Stress-Temperature Relationship in Compression Mode in Cu-Al-Ni Shape Memory Alloys

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Compression tests were performed at different temperatures in an 82.5%Cu-13.5%Al-4.0%Ni (mass %) single crystal, a composition giving the β' (18R) thermally induced martensitic phase. In all cases, the non-twinned γ' (2H) martensite was obtained after compression, so, the $\beta' \rightarrow \gamma'$ or $\beta \rightarrow \gamma'$ martensitic transformations were induced, depending of the test temperature. The critical stress vs. temperature, σ_c-T , relationship was established for both types of transformations, obtaining a negative slope $d\sigma_c/dT$ (considering compressive stresses as negative) for the austenite-martensite transformation and a small positive slope for the martensite-martensite. The experimental $d\sigma_c/dT$ values were compared with those calculated from the Clausius-Clapeyron type equation and reasonable good agreement between them was obtained. For these calculations, the entropy changes $\Delta S^{\beta'-\gamma'}$ and $\Delta S^{\beta-\gamma'}$ were directly obtained from the calorimetric runs performed after each mechanical test.

(Received December 22, 2003; Accepted March 19, 2004)

Keywords: shape memory alloys, mechanical cycles, stress-temperature relationship, differential thermal analysis

1. Introduction

The stress induced martensitic transformation in Cu-Al-Ni shape memory alloys (SMA) is strongly dependent on the alloy composition, crystal orientation, heat treatment, temperature, applied stress, and sense of loading. Depending on these parameters a wide variety of austenite to martensite and martensite to martensite transitions can occur. The influence of the different parameters on the transformation characteristics has been widely studied for tensile experiments [see for example,¹⁻⁵]. However, only few works⁶⁻¹⁰ have studied the effects of applying compressive stresses.

A linear relationship between the critical stress to induce the transformation (σ_c) and the temperature is predicted by a modified Clausius-Clapeyron equation.¹¹ This σ_c-T dependence has been experimentally established in practically all SMA systems for the parent-martensite transformations and in particular, for the Cu-Al-Ni SMA.^{1-3,7,12,13} For these alloys the σ_c-T phase diagrams corresponding to parent-martensite transformations, are well established for compositions giving γ' (2H) thermal martensite at zero stress.^{1,2,4,13,14} However much less quantitative data are available for the compositions giving β' (18R) thermal martensite at zero stress.

The behaviour of the intermartensitic $\beta'-\gamma'$ transformation is also not completely established. Otsuka *et al.*^{1,2,15} obtained a small and negative (considering tensile stresses as positive) slope $d\sigma_c/dT$. In that case the stress induced β' was transformed to γ' by cooling and unloading. On the other hand, Novak and co-workers¹⁴ have established, according to their stress-temperature diagrams for Cu-Al-Ni, that $d\sigma_c/dT \approx 0$ for $\beta'-\gamma'$ transformation. A similar, practically temperature independent σ_c-T relationship was obtained by Ahlers *et al.*¹⁶ for the same transformation in Cu-Zn-Al alloys, by means of tensile experiments. Numerical values for $d\sigma_c/dT$ obtained from these works range from -0.7 to $+3$ MPa/K when considering a series of different samples.

An additional problem appears when comparing the experimental $d\sigma_c/dT$ values, obtained directly from the

stress-strain curves at different temperatures, with the theoretical prediction given by the Clausius-Clapeyron-type equation: the lack of reliable data for the entropy change $\Delta S^{\beta'-\gamma'}$. Therefore it is clear that more systematic and as accurate as possible data are needed, paying attention to simplify the thermomechanical paths. For instance, in compositions giving β' thermal martensitic phase at zero stress, the γ' phase is induced when applying compressive stresses. Moreover, more accurate ΔS values can be directly obtained from calorimetric runs, avoiding rough estimations as $\Delta H/T_0$, which can be misleading in cases as that of $\beta' \rightarrow \gamma'$, where the previous experiments show clearly that $\Delta S^{\beta'-\gamma'}$ should be rather small.

In this paper, the results of systematic mechanical experiments in compression, performed at different temperatures and from different initial states (β -parent phase, β' martensitic phase or a mixture of both) are reported together with the data obtained from the calorimetric measurements. From the $\sigma-\epsilon$ curves obtained at each temperature, the values of critical stress have been determined. The σ_c-T relationship for martensite to martensite $\beta' \rightarrow \gamma'$ and parent to martensite $\beta \rightarrow \gamma'$ transitions has been obtained and the experimental results have been compared with those predicted by the Clausius-Clapeyron equation, in which entropy change values obtained from calorimetric runs and strain values got from the compression tests have been used.

