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In situ X-ray study of order–disorder phase transitions in Cu–Al–Be melt spun ribbons

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Abstract The disorder–order phase transitions in Cu–Al–Be shape memory alloys were studied by in-situ X-ray diffraction. Isothermal measurements in an inert gas chamber were made on ribbons of Cu–Al–Be alloys, obtained by melt spinning. A position sensitive detector was used for a fast record of the X-ray signal on a θ–θ geometry diffractometer. Each ribbon was used as the heating element, avoiding the need of a heating sample holder and obtaining a better measurement of the temperature with a thermocouple attached directly to the ribbon. The order transition was followed at different temperatures after a high temperature annealing (700 °C) in the disordered β-phase region. A first order transition was observed from disordered β (A2) to ordered β_1 (DO_3), without prior β (B2) ordering. No precipitation was detected during this fast measuring procedure.

Introduction

Phase diagrams of some copper based alloys show a high temperature stable disordered body centered cubic β-phase of A2 type. It has been observed that the cubic A2 structure of this β-phase undergoes ordering reactions on cooling below the eutectoid temperature, first to a B2 (CsCl type) and then to a DO_3 (Heusler type) ordered structures [1]. On further cooling, the ordered phase undergoes a martensitic transformation when the alloy is rapidly cooled [2]. Such transformation is responsible for the shape memory behavior.

Many studies have been performed about these ordering transitions in Cu–Zn–Al for different alloy compositions and the critical temperatures for the B2 and DO_3 order transitions have been determined [3]. It has been established that the ordering process is assisted by vacancy diffusion during cooling, as shown in positron annihilation measurements [4]. Also, it has been shown that the martensitic transformation start temperature (M_S) changes with the degree of ordering [5]. In those studies the ordering processes have been identified as second order type transitions, with transformations on cooling proceeding from A2 to B2 to DO_3.

Previous X-Ray diffraction studies on powders of Cu–Al–Be alloys show that the ordering transitions to DO_3 is first order [6], differing from Cu–Zn–Al and Au–Cu–Zn alloys, and that a single ordering transition from A2 to DO_3 occurs on cooling, in contrast to the A2–B2–DO_3 sequence observed in Cu–Zn–Al.

The β-phase stability has been studied earlier by means of Differential Scanning Calorimetry to trace precipitation of α and γ_2 stable phases, and C curves in a T-T-T diagram were determined [7-10]. The α-phase is a copper rich phase with a fcc structure, and γ_2-phase (Cu_9Al_4) has a cubic complex structure where lattice parameter is about three times that of β-phase [2]. Further thermoelectric power measurements and transmission electron microscopy (TEM) were used to corroborate those results [11]. Also, in recent work optical and transmission electron microscopies were used to follow the precipitation kinetics in these alloys [12].

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A previous study of X ray diffraction on Cu_3Al reported the A2–B2–DO_3 ordering sequence [13], but this result has been questioned by Jurado et al. [6], who believe that during these measurements γ_2 decomposition took place, affecting the identification of the ordered phases.

The aim of this work is to study the ordering process on ribbons of Cu–Al–Be alloy produced by the melt spinning technique, to verify the nature of the ordering transition. Considering the kind of sample (ribbons) one can expect to have a more precise measurement of temperature. Also, the grain sizes in the melt-spun ribbons were smaller than 50 μm assuring good diffractometry measurements.

Experimental

Ribbons of Cu–12 wt% Al–0.44 wt% Be (C2) and Cu–11.66 wt% Al–0.44 wt% Be (C3) alloys were obtained by the process of melt spinning. These compositions are near the eutectoid one. The ribbon thickness was about 0.1 mm and 3.5 mm wide. M_S temperatures of −63 °C and −60 °C, respectively, were measured by Differential Scanning Calorimetry.

In situ X-ray diffraction measurements were performed by using the ribbons as the heating element. A thermocouple was fixed to the ribbon by welding it with a ''home made'' point welding system. Figure 1 shows the configuration used in the diffraction experiments. The whole set was inside a vacuum chamber and an argon flux was injected after obtaining a primary-vacuum with a mechanical pump.

A position sensitive detector was used to simultaneously record a 12° angular diffracted signal. This allowed us to perform fast response experiments, and follow the evolution of the diffraction peaks, well before precipitation could appear.

Heat treatments were carried out using the following routines:

1. Heating at 700 °C during 15 min to obtain the disordered β-phase.
2. Step quenching at different intermediate temperatures (200 °C/min approx.).
3. Measuring at each temperature for 15 min.
4. Increasing temperature up to 700 °C and measure again.

The heat treatments are shown in Fig. 2, where the times are approximated. This experimental procedure is different from the one used by Jurado et al. [6] in a similar order disorder study made on Cu–Al–Be powders, where they report that following the above procedure allows them to precipitate the stable phases. However, in our case the use of a ribbon with a high dissipative surface with respect to volume, and the fast measurement procedure as well as the continuous flux of argon allowing a fast cooling rate might be the reason why no precipitation was observed in our case, as will be explained later.

