring permanent (plastic) deflection f_p , after room temperature (RT) loading-unloading in bending and residual deflection f_{res} , after heating above A_f temperature and air-cooling, as previously detailed [8].

3. Experimental results and discussion

Each of the DSC thermograms, recorded on heating up to 1073 K, typically revealed the existence of up to four endothermic peaks, as shown in Fig. 1.

Basically, in any Cu-base SMA, the endothermic peak located above 773 K would correspond to β_1 -austenite disordering [24]. In Cu-Al-Ni SMAs, up to two disordering reactions can take place with increasing temperature: (i) $D0_3 \rightarrow B2$ ($D0_3$ disordering) at lower temperatures and (ii) $B2 \rightarrow A2$ ($B2$ disordering) at higher temperatures [25]. Therefore it was assumed that the two endothermic peaks, located above 800 K, would correspond to the above two disordering reactions and were designated accordingly, in Fig.1. It seems that austenite disordering is more prominent at alloys 3 and 12 and less visible at alloy 4.

On the other hand, it is known that γ -phase

precipitation occurs in martensitic high-aluminium Cu-Al-based alloys, during aging at about 570 K, being accompanied by an exothermic reaction [26]. Other authors reported γ -phase formation, besides martensite, after ageing (823K/ 3-3.6 ksec) followed by water quenching of Cu-Al-Ag SMAs [27]. The secondary phase, formed in this way, did not take part to the martensitic transformation [28]. For this reason γ precipitation was assumed on the thermograms of all the alloys under study, in Fig.1.

Considering that the alloys under study are martensitic, they would normally undergo reverse martensite transformation (RMT) on heating. Owing to martensite stabilization observed at Cu-Al-Be single crystals, the reverse transformation can be produced in two stages: (i) a low-temperature endothermic partial reverse martensitic transformation (LT-RMT), also called bulk transformation, caused by reverse motion of interfaces and (ii) a high-temperature endothermic reverse martensitic transformation (HT-RMT) consisting in renucleation of fine austenite lamellae, as a direct effect of martensite stabilization. These transformations were assumed in Fig.1, in accordance with their respective positions reported at Cu-Al-Be [19-22].

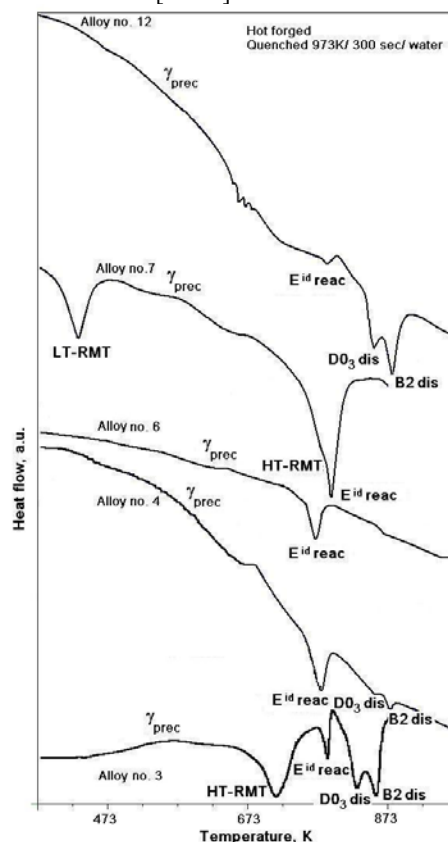


Fig. 1. DSC thermograms recorded during the heating of the five experimental alloys in hot forged and quenched condition. Assumed phase transitions are: γ_{prec} - γ -phase precipitation; LT-RMT - low temperature reverse martensitic transformation; HT-RMT high temperature reverse martensitic transformation; $E^{id} reac$ - eutectoid reaction; $D0_3 dis$ - $D0_3$ disordering and $B2 - B2$ Disorder.

Low-temperature reverse martensitic transformation (LT-RMT) was depicted only for alloy 7. High-temperature reverse martensitic transformation (HT-RMT) was clearly revealed at alloy 3. At alloy 7 it overlaps eutectoid reaction (E^{id} reac) which should be normally present at about 770 K at each of the alloys under study [19, 22].

It must be noted that most the phase transitions marked in Fig.1 are only informative, being simply assumed in accordance with the results reported at Cu–Al–Be single crystals. The accurate identification of the recorded peaks is beyond the scope of the present paper, which focuses on heat treatment effects on γ -phase precipitation within martensitic matrices. Such an effect is illustrated in Fig.2 in the case of alloy 12.