2. Experimental Procedure

Single crystals with composition 82.5%Cu-13.5%Al-4.0%Ni (mass %) were used. The dimensions of samples (5 mm diameter and 2.3 mm length) allow using them for calorimetric measurements before and after the mechanical testing. The specimens were submitted to a thermal treatment consisting of 15 min at 1120 K and quenching in water at room temperature. The thermal martensitic transformation obtained after quenching is a $\beta \rightarrow \beta'$ (18R) transformation with temperatures $M_s = 335$ K, $M_f = 290$ K, $A_s = 320$ K and $A_f = 370$ K. Compression stress-strain tests along $[001]_\beta$

Fig. 1 Stress-strain curves (in absolute values), obtained at different temperatures. The sample was in β' martensitic phase before applying stress.

Fig. 2 Stress-strain curves (in absolute values), obtained at temperatures for which the sample was, initially, mostly in parent phase.

direction, under displacement control and at a crosshead speed of 0.2 mm/min (strain rate of $1.3 \times 10^{-3} \text{ s}^{-1}$) were carried out at different temperatures using a Zwick mechanical testing machine. Subsequent calorimetric runs were performed in a TA DSC-2920 calorimeter at 10 K/min cooling/heating rate.

3. Results and Discussion

3.1 σ - ϵ curves

The compression tests were done, after the thermal treatment, at different temperatures for which the sample was initially in the thermally induced β' martensitic phase ($T < A_s$), partially in the martensitic and β phase ($A_s < T < A_f$) or in parent phase ($T > A_f$). In all cases the sample was deformed till a maximum strain of 10%, enough to ensure that the entire specimen was transformed to the new phase. Previous results⁹⁾ have shown that the mechanically formed martensitic phase is the non-twinned γ' (2H).

The σ - ϵ curves (σ and ϵ in absolute values) corresponding to the temperatures for which the sample is, before applying stress, completely (or almost) in β' martensite phase, are presented in Fig. 1. In these cases, the γ' martensite has been obtained from the β' martensite. In this range of temperatures it can be observed that the magnitude of the stress required for reorientation slightly decreases with increasing temperature. Figure 2 shows the ensemble of σ - ϵ curves obtained at temperatures for which the sample is, initially, mostly in parent phase. In these cases the sample suffers the transition from the β parent phase to the γ' martensite. As it is known, when increasing the temperature higher values of stress (in absolute value) are needed in order to induce the new phase.

The critical stresses as a function of temperature for both $\beta \rightarrow \gamma'$ and $\beta' \rightarrow \gamma'$ transformations are shown in Fig. 3. Two linear stages can be observed: one with positive slope, corresponding to the β' reorientation towards γ' , and the other with negative slope, which corresponds to the martensitic phase obtained from the parent phase ($\beta \rightarrow \gamma'$). The slopes of both linear relationships have been determined giving a value of $d\sigma_c/dT = +1.2 \text{ MPa/K}$ and $d\sigma_c/dT =$

Fig. 3 Plot of the critical stress σ_c vs. Temperature. Two branches can be observed corresponding to the $\beta' \rightarrow \gamma'$ (left) and $\beta \rightarrow \gamma'$ (right) transformations.

-2.5 MPa/K respectively. The critical stress values have been determined by the method of tangents intersection. If the plateau stresses are considered (for example the stress corresponding to a 6% of deformation), the obtained $\sigma_c - T$ slopes are $+1.0 \text{ MPa/K}$ and -2.6 MPa/K .

By extrapolating the $\sigma_c - T$ linear relationship to zero stress we get, in the case of $\beta' \rightarrow \gamma'$ line, that $T_c^{\beta' \rightarrow \gamma'} (\sigma = 0) = 371 \text{ K}$; this would be the temperature of a hypothetical spontaneous $\beta' \rightarrow \gamma'$ transformation on heating, which does not manifest because the reverse martensitic transformation $\beta' \rightarrow \beta$ occurs before (at lower temperatures). In the same way the extrapolation to zero stress of the straight line corresponding to the $\beta \rightarrow \gamma'$ transformation gives $T_c^{\beta \rightarrow \gamma'} = 323 \text{ K}$, this temperature is lower than $M_s^{\beta \rightarrow \beta'} = 335 \text{ K}$, in agreement with the formation of β' upon cooling from parent phase.

