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MARTENSITIC TRANSITION ENTROPY CHANGE AND ELASTIC CONSTANTS OF Cu-Al-Be ALLOYS

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Abstract. Measurements of the enthalpy (ΔH) and entropy (ΔS) changes associated with the martensitic transformation of Cu-Al-Be single crystals of different compositions, were performed by differential scanning calorimetry. In addition, the elastic constants of the body-centered-cubic parent phase single crystals were measured as a function of temperature, using the ultrasonic pulse-echo frequency varying - phase detection method, and the value of the elastic anisotropy ($A=C_{44}/C'$) was computed at the martensitic transformation temperature. The results are in good agreement with a theoretical expression obtained according to models previously proposed, which relates ΔS to the elastic anisotropy of the parent phase at the martensitic transformation temperature.

1.-Introduction.

Cu-based alloys with a b.c.c. high temperature phase exhibiting a thermoelastic martensitic transformation have been extensively studied, mainly because of the interest in their technological applications as shape memory materials [1]. Great attention has therefore been paid to the thermodynamics and kinetics of the martensitic transformation, and multiple studies have consequently been performed [2,3]. At the same time, looking for a better understanding of the microscopic mechanisms driving the transformation, people has performed a lot of studies of the elastic response of the material and its relationship with the mechanical stability of the phases [4]. However, only a few attempts have been made in order to relate both the thermodynamic and the elastic properties. The present work is a first attempt in trying to relate these two type of properties in the case of Cu-Al-Be shape memory alloys. We note that for this particular system, no measurements of enthalpy and entropy changes during the martensitic transformation had been reported previously, to our knowledge, in the literature. Also, in the case of the elastic constants of this alloys only a few measurements have been recently published [5].

2.-Single crystal preparation.

Polycrystalline rods (l ~ 10 cm, ϕ ~ 1.5 cm) of CuAlBe alloys were obtained by inductive fusion of electrolytic Cu with proper amounts of Cu-4%Be commercial alloy and Al, under an Ar-rich atmosphere. The polycrystalline rods were quartz encapsulated in vacuum and single crystals (l ~ 7 cm, ϕ ~ 1.4 cm) were grown by a modified Bridgman method.

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The single crystals were crystallographically oriented using the back-Laue x-ray diffraction method, and cut parallel to the (110) planes of the parent β-phase, to an accuracy better than two degrees, with a low speed diamond saw. Samples for the elastic constants measurements were approximately 1 cm long and those for the calorimetric measurements 0.1-0.2 cm thick. Table I shows the weight composition of the single crystals used in this work, as measured by Plasma Emission Spectroscopy.

Table I. Weight composition of the alloys.

ALLOY	Cu	Al	Be
CAB 56	87.88	11.65	0.47
CAB 04	88.01	11.50	0.49
CAB 21	87.87	11.63	0.50
CAB 17*	87.67	11.79	0.54
CAB 05**	87.90	11.50	0.60
CAB 01	87.84	11.38	0.78

* polycrystal, ** nominal composition.

3.-Calorimetric measurements.

Differential scanning calorimetry measurements of the whole set of single crystals were made on a high sensitivity calorimeter with two semiconducting thermoelectric power (Peltier) elements mounted differentially on a high thermal inertia Cu-block [6]. A four point Pt-100 resistance embedded on the Cu-block was used for the temperature measurements. Typical temperature rates were of about 0.5 to 2 K/min.

Enthalpy and entropy differences between the martensitic and parent phase were obtained by integration of the thermograms. Large temperature scans were necessary in order to cover the whole extension of the calorimetric peaks. Such a large transformation temperature range seems to be characteristic of these Cu-Al-Be alloys, as shown for instance in the typical calorimetric curve of Fig. 1, where differences between M_s and M_f (or between A_s and A_f) temperatures as large as 60K can be observed. This transformation behavior made the enthalpy and entropy measurements quite difficult, since the choice of the integral limits was not easy. A base line proportional to the transformed fraction at each temperature was constructed by an iterative integral method between two temperatures, one below and the other above the transformation range and far enough from the peak region. Following this method enthalpy and entropy were obtained with uncertainties of around 6% and 8%, respectively. Figure 2 shows the hysteresis curves associated with the martensitic and reverse transformations of the alloys studied.

