

# Phase transformations during continuous cooling of polycrystalline $\beta$ -CuAlBe alloys

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Received 29 October 2007; received in revised form 17 December 2007; accepted 19 December 2007

Available online 26 December 2007

## Abstract

The transformations during continuous cooling and their effect on the thermoelastic behaviour of  $\beta$ -CuAlBe shape memory alloys have been studied by electrical resistometry, microscopy and differential calorimetry. Under slow cooling rates, the alloys show hypereutectoid behaviour as a result of the addition of Be. The sequence of  $\gamma_2$  and  $\alpha'$  precipitation and the ordering of  $\beta$  phase were clearly identified. A quasi-binary phase diagram with variable Be content is proposed. Small modifications in the Be content cause noticeable changes in the ranges of phase stability. The precipitation could be avoided with high cooling rates. The precipitation processes produce changes in the matrix composition, which affect the critical temperatures of ordering as well as the  $\beta$ -martensite transformation.

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**Keywords:** Metals and alloys; Precipitation; Phase transitions; Shape memory; Metallography

## 1. Introduction

The Cu–Al system shows a disordered bcc  $\beta$  phase, stable at high temperatures. The stability range of  $\beta$  becomes narrower at lower temperatures, showing a eutectoid transformation at 830 K for approximately 24 at% Al. At temperatures below the range of stability of  $\beta$ , the equilibrium phases are:  $\alpha$ , a low Al fcc structure, and  $\gamma_2$ , a higher Al  $\text{Cu}_9\text{Al}_4$  phase [1,2]. The equilibrium phases can be suppressed by rapid cooling from high temperature, and metastable  $\beta$  phase is retained at room temperature (RT). During cooling, the disordered  $\beta$  phase orders to a  $\text{DO}_3$  structure ( $\beta_1$ ), and at lower temperature it transforms martensitically to a 18R structure. For the eutectoid composition, the order transition occurs at around 850 K, and the martensitic transformation takes place at approximately 570 K [3].

The martensitic transformation of  $\beta$  phase is responsible for the shape-memory properties exhibited by Cu–Al alloys. However, the martensitic transformation starting temperature,  $M_s$ ,

is too high for practical applications. The addition of third elements, such as Be, Mn and Ni, has proved to be effective in stabilizing the  $\beta$  phase and lowering the  $M_s$  [4–6]. Particularly, the addition of small amounts of Be results in an important decrease of  $M_s$ ,  $-114$  K each 1 at%, without a change in the nature of the martensitic transformation [7]. This decrease in  $M_s$  enlarges the temperature range at which the shape-memory effect is operative, making Cu–Al–Be an interesting smart system.

The aim of this work is to study the microstructure evolution of the metastable  $\beta$  phase during continuous cooling in two Cu–Al polycrystalline alloys with Be additions of 3.26 and 2.98 at%. The decomposition, ordering, and martensitic transformation of  $\beta$  phase were monitored by electrical resistivity measurements, microscopical examinations, and differential scanning calorimetry (DSC). The behaviour of these alloys is compared to that of  $\beta$  Cu–Al [1,8] alloys, and  $\beta$  Cu–Al alloys with different contents of Be [7,9].

## 2. Experimental procedure

The Cu–22.60Al–3.26Be (at%) and Cu–22.66Al–2.98Be (at%) polycrystalline alloys were commercial alloys obtained from Trefimetaux (France). The

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chemical composition was determined by atomic absorption spectrophotometry. The grain size in the as-received samples was around 0.06 mm. The nominal martensitic transformation temperature  $M_s$  is 217 K for the 3.26 at% Be alloy, and 261 K for the 2.98 at% Be alloy [7]. The heat treatments, carried out in a resistance furnace, include a heating stage at 1073 K in the  $\beta$  field, followed by continuous cooling at different rates between 3 and 470 K/min. The electrical resistivity was monitored using a standard four-point probe technique. Samples of 10 mm length, and 3 mm  $\times$  1.5 mm rectangular section were used. The temperature was monitored using a chromel–alumel thermocouple spot welded to the sample. Changes in the microstructure were followed by observing at RT quenched specimens from selected temperatures along the cooling curves. The cooling rate corresponding to these quenches was around  $10^4$ – $10^5$  K/min. For light microscopy (OM) and scanning electron microscopy (SEM) observations, the samples were electropolished in a saturated solution of chromium trioxide in phosphoric acid at  $\sim 4$  V. Some of them were suspended a few seconds in a solution of ferric chloride in order to reveal phase microstructure details. The volume fraction of  $\gamma_2$  phase was estimated as the relative area occupied by the precipitates with respect to the total area. For the range of the precipitates size, the  $f_{V\gamma_2}$  value estimated by the areal analysis would be within  $\pm 10\%$  as the relative error [10]. Calorimetric measurements were performed with a Rheometric DSC calorimeter.