The straight lines in Fig. 3, representing the phase boundary between β' and γ' and β and γ' phases, provide a schematic phase diagram for the present composition and orientation of the compression axis, which shows that by applying compressive stresses the final martensitic phase is always the non-twinned γ' independently whether the initial state was the parent β -phase or the β' martensitic phase. So, for the present alloy composition, the γ' phase is the most stable phase at high enough absolute values of compressive stress. At low temperatures and stresses the stable phase is the β' and for high temperatures and small stresses the stable

phase is the β parent phase.

From the form of the stress-strain curves obtained after thermal treatment it is interesting to observe the differences between those σ - ε curves corresponding to martensite-martensite and those corresponding to the parent-martensite transition. In the first case a nearly horizontal plateau is obtained once the critical stress is reached.

In these curves a sharp decrease of stress close to 20 MPa (indicated by an arrow in Fig. 1) can be observed just before the elastic deformation of the final phase. Similar stress drop but occurring at the beginning of the plateau has been referred in several works when compressing from parent phase.^{4,6)} The authors related this effect to the growth of the γ' phase after the initial formation of β' needles. Otsuka and co-workers in¹⁾ associated the stress drop to the fast movement of the interfaces. This is supported by measurements of the phase interface velocities, which indicate that interfaces move one order of magnitude faster in compression than in tension.⁵⁾ Following these ideas, in the present case the stress drop could indicate a fast completion of the $\beta' \rightarrow \gamma'$ process.

In the curves corresponding to the parent-martensite transformation, a continuous and smooth increase of stress is needed in order to obtain the new phase. Previous papers¹⁷⁾ related such increase of stress to the latent heat released during the phase transformation. This could explain the differences between the almost horizontal reorientation plateau (where no significant latent heat is produced) and the smoothly increasing loading curve corresponding to the parent-martensite transformation. The latent heat effects are enhanced when increasing the crosshead speed of the loading-unloading processes. However in the present case, experiments carried out by increasing in two orders of magnitude the crosshead speed do not reveal important changes in the slope of the σ - ε curves. Consequently, the used crosshead speed can be considered slow enough to ensure that these heat effects are only marginal and other reasons (for instance, the difficult $\beta \rightarrow$ non-twinned γ' transformation) have to be considered for the slope increase.

The $\beta \rightarrow \gamma'$ transformation strain values obtained are higher than those of $\beta' \rightarrow \gamma'$, and close to 8%. This value is in agreement with theoretical calculations for β to detwinned γ' .¹⁸⁾ When the test temperature is higher than A_f and consequently, some amount of material is able to retransform upon unloading, a decrease of the permanent deformation is observed in the curves corresponding to the parent-martensite transformation.

3.2 Calorimetric results

From the calorimetric runs performed after the mechanical tests (Fig. 4) it can be observed that a burst peak (γ' -type transformation) appears in the first heating at temperatures higher than those obtained after thermal treatment. In the second cycle the temperatures come back to the normal values corresponding to a β - β' transformation. Therefore a martensite stabilisation effect is produced, directly related to the permanent deformation that remains in the sample when unloading and leading to the large hysteresis shown by the mechanically formed martensite. This stabilisation has been studied in detail in a previous paper.⁹⁾ The stabilisation degree is slightly higher for the set of mechanical tests

Fig. 4 Thermograms obtained after the mechanical tests performed at different temperatures. The sharpest curve corresponds to the re-transformation of the mechanically formed γ' -martensite (first heating) and the smoother one to the reverse transformation of the second thermal cycle (2nd heating).

performed at lower temperatures (*i.e.* $T < 330$ K) than in those performed at higher temperatures (Fig. 4). As a general trend, the low temperature σ - ε curves (Fig. 1) present a shorter plateau and an important additional deformation of the mechanically formed γ' phase before unloading. Otsuka *et al.*¹⁹⁾ proposed that this deformation can be due to the slip of partial dislocations which are very mobile and abundantly present in the γ' martensite. This deformation can contribute to the higher stabilisation.

