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An Experimental Study of the Coupling Between the Order-Disorder Transition and the Martensitic Transformation in Cu-Al-Be Shape Memory Alloys

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Abstract: Order-disorder transitions in Cu-Al-Be alloys have been studied by means of X-ray diffraction measurements. Assuming that different ordered degrees can be "frozen" with suitable heat treatments, their effect on the martensitic transformation has been analized by microcalorimetry. The results indicate a change in the temperature of the martensitic transformation directly related to the change of the order degree: disordering stabilizes the martensite phase. Other effects observed after specific heat treatments have been associated to the vacancies retained after the quench. Additional elastic neutron scattering experiments provide data to fit the temperature changes to a previous proposed model.

1. INTRODUCTION

A number of Cu-based alloys undergo at a temperature M_s a martensitic transformation (MT) from a high-temperature bcc phase to a close-packed structure [1]. Although the close-packed structure is energetically more favorable, the bcc high-temperature phase is stabilized by a large vibrational entropy [2]. The interest of these alloys stems from their technologically important shape-memory properties, which are directly associated to the MT.

Furthermore, most of these alloys undergoing a MT exhibit ordered structures below a certain temperature T_c ($T_c > M_s$) [3]. In the case of Cu-Zn-Al alloys, it has been shown that the degree of atomic order at low temperature can be controlled by means of suitable heat treatments [4], and that the induced changes affect the relative stability between the bcc and the close-packed phases [5].

Cu-Al-Be alloys display at high temperatures (above 970K), a bcc structure (β-phase). Below the range of stability of the β-phase, the equilibrium phases are the so-called α (fcc structure) and γ_2 (Cu_9Al_4 stucture) phases [6]. The β-phase can be metastabilized at lower temperatures by suitable cooling. It is during this cooling that the β-phase goes through different ordered states. Once metastabilized, below the eutectic point/line, the β-phase undergoes, upon further cooling, a MT towards a close-packed structure. This close-packed structure is an orthorombic (18R) structure in the case of Cu-Al-Be alloys close to the stoichiometric Cu_3Al composition.

The aim of this work is to study the coupling between the order-disorder transition and the martensitic transformation in Cu-Al-Be alloys. For this purpose, we have studied the order-disorder transition in a family of composition related Cu-Al-Be alloys by means of X-ray powder diffraction measurements. Additional elastic neutron scattering experiments were performed for completeness.

We have also used differential scanning calorimetry to measure the change in the thermodynamic quantities characteristic of the MT after different heat treatments.

This paper is organized as follows. In Section 2 we describe the experimental procedure and give the data we obtained on the X-ray diffraction measurements, the neutron scattering experiments and the calorimetric study. In Section 3, the discussion and conclusions of this work are presented.

2. EXPERIMENTAL DETAILS AND RESULTS

Single crystals grown by the modified Bridgman method were used in the measurements. Their atomic composition and characteristic temperatures are given in Table I. T_c values are taken from the X-ray diffraction results (see next subsection).

Table I: Atomic composition, T_c and M_s for the investigated alloys. Uncertainties in T_c are $\pm 10K$, and in M_s, $\pm 1K$. The values with (*) are taken from [7].

sample	Cu	Al	Be	$T_c(K)$	$M_s(K)$
cab56	74.08	23.13	2.79	813	275
cab21	73.97	23.06	2.97	803	240
cab51	73.73	22.72	3.55	793	150
cab90	71.77	22.73	5.50	788	—
cab91	69.77	22.19	8.04	793	—
cabB	74.24	22.84	2.91	—	227*
cabC	73.98	23.06	2.97	—	228*

2.1 X-ray diffraction and neutron scattering measurements.

We started the study of the order-disorder transitions in Cu-Al-Be from the assumption that the different possible ordered structures for the β-phase are the $A2$, the $B2$, and the DO_3 (or the equivalent $L2_1$) [6]. The DO_3 and $L2_1$ structures are equivalent in the sense that they give rise to the same Bragg reflections, but they can be distinguished by the corresponding intensity values. The Bragg reflections associated to the different ordered structures are: k,k,l all odd for the DO_3 or $L2_1$ superstructure (example (111)); h,k,l all even and $h+k+l=4n+2$ with n integer for the B2 superstructure (example (200)); h,k,l all even and $h+k+l=4n$ for the A2 fundamental reflections. For a detailed description of these structures, see [3]. Depending on the different degrees of order within the sublattices the intensity of the associated peaks range from zero to the maximum value.

X-ray powder diffraction measurements were performed in a Bragg-Brentano diffractometer equipped with a high temperature chamber and a position sensitive detector. We used the Cu $K\alpha$ radiation ($\lambda = 1.5418\AA$). Powder specimens were made from the single crystals by using a diamond file. The typical mass of the powder samples was $10^{-2}g$. All the measurements were performed in a primary-vaccuum atmosphere in order to avoid oxidation of the powder particles. Due to their small size, surface oxidation might reduce the intensity of β-phase peaks.