### 3. Results

The behaviour of the Cu–22.60Al–3.26Be (at%) is described in detail in what follows. Fig. 1 shows a plot of the relative electrical resistivity against temperature obtained by continuous cooling from 1073 K, for two cooling rates.  $R_0$  is the electrical resistivity value at 900 K, that is in  $\beta$  phase.

Microscopy observations were done after quenching samples every 10 K or less along the cooling curve. For cooling rates slower than 100 K/min, the decomposition of  $\beta$  phase was observed. For faster cooling rates precipitation was observed neither by OM nor by SEM. For the slowest cooling rate, 3 K/min, the sequence of transformations could be well determined. The first precipitates were observed by SEM after quenching from 873 K, point (a) in Fig. 1. Fig. 2 shows the microstructures corresponding to points (a)–(f) marked on the cooling curve. From approximately 873 to 770 K, the nucleation and growth of pro-eutectoid  $\gamma_2$  phase takes place, as shown in Fig. 2a–c. The precipitates exhibit dendritic morphology, and appear uniformly distributed along the whole sample, indicating that the

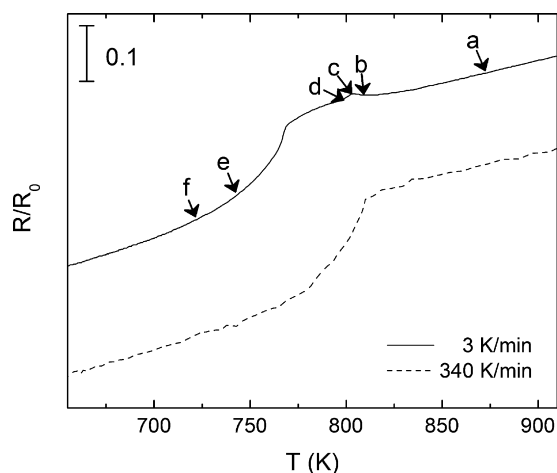


Fig. 1. Change in relative electrical resistivity during continuous cooling from 1073 K, for different cooling rates. The curves are vertically shifted for clarity.

grain boundaries do not act as preferential nucleation sites. As the temperature decreases, the dendrite primary arms grow and secondary arms appear also in preferential directions according to the orientation of each grain (Fig. 2c). The grain boundaries appear decorated by  $\gamma_2$  phase. At 808 K, the volume fraction of  $\gamma_2$  phase is approximately 20%, and increases up to around 50% at 800 K.

Between around 800 and 770 K, besides  $\gamma_2$  precipitates, the presence of martensite plates are observed (Fig. 2d). Long parallel needles are organized in groups with preferential orientations and formed one after the other. The  $\beta$  phase has transformed almost entirely to martensite during quenching, indicating that the martensitic transformation temperature,  $M_s$ , has raised to values above room temperature.

Between around 770 and 720 K, the decrease of the  $\gamma_2$  dendrites size is observed, together with the appearance of rosette-shape regions, similar to those observed in Cu–Al alloys [8], corresponding to ordered  $\beta_1$  phase. The formation of thin envelopes around  $\gamma_2$  phase is also seen in Fig. 2e. Further cooling leads to the amalgamating of the rosettes with the envelopes, suggesting that both consist of  $\beta_1$  phase. It is worth noting that martensite is not observed at RT in this stage. Particles of  $\alpha'$  phase are formed in  $\beta_1$  zones on further cooling (Fig. 2f). Fig. 2f\* corresponds to a SEM image of one of these zones. The  $\alpha'$  particles have the form of thin platelets, and correspond to low-temperature  $\alpha$  phase, similar to that observed in Cu–Al alloys [8]. At RT the structure is similar to that of Fig. 2f at 720 K.

For cooling rates higher than 100 K/min, precipitation is inhibited. However, the relative resistivity–temperature curves at cooling rates as high as 340 K/min show a marked break, as shown in Fig. 1. This could be associated to the disorder–order transition of  $\beta$  phase, from A2 to DO<sub>3</sub>, which cannot be avoided even at the highest cooling rates [3]. Fig. 3 presents typical ordering curves obtained from the evolution of  $dT/dt$  with  $T$ , and from calorimetric measurements on cooling from 950 K. Both techniques give similar results. The ordering process of  $\beta$  phase is observed at around 800 K when the faster cooling rates are applied. In the slow cooling rate curve (3 K/min), the ordering process is observed at a lower temperature, around 770 K (Fig. 3b). The change in the ordering transformation temperature as a function of the cooling rate suggests that the precipitation interferes with the ordering process. The ordering process is also identified by OM when cooling is made at low rates, with the appearance of rosette-shape regions corresponding to ordered  $\beta_1$  phase (Fig. 2f).