In the thermograms corresponding to the mechanical cycles carried out at $T > 340$ K, it is possible to observe a small displacement to lower temperatures of the peak related to the stabilised martensite. By increasing the test temperature the shape of the peak changes, its enthalpy change diminishes and a small peak appears at lower temperatures (marked by an arrow in Fig. 4, curve at 387 K). This peak is related to the amount of material which re-transforms to the parent phase when unloading at high temperature. When removing the sample from the furnace, this part of the sample transforms to the β' thermally induced martensitic phase and comes back to the parent phase when heating in the calorimeter. When increasing the temperature of the compression test, more amount of material is able to revert to the parent phase on unloading (see curves at 377 and 387 K in Fig. 2), and so less amount of sample remains stabilised.

3.3 Clausius-Clapeyron equation

From the mechanical and calorimetric data it is possible to compare the $d\sigma_c/dT$ values obtained from the slope of σ_c - T points with that calculated from the Clausius-Clapeyron equation:

$$\frac{d\sigma_c}{dT} = - \frac{\Delta S \rho}{\varepsilon_t}$$

where ΔS and ε_t are the entropy change and transformation strain respectively, and ρ is the molar density, which has been measured to be 0.131 mol/cm³. In case of the $\beta' \rightarrow \gamma'$ transformation, the corresponding $\Delta S^{\beta' \rightarrow \gamma'}$ can be obtained

Table 1 Values of the entropy changes (ΔS) and transformation strain (ε_t) for the different cases considered. The experimental errors estimated for these magnitudes are ± 0.05 J/molK and ± 0.005 , respectively. The slope $d\sigma_c/dT^{(1)}$ is calculated from the Clausius-Clapeyron equation using the experimental strain; $d\sigma_c/dT^{(2)}$ is calculated from the Clausius-Clapeyron equation subtracting to the experimental strain the deformation corresponding to the β' reorientation (≈ 0.025), see text for details. $d\sigma_c/dT^{(3)}$: slope from σ - T linear fit of σ values determined by the tangents intersection method and $d\sigma_c/dT^{(4)}$: slope obtained from σ - T linear fit of the σ values corresponding to the plateau of the σ - ε curve.

	ΔS (J/molK)	ε_t	$d\sigma_c/dT^{(1)}$ (MPa/K)	$d\sigma_c/dT^{(2)}$ (MPa/K)	$d\sigma_c/dT^{(3)}$ (MPa/K)	$d\sigma_c/dT^{(4)}$ (MPa/K)
$\beta' \rightarrow \gamma'$	0.15	-0.050	0.4 ± 0.2	0.8 ± 0.3	1.2 ± 0.1	1.0 ± 0.1
$\beta \rightarrow \gamma'$	-1.30	-0.075	-2.3 ± 0.2	—	-2.5 ± 0.1	-2.6 ± 0.1

from two consecutive calorimetric runs performed after the compression test. The entropy changes measured in the first and second heating runs correspond to $\gamma' \rightarrow \beta$ and $\beta' \rightarrow \beta$ transformations, respectively. Consequently, for the $\beta \rightarrow \gamma'$ transformation, the entropy change is directly obtained from de calorimetric signal, while for the $\beta' \rightarrow \gamma'$ one, it can be evaluated as $\Delta S^{\beta' \rightarrow \gamma'} = \Delta S^{\beta' \rightarrow \beta} - \Delta S^{\gamma' \rightarrow \beta}$. The experimental values averaged among all the measurements performed are: $\Delta S^{\beta' \rightarrow \beta} = 1.45$ J/molK and $\Delta S^{\gamma' \rightarrow \beta} = 1.30$ J/molK. In its turn, the transformation strain ε_t has been directly obtained from the σ - ε curves by considering the deformation associated to the “plateau” of the curve, the region between the two linear deformation parts. The different values involved in the Clausius-Clapeyron equation are presented in Table 1, together with the experimental slopes of the σ_c - T diagrams.

From Table 1 it can be observed that the values obtained for the $\Delta S^{\beta' \rightarrow \gamma'}$ are very small and positive, leading, as ε_t is negative in a compression test, to $d\sigma_c/dT > 0$, in agreement with the present experimental results. It is worth to comment that Otsuka *et al.*¹⁾ obtained a small but *negative* value of the $d\sigma_c/dT$ slope for the $\beta' \rightarrow \gamma'$ transformation, using the enthalpy change values of the $\beta \rightarrow \beta'$ and $\beta \rightarrow \gamma'$ transformations. It has to be noted that the authors calculated the entropy change values by dividing the enthalpy change by a constant temperature ($T_o = 300$ K). This approximation can be critical when the differences between $\Delta S^{\beta \rightarrow \beta'}$ and $\Delta S^{\beta \rightarrow \gamma'}$ are small, as in the present case. Pelegrina and Ahlers obtained either positive or negative slopes for the temperature dependence of the critical resolved stress in CuZnAl alloys, depending on electronic concentration and Schmid factor.¹⁶⁾