Results and discussion

A typical diffraction pattern obtained at room temperature from a quenched Cu–Al–Be alloy ribbon is shown in Fig. 3, where the main reflections from each order structure are clearly identified.

X-ray spectra from ribbon C3, following the heat treatments described before, are shown in Fig. 4. First to note is that the ordering transition occurs well before precipitation, since no precipitations peaks were present in the diffraction patterns. Actually, as mentioned in a previous study of the precipitation kinetics in these alloys shows that gamma precipitates start to be detected by calorimetry, thermoelectric power, transmission electron microscopy

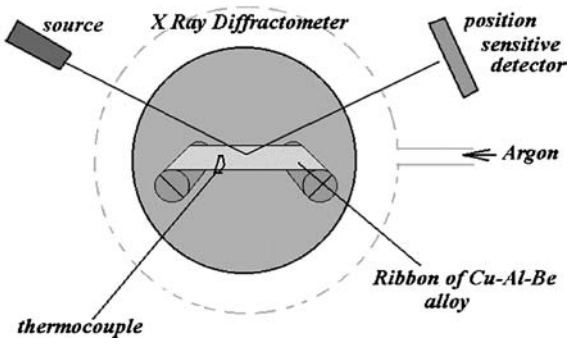

Fig. 1 Cu–Al–Be ribbon used in the experimental set-up for in-situ θ–θ X-Ray Diffraction measurement

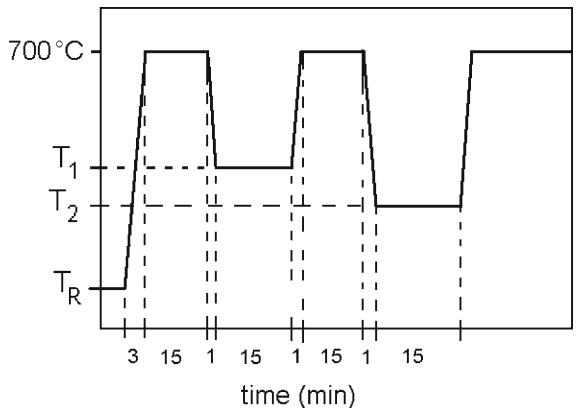

Fig. 2 Heat treatment of the ribbons in the in-situ measurement

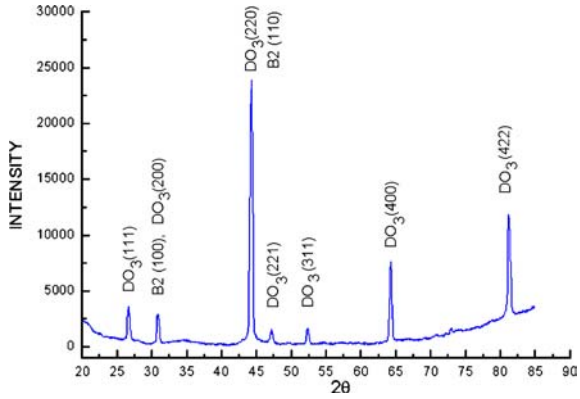

Fig. 3 Typical diffraction pattern of a Cu–Al–Be ribbon at room temperature

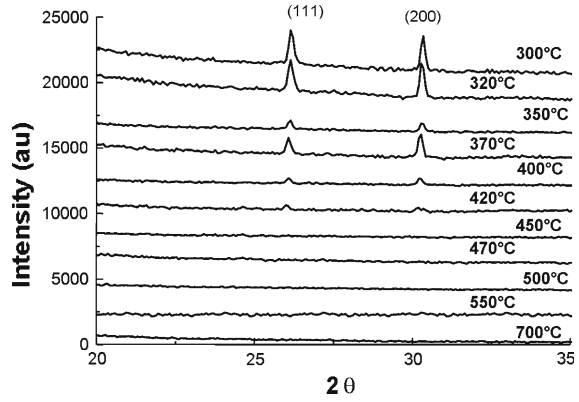

Fig. 4 Ordering peaks evolution during the heat treatment: measurements carried out for descending temperatures. Peaks are indexed from DO_3 ordered phase