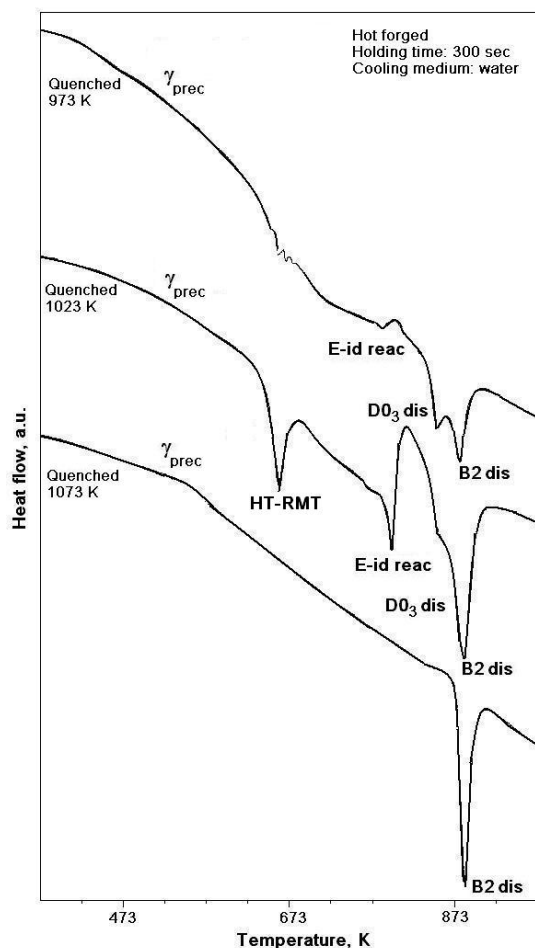


Fig. 2. DSC thermogram recorded during the heating of alloy 12, illustrating the effects of quenching temperature.

It seems that, with increasing quenching temperature from 973 to 1073 K the two disordering reactions, observed at alloy 12 in initial state, tend to become less distinctive, in such a way that only B2 disordering becomes noticeable at the specimen quenched from 1073 K. On the other hand, both eutectoid reaction and high temperature reverse martensitic transformation seem to be firstly enhanced by increasing quenching temperature from

973 to 1023 K. However, further increase of quenching temperature, from 1023 to 1073 K, induces such a martensite stabilization effect that no reverse martensitic transformation is noticeable within the thermal range of sensibility of the DSC unit, namely 373–973 K.

This behaviour could be caused by the more intensive precipitation of γ -phase, noticeable on the thermogram of the alloy quenched from 1073 K. The intense precipitation of γ -phase causes such an advanced Al depletion of the martensite matrix that the critical temperature for reverse martensitic transformation increases so much that it overlaps on B2 disordering. In other words, both austenite formation and its disordering occurred at the same temperature.

In order to reveal the typical structure obtained by quenching, Fig.3 illustrates the representative aspects of the OM micrographs of the alloys under study.

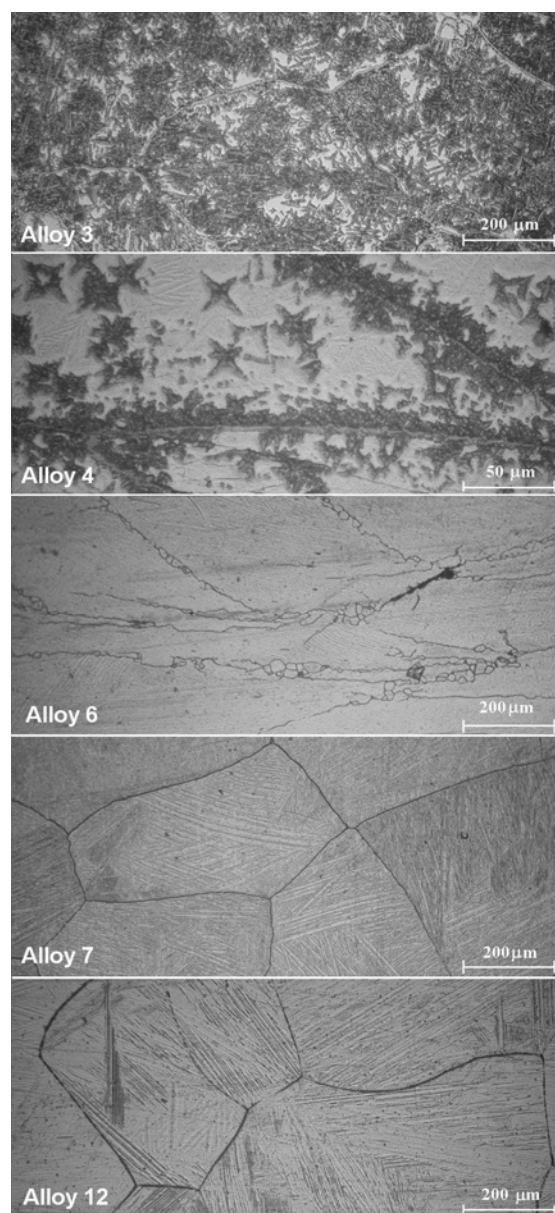


Fig. 3. Typical OM micrographs of the alloys under study in quenched condition.

Obviously, martensite is noticeable in all of the structure of alloys 7 and 12 and in some isolated regions of alloys 4 and 6. On the other hand, γ -phase is present in alloys 3 and 4.

It follows that the only alloy that contains γ -phase and does not contain readily noticeable amounts of martensite is alloy 3. A more comprehensive study of the structure of alloy 3 can be performed by means of the SEM micrographs shown in Fig. 4.