The procedure to study the order-disorder transitions in our system is as follows: First of all, the powder is annealed in the high temperature chamber at a T_h temperature in the β-phase equilibrium region for around 20 minutes; then it is cooled down to room temperature. This cooling takes approximately 4 minutes. This heat treatment is needed to improve the crystallinity of the powder. Measurements start by heating up again the powder to T_h and running a large angle range scan (> 40 degrees). After this scan, different scans are conducted at selected temperatures: some of them in a small angular region comprising the (111) and (200) peaks, and others around the (220) peak ; each scan takes approximately 3 minutes time.

After each measurement at a selected temperature, and prior to a new change in temperature, the powder was heated up again to T_h in order to get a fixed initial reference state ($A2$) for the next measurement, and also to eliminate possible precipitates of the α and γ_2 phases that could have grown during the preceding measurement. Each time that the sample was at T_h, a long scan was performed. Cooling and heating rates were choosen as fast as possible (2K/s) in order to minimize the growth of precipitates.

The procedure explained above was followed for different temperatures and for the first five compositions given in table 1. T_h values were 973K for cab21 and cab51, 1073K for cab56 and cab90, and 1123 for cab91. The reason for having different T_h values is that for some compositions, the peaks of precipitates did not disappear at 973K and therefore, a higher T_h value was needed.

The (111), (200) and (220) β-phase peaks were integrated for each temperature T, once corrected for the background. Also, noise and contamination contributions to the peaks were eliminated by substracting, from the integrated area at T, the corresponding integrated area in the previous T_h scan. The resulting values are plotted in figure 1. The integrated intensities of the superlattice peaks have been normalized to the total amount of β-phase present, by dividing by the (220) intensity. Typical estimated errors are $\sigma \approx 10^{-3}$. The (220) β-phase peak is at the same scattering angle value as one of the peaks of the γ_2-phase. For this reason, when γ_2-phase has been detected, the integrated area of the (220) β-phase peak has been corrected for the γ_2-phase contribution.

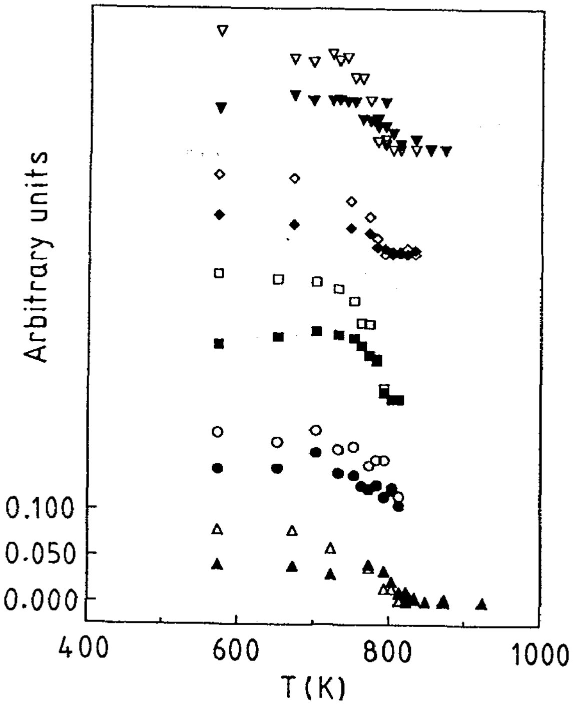

Fig.1. Normalized intensities of superstructure peaks: I(111)/I(220) (open symbols), and I(200)/I(220) (filled symbols) for cab56 (△), cab21 (○), cab51 (□), cab90 (◇) and cab91 (▽) compositions.

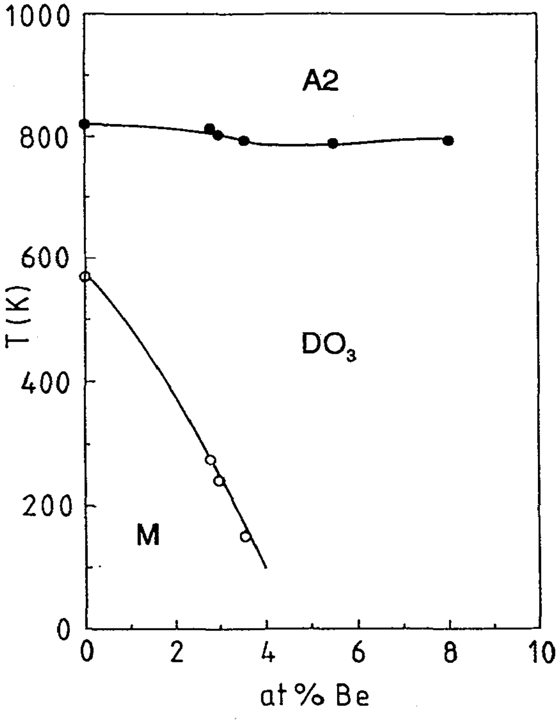

Fig.2. Phase diagram of the Cu-Al-Be investigated alloys: (●) are the T_c data and (○) the M_s values. Solid lines are a guide to the eyes.