Table II gives the enthalpy and entropy mean values measured for the martensitic and reverse transformations of the different samples. Also shown in Table II are the M_s, A_s and M_f, A_f temperatures measured at 5% and 95% of transformed fraction, respectively.

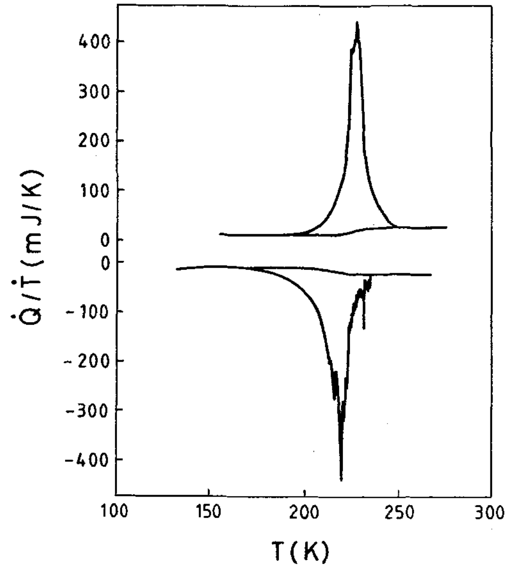

Fig. 1.- Calorimetric curves for alloy CAB 21, showing the martensitic and reverse transformations. Notice the large extension of the peaks towards the low temperature region.

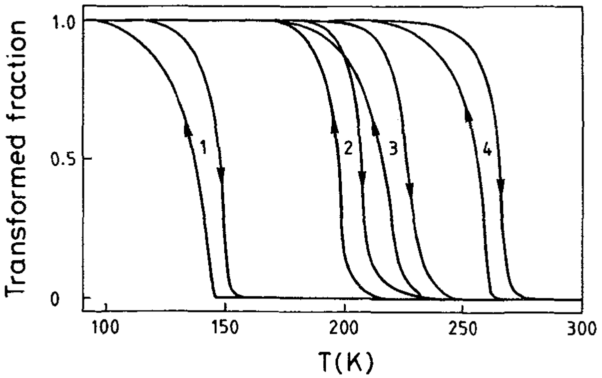

Fig. 2.- Transformation cycles for samples CAB05 (1), CAB17 (2), CAB21 (3) and CAB56 (4). Notice again the large extension of the transformation towards the low temperature region.

Table II. Enthalpy (ΔH in J/mol) and entropy (ΔS in J/Kmol) mean values of the martensitic and reverse transformations, and mean values of the M_s, M_f, A_s and A_f temperatures (in K) measured at 5% and 95% transformed fraction, respectively.

ALLOY	M_s	M_f	A_s	A_f	$\Delta H^{\beta\text{-}M}$	$\Delta H^{M\text{-}\beta}$	$\Delta S^{\beta\text{-}M}$	$\Delta S^{M\text{-}\beta}$
CAB 56	272	230	247	271	-354	359	-1.39	1.37
CAB 04	251	188	209	239	-297	297	-1.40	1.34
CAB 21	240	190	211	238	-294	326	-1.34	1.44
CAB 17	221	181	194	219	-259	288	-1.32	1.39
CAB 05	153	112	127	152	-198	206	-1.44	1.41

4.- Elastic constants measurements.

Ultrasonic wave velocities measurements were made along the [110]β direction. X and Y-cut quartz transducers were used to generate and detect 10 MHz ultrasonic pulses. Satisfactory acoustic coupling could be achieved above room temperature using Dow Resin 276-V9 and below room temperature with Nonaq stopcock grease. Ultrasonic pulse transit times were measured using the phase sensitive detection technique [7] capable of resolution of velocity changes to 1 part in 10^6 and particularly well suited for determination of temperature induced changes in velocity. The sample was placed on a copper plate whose temperature was monitored with an embedded Pt-100 resistance. Cooling was performed by introducing the sample holder into a Dewar vessel with liquid nitrogen in its bottom. The cooling rate was 0.5 K/min approximately, which is slow enough to ensure that the sample was at the same temperature than the copper plate. In addition, some measurements were taken at constant temperature in order to confirm that the ultrasonic time measurements did not depend on the cooling rate.