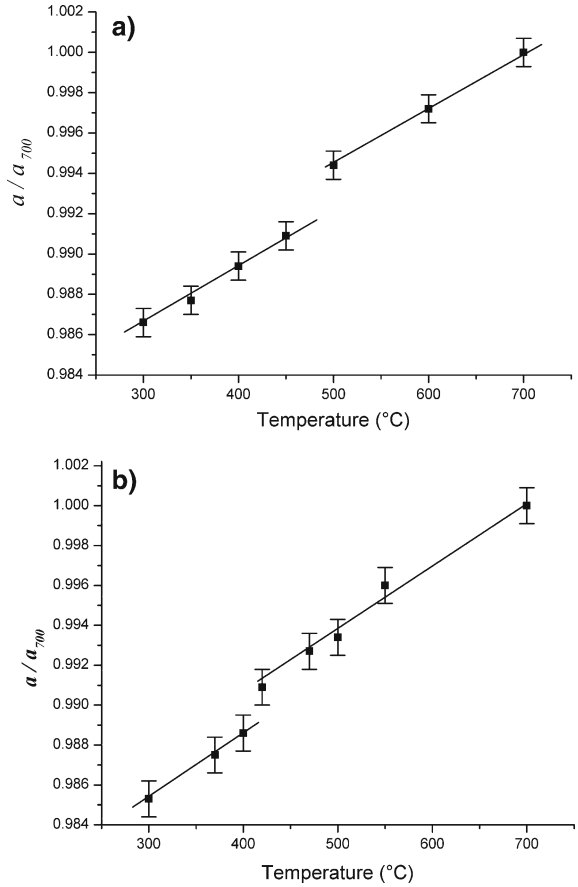

Fig. 5 Temperature dependence of the lattice parameter from (220) reflection normalized by its value at 700°C. (**a**) Ribbon C2, (**b**) Ribbon C3

and optical microscopy only after about 1 h of isothermal ageing at 500 °C.

In Fig. 4, the ordered phase peaks start to be detectable between 450 °C and 420 °C for this composition. Important enough is to note that both the peaks associated to DO_3 appear simultaneously, with no prior appearance of the characteristic B2 peak. Therefore, it seems that the ordering transition occurs directly from A2 to DO_3, without the intermediate formation of B2, as it was also concluded by Jurado et al.

Figure 5 shows the temperature dependence of the lattice parameter of the β-phase for both samples, obtained from the main peak (220) normalized by its value at 700 °C. It can be noticed in Fig. 5 that is a clear discontinuity in the lattice parameter at a temperature corresponding to the disorder–order transition, which must correspond to a discontinuity in the volume, indicating a first order transition. This result also corroborates the results reported by Jurado et al. [6].

It is also noticeable that the slope of the lines, corresponding to linear thermal expansion coefficient, is similar in both temperature ranges, above and below the transition. The average thermal expansion coefficient measured was close to 3×10^{-5} K^{-1}.

In addition, differential thermal analysis (DTA), evidenced endothermic and exothermal peaks close to the order–disorder transition temperatures, like the one shown in Fig. 6. The DTA was obtained by heating at a rate of 10° C/min up to 660 °C and then switching the oven off to allow cooling; therefore the cooling rate was slower than the heating rate. This result is interesting enough, since it evidences a first order transition.

However this result is controversial with the conclusion reported by Soltys [13] in Cu_3Al, who concludes that there is an intermediate transition to the B2 ordered phase. Here it should be noticed that the compositions used in this work and also those in the Jurado's study, are close to the stoichiometric DO_3 composition and therefore no intermediate transition to B2, that involves a shorter range order process, is required. Jurado et al. argue that precipitation of γ_2-phase might be the reason why Soltys concludes that B2

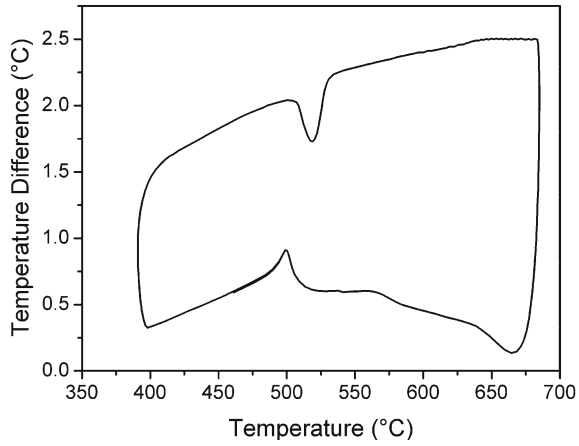

Fig. 6 Differential Thermal Analysis showing the endothermic and exothermal peaks near the order–disorder transition of a Cu–Al–Be ribbon C2

forms prior to DO_3, since the peak used to identify B2 is close to one of γ_2.

An alternative analysis could be that the shift in composition associated to the formation of γ_2 could deviate towards Cu rich region, far enough from the stoichiometric one, therefore the formation of B2 might be necessary, since it means a shorter range order transition. In this sense, it is interesting to note that studies of order in eutectic Cu–Zn–Al alloys by Ahlers [14] and resumed by Jurado [6] shows that as the Zn content decreases to nearly zero, the gap in the transition temperatures from A2 to B2 to $L2_1$ becomes close to zero, indicating the possibility to obtain a direct A2 to $L2_1$ order transition at an extrapolated Zn content of about 5 at%, that is to say near the stoichiometric Cu_3Al, a conclusion that agrees with the present results and these of Jurado et al. Further loses in Al (as in Soltys case) could increase the gap again allowing the intermediate ordering transition to the B2 phase. However, more work is needed to clarify these discrepancies.

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