The (111) and (200) β-phase peaks were found to appear and grow simultaneously at the same temperature T_c, which depended on the composition. The fact that the (111) and (200) β-phase peaks appear together in these Cu-Al-Be alloys indicates that there is a single order-disorder phase transition: from a $A2$ structure to a DO_3 (or $L2_1$). This order-disorder transition starts at a temperature denoted by T_c. The values found for T_c are listed in table I.

Also, the change in the lattice parameter with respect to the value at T_h has been determined for the (220) reflection. In addition to the normal variation with temperature, a small discontinuity in the lattice parameter has been observed at a temperature very close to the T_c value.

We have computed the different structure factors assuming a uniform mean thermal vibrations in all the sublattices. The values found for (111) and (200) intensity are in better agreement with a DO_3 superstructure than with a $L2_1$.

In figure 2, we present the phase diagram obtained from the X-ray measurements and from the calorimetric results (see next subsection). The M_s and T_c values for the stoichiometric Cu_3Al obtained from the literature [8] are also shown. cab90 and cab91 samples do not transform into martensite at any temperature below 77K [9]. The T_c points separate the region of stability of the $A2$ ordered β-phase from that of stability of the DO_3 ordered β-phase. The M_s points separate the region of stability of β-phase from the region of stability of martensite (M).

Elastic neutron scattering experiments were performed using a constant-incident neutron energy triple-axis spectometer (HB1-A, at ORNL). Two single crystals (cabB and cabC in table 1) of 14.72g and 14.83g were studied prior and after heat treatment. The heat treatments consisted in annealing the sample at 1085K for 20 or 30 minutes, air-cooling down to T_q and quench into water at room temperature. T_q values were 633K, 653K and 1073K. It was found that before any heat treatment there was a small amount of precipitates (mainly α) and martensite phase in the samples, which did not change appreciably after the different heat treatments. In all cases the amount of precipitates in the sample was extremely small (typically, the relation between maximum intensities was 1/1000) in comparison with β phase peaks. Nevertheless a striking feature consisting of a non-uniform distribution of the precipitates was found: they showed symmetric distribution along specific crystal directions.

Also, no change in the TA_2 [110] phonon branch was observed after the heat treatments. Neutron scattering experiments to compute the degree of disorder achieved after the quench have showed that after a heat treatment in sample C with $T_q = 1073K$, the (111)/(220) and (200)/(220) values have been reduced to the 10% and 15% respectively. The same measurement performed on a Cu-Zn-Al sample, gives changes of the order of 20%.

2.2 Calorimetric measurements.

In our calorimetric study we used single crystals cab56, cab21 and cab51 of masses typically between 0.4 and 0.8g. Scanning calorimetric measurements were made on a high sensitivity microcalorimeter. The technical details are given elsewhere [10].

The single crystals are subjected to different heat treatments: First, the sample is annealed at T_a for 3 or 10 minutes. Then, it is air cooled down to a temperature T_q and it is quenched into either a mixture of ice and water (cab21, cab51), or water at room temperature (cab56). Just after the quench, a first calorimetric run is performed. 23 hours after the first run, a second calorimetric run was conducted in order to separate non-permanent effects from permanent effects. The T_a values used were 973K for cab21 and cab51 and 1073K for cab51 and cab56. These values were found to be the best suitable for these compositions.

Different heat treatments were conducted on the different specimens for a set of T_q values ranging from 350K to 1075K. Also, for all the set of compositions, a reference heat treatment was performed: This reference heat treatment consisted of an air cooling from T_a down to room temperature and an annealing of two days prior to the calorimetric runs. The M_s values appearing on table 1 are those obtained from these reference heat treatments.

From the recorded thermal curves the martensite start and finish temperatures (M_s, M_f) can in principle be obtained. We adopted as a characteristic temperature of the transformation the temperature of the maximum of the thermal curve (T_M). That choice was motivated by the difficulty of a precise determination of M_s, due to the jerky character of the transition and the presence of some premonitory effects, both induced by some of the heat treatments (see [11]) in cab56 and cab21. The jerkier character was found for $T_q = 823K$ for both cab21 and cab56.

In figure 3, the shift in the heating T_M values with respect to the T_M value for the reference heat treatment, are plotted for the different compositions and samples as a function of T_q, both for the first and second calorimetric runs.