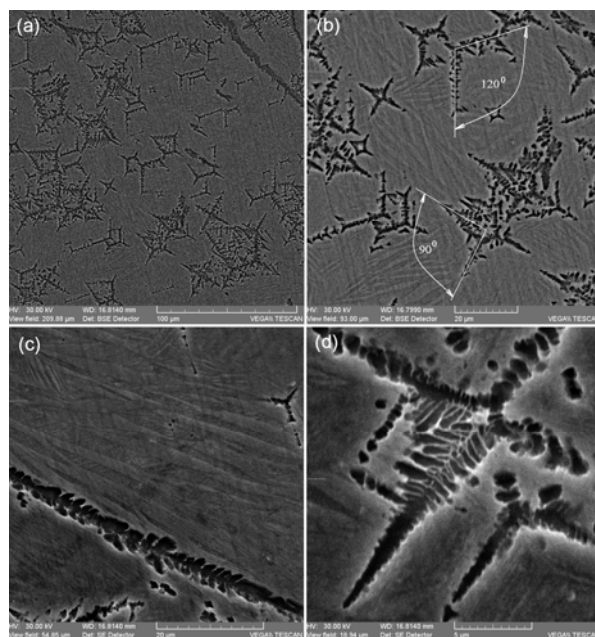


Fig. 4. SEM micrographs illustrating γ -phase morphology in alloy 3: (a) typical morphologies of γ -phase precipitates, 1000:1; (b) detail of γ -phase precipitates with dendrite arms at 90° and at 120° , 2400:1; (c) detail of the martensitic area, 4120:1; (d) morphology of dendrite aggregates with main arms at about 90° .

Fig.4 shows that martensite and γ -phase precipitates coexist in the structure of alloy 3. It is noticeable that γ -phase dendrite arms are located at about 90° and at about 120° without any connection with martensite plates. In other words, there does not seem to be any orientation relationship between γ -phase precipitates and martensite plates. Therefore, there is no reason to assume that the two phases are coherent.

Under these circumstances, bending tests were performed on specimens of alloys 3 and 4, which contain γ -phase precipitates, in order to check the existence of free-recovery shape memory effect (SME) in the presence of γ -phase. As previously explained [8], firstly the ultimate deflections to failure ($f_{\max}$) were determined, and then the values of permanent deflection (f_p) and residual deflection (f_{res}) were measured after RT loading-unloading in bending and heating-cooling, respectively, in order to trigger free-recovery SME.

Fig.5 illustrates the variation tendencies of shape recovery degree, determined as $(f_p - f_{\text{res}}) / f_p \times 100$ as a

function of relative permanent deflection $(f_p / f_{\max}) \times 100$.

It appears that the higher the relative permanent deflection, the larger the shape recovery degree. In the case of alloy 3 this increase has a saturation tendency which is absent in the case of alloy 4. Moreover, for the same value of relative permanent deflection, shape recovery degree is always higher at alloy 3 than at alloy 4.

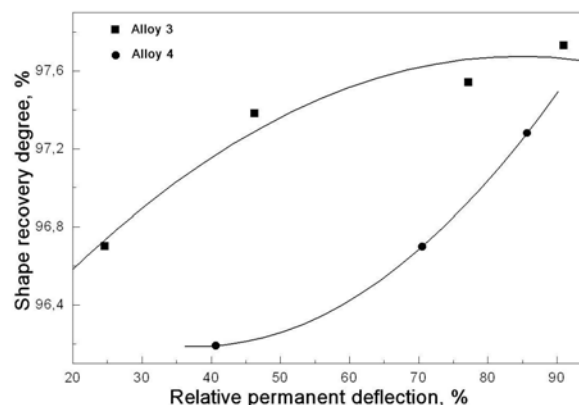


Fig. 5. Variations tendencies of shape recovery degree as a function of relative permanent deflection at alloys 3 and 4.

The above observation suggests that martensite reversion is less impeded in alloy 3 than in alloy 4. Alloy 4 should contain martensite with higher stabilization degree. This assumption is confirmed by comparing DSC thermograms of alloys 3 and 4, from Fig.1. The alloy with more important reverse martensitic transformation, i.e. alloy 3, is characterized by higher shape recovery degrees. Conversely, the DSC thermogram of alloy 4 reveals a higher stabilization degree of martensite, due to the absence of the endothermic peak corresponding to reverse martensite transformation.

4. Conclusions

(i) the stabilization of thermally induced martensite was revealed on the DSC thermograms recorded during heating of five martensitic Cu-Al-Ni-Fe-Mn SMAs;

(ii) the structure of the martensitic alloys under study contained γ_2 - phase precipitates, the formation of which was associated with flat exothermic peaks, on then DSC thermograms;

(iii) with increasing quenching temperature, γ_2 - phase precipitation becomes more important, causing Al-depletion of the martensite matrix, in such a way that high-temperature reverse martensite transformation, eutectoid reaction and order-disorder transitions overlap;

(iv) γ_2 -phase precipitates had two specific morphologies, as a result of dendrite arms orientation at about 90° and about 120° , respectively and were incoherent with martensite plates;

(v) a direct connection was emphasized between the

decrease of shape recovery degree and the increase of martensite stabilization.

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