When comparing the absolute value of $d\sigma_c/dT$ obtained from the Clausius-Clapeyron equation with those given by the slope of the σ_c - T linear relationship for the $\beta' \rightarrow \gamma'$ transformation, a smaller value is obtained in the first case. The reasons for this discrepancy can be found in the difficulty for getting a correct determination of the strain corresponding to the $\beta' \rightarrow \gamma'$ transformation. The strain determined from the σ - ε curves includes the strain corresponding to the unravelling of the self-accommodated β' martensite plates together with the $\beta' \rightarrow \gamma'$ transformation itself, consequently it is an overestimation. In order to correct the deformation value, we can use the published results⁹⁾ of partial mechanical cycles up to different strains performed in the same alloy. Due to the different hysteresis of the β' and γ' martensites, they retransform separately to the parent phase, which allow us to detect the presence of each phase. From the partial

compression tests and subsequent calorimetric heating runs reported in⁹⁾ we can see that for low compression strains, no γ' is detected in the thermograms, so the compression only causes the unravelling of the β' plates. The strain value from which the γ' retransformation peak starts to appear is $\sim 2.5\%$. If this value is subtracted from the present experimental strain values, we obtain the result for $d\sigma_c/dT^{(2)}$ shown in the table, which is closer to those obtained from the σ_c - T slope ($d\sigma_c/dT^{(3)}$ and $d\sigma_c/dT^{(4)}$) but still lower. This fact indicates that the strain correction is not enough, *i.e.* above 2.5% compression the γ' phase starts to be formed, but the remaining thermal β' phase is still unravelling. On the other hand, if instead of calculating the slope from the entropy and strain values, we use the Clausius-Clapeyron equation to calculate the deformation from the experimental slope of the σ_c - T relationship and the entropy and density values, the obtained strains are 0.020 and 0.016 (for $d\sigma_c/dT = 1.0$ and 1.2, respectively). These values can give us an idea of the contribution of the $\beta' \rightarrow \gamma'$ transformation to the total strain.

Finally, in the case of the parent-martensite transformation, $\beta \rightarrow \gamma'$, the compression causes purely the martensitic transformation, so the value of $d\sigma_c/dT$ given by the Clausius-Clapeyron equation using the experimental strain is very close to the experimental slope.

4. Conclusions

(1) The σ_c - T relationship has been determined in a wide interval of temperature, which includes austenite-martensite and martensite-martensite transformations for a Cu-Al-Ni alloy in compression mode. The stress-temperature relationship is different for both types of transformation: while a negative slope is obtained for parent-martensite ($\beta \rightarrow \gamma'$) transformation (taking into account the negative sign of the compressive stress), a positive σ_c - T slope is obtained for the martensite-martensite ($\beta' \rightarrow \gamma'$) transformation. In the latter case, this fact has been clearly established by inducing directly the γ' from the thermally formed β' , thus avoiding complicated thermo-mechanical paths.

(2) The $d\sigma_c/dT$ values for both regimes have been determined and compared with those calculated from a Clausius-Clapeyron type equation, which includes mechanical and calorimetric results. Direct calorimetric measurements allowed to determine $\Delta S^{\beta \rightarrow \gamma'}$ and $\Delta S^{\beta' \rightarrow \gamma'}$, therefore, rough estimations for ΔS as $\Delta H/T_o$ have been avoided as elements in the equation. A reasonable good agreement between experimental and calculated $d\sigma_c/dT$ values has been obtained for the $\beta \rightarrow \gamma'$ transformation. In the case of

$\beta' \rightarrow \gamma'$, the experimental strain includes a contribution caused by the unravelling of the self-accommodated β' martensite plates, which needs to be subtracted.

(3) From the mechanical and calorimetric data it is possible to draw a schematic phase diagram which sets the “stability” limits in the σ_c – T plane between either β' or β and the γ' phase, induced by compression.

Acknowledgements

Partial financial support from the DGI (proj. numbers MAT2000-0862-C03-02 and MAT2002-00319) is acknowledged.

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