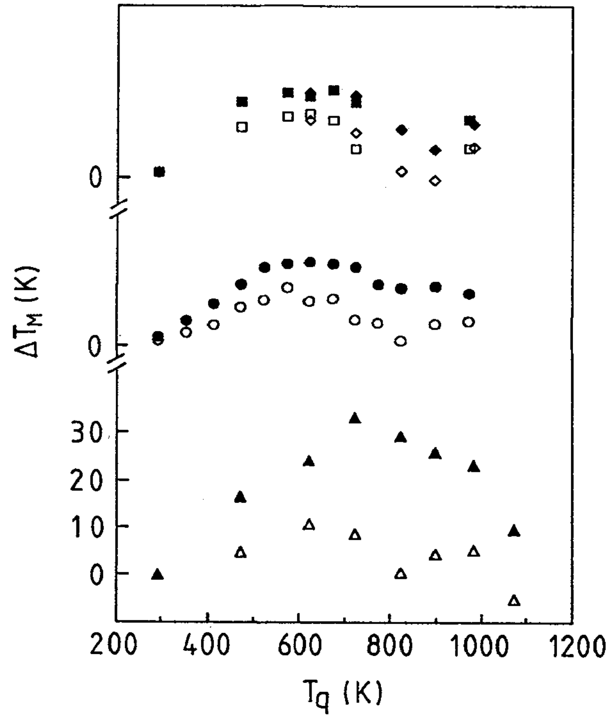

Fig.3. T_M minus T_M for the reference heat treatment versus T_q for the first (filled symbols) and second (open symbols) heating runs. The different composition values have been shifted for a better view: cab56 (△), cab21(○) and cab51(□), (◇).

3. DISCUSSION AND CONCLUSIONS.

From the X-ray diffraction study it is concluded that in these Cu-Al-Be alloys there is a single order-disorder transition from a A2 structure to a DO_3 structure (rather than a $L2_1$). This transition seems to be a first-order transition according to the change in the lattice parameter at T_c.

On the other hand, neutron scattering measurements reveal that with the heat treatments one does not increase the amount of precipitates within the samples, but the order degree can be changed. Therefore, one can assume that the heat treatments performed in the calorimetric study modify the order degree in the sample; and that the changes in the T_M values are a direct consequence of the coupling between the order-disorder and the martensitic transformations. This is confirmed by the behaviour of the T_M values for the second run: They tend to approach the standard heat treatment T_M value, wich is considered to be the one with the largest order degree.

In all cases the disorder increases the T_M value and, thus, stabilizes the martensite phase. For all the compositions in figure 3 the second run results are qualitatively and quantitatively the same. Also the first run results are similar in the cab51 and cab21. In cab56, an "extra" shift of T_M is found in the first heating run (but not in the cooling). We attribute that to a possible stabilization of martensite after the heat treatment for the M_s value in cab56 is close to the room temperature value and it is increased with heat treatments. Just after the quench the cab56 sample is likely to be in martensite phase. In cab56 the maximum difference in T_M for the first and second heating run (see fig.3) corresponds to $T_q = 823K$, so following our hypothesis, this T_q value would correspond to the maximum amount of martensite stabilized by the quench. If one assumes that the quenched-in vacancies and vacancy clusters are responsible for the stabilization of martensite [12], the larger amount of retained vacancies is reached for $T_q = 823K$. Also, the jerkier character of the MT was observed for $T_q = 823K$, then it seems logical to conclude that the interface pinning caused by vacancies retained after the quench would be the origin of the jerky character of the transformation. In the second runs, the jerkier character was always absent. That can be understood by assuming that the mobility of vacancies in the martensite phase is much lesser than in the β phase, similarly to what has been observed by positron annihilation in the Cu-Al-Ni alloy system and in Cu-Al-Be alloys with some Ti or Cr impurities [12],[13]. Therefore, once the reverse transformation has taken place, the vacancies can easily be removed and do not produce the jerky effect.

Recently, a theoretical relationship between T_M and the order parameter (s) has been proposed [14]. For $T_q = 1073K$, neutron scattering results show that $s^2(T_q) \sim 0.85s_o^2$. Inputing this value in equation (1) of reference [11], we obtain $\delta T_M = \delta M_s \sim -8K$. This value is in very good agreement with the change in T_M measured calorimetrically for sample B ($\delta T_M = -10K$, for $T_q = 673K$).

For the cab51 composition, in the X-ray measurements it was noticed that it was easier to avoid the growth of the γ_2 phase in comparison with the other compositions. Also the jerky character of the MT was practically absent in its calorimetric runs. These features could be correlated each other. These points, together with the symmetries showed by the precipitates in the neutron study, indicate that, besides the disorder, other effects such as the precipitates precursors or dislocations play a role in driving the MT. From this work, there is no doubt about the influence of the disorder on the shift of T_M, but it seems that the disorder has a "specific effect", while the whole MT properties are not solely determined by the degree of order.

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