In Table III we present the value of C_{44}, C' ($=(C_{11}-C_{12})/2$), C_L ($=(C_{11}+C_{12}+2C_{44})/2$) and the elastic anisotropy A ($=C_{44}/C'$) at room temperature for the four crystals investigated. C_L and C_{44} show the usual behavior of linearly increasing as the temperature drops. However, similarly to other Cu-based shape memory alloys [8], C' decreases with temperature. This partial softening of the slow shear mode is related to a lattice instability towards a martensitic transformation. A linear fit has been performed to the data in order to obtain the slopes ($C_{IJ}^{-1}dC_{IJ}/dT$) in Table III.

Table III.- Room temperature values of the elastic constants in GPa, relative thermal variation Γ_{IJ} $=(C_{IJ}^{-1}dC_{IJ})/dT$ in 10^{-4} K^{-1} and elastic anisotropy, and value of the anisotropy extrapolated at M_s.

ALLOY	C_L	C_{44}	C'	Γ_L	Γ_{44}	Γ'	A	A(M_s)
CAB 56	224.5	94.9	7.15	-2.33	-3.90	4.59	13.27	13.53
CAB 21	223.9	92.9	7.11	-2.35	-3.84	4.59	13.07	13.68
CAB 05	224.1	90.9	7.68	-2.19	-3.72	4.41	11.83	13.38
CAB 01	222.9	94.4	8.97	-2.11	-3.58	4.01	10.52	---

5.- Discussion.

Several features can be pointed out from our experimental results. First we want to stress the great difficulty encountered in measuring the enthalpy and entropy values set in Table II, mainly because of the large and gently extension of the thermogram peaks towards the low temperature region. An experimental situation that very much difficult the definition of M_f and A_s temperatures, and therefore increased the incertitude in the integration of the area of the peaks. Note for instance that typical M_f-M_s differences in Figure 2 are of about 60k.

It should be noted that, within the experimental incertitude, the values of entropy in Table II are quite similar for the different measured alloys. This situation, together with the significant linear decrease of the M_s temperature with small increases in Be content, results in a monotonic decrease in the enthalpy values for increasing Be.

Another important feature in our results is the constancy of the anisotropy factor A, extrapolated at the M_s temperatures, for all the studied single crystals (see Table III). It should be noted here that the same value of A (~13.5) is calculated by extrapolation for alloy CAB 01 at its "expected" M_s temperature (~-25K), obtained by extrapolation of the curve giving the variation of Ms with Be content in Cu-Al-Be alloys [9]. Such a constancy in both the anisotropy factor A and the entropy change ΔS, that we have found for Cu-Al-Be, is consistent with the theoretical expression [10]:

$$\Delta S = \frac{3}{2} R\alpha \ln[z(1+\frac{q_2}{q_1}A^{-1})]$$

where R is the gas constant, α is the fraction of soft modes, q_1 and q_2 are the coordination numbers for nearest and next nearest neighbors in the parent phase, z is the ratio between the number of first nearest neighbors in the parent and in the martensitic phases, respectively, and A is the anisotropy factor at the transition temperature. The substitution in this equation of the values corresponding to the martensitic transition in Cu-Al-Be ($z=2/3$, $q_1=8$, $q_2=6$, $A=13.5$), and taking $\alpha \approx 0.25$ results in a value for the entropy change of about -1.1 J/Kmol, which is in good agreement with our experimental results. The value of α used in this calculation is the one previously reported from low temperature C_p measurements in Cu-Zn-Al shape memory alloys [11].

More work about this latter question and other related phenomena is in curse, and a more extensive report will be presented in the next future.

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