In order to analyze the precipitation effect on the  $\beta$ -martensite transformation, DSC cycles through the martensitic transformation temperature range have been carried out on specimens quenched from selected temperatures along the cooling curves. The samples were cooled down to 198 K to complete the  $\beta$ -martensite transformation and then heated up to 473 K in the calorimeter. With this procedure the reverse transformation to  $\beta$  was monitored. Fig. 4 shows the thermograms obtained on heating. Sample quenched from 1073 K is the reference specimen without precipitation. As a consequence of precipitates, the heat peaks become broader and flatter. In addition, signifi-

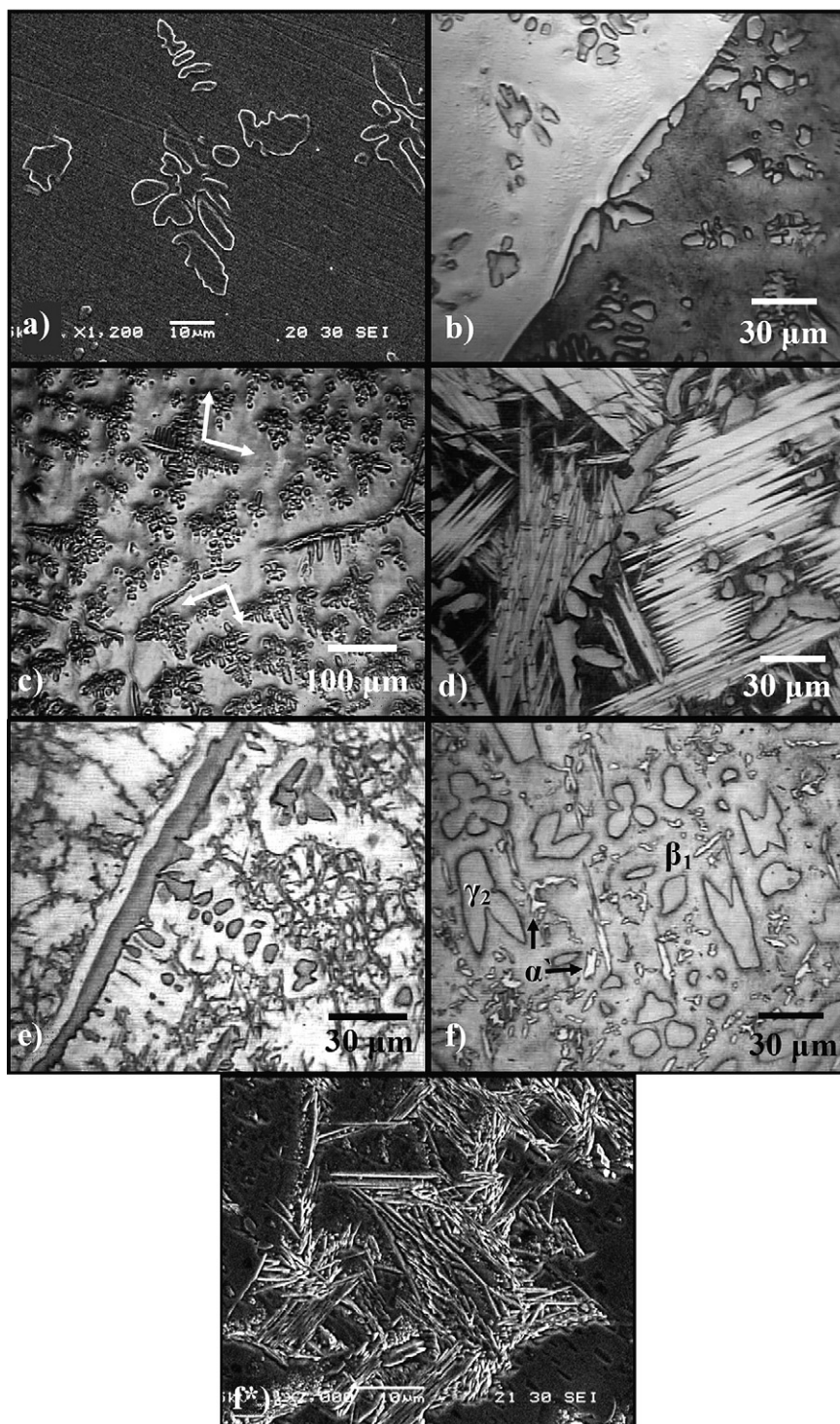


Fig. 2. Micrographs corresponding to points a–g on the cooling resistivity curves in Fig. 1: (a) 873 K; (b) 808 K; (c) 800 K; (d) 797 K; (e) 743 K; (f) 722 K; (f\*) shows a detail of  $\alpha'$  phase. See text.

cant changes in the transformation temperatures are observed, particularly for quenching temperatures between 808 and 783 K, where the transformation temperatures are shifted above RT.

The general behaviour of the Cu–22.66Al–2.98Be (at%) alloy was qualitatively similar as regards to the phase transformation sequence. However, changes in the characteristic

temperatures were measured. The results are analyzed in the next section in relation to the differences in Be content.

#### 4. Discussion

The sequence of phase transformations taking place in the studied alloys during continuous cooling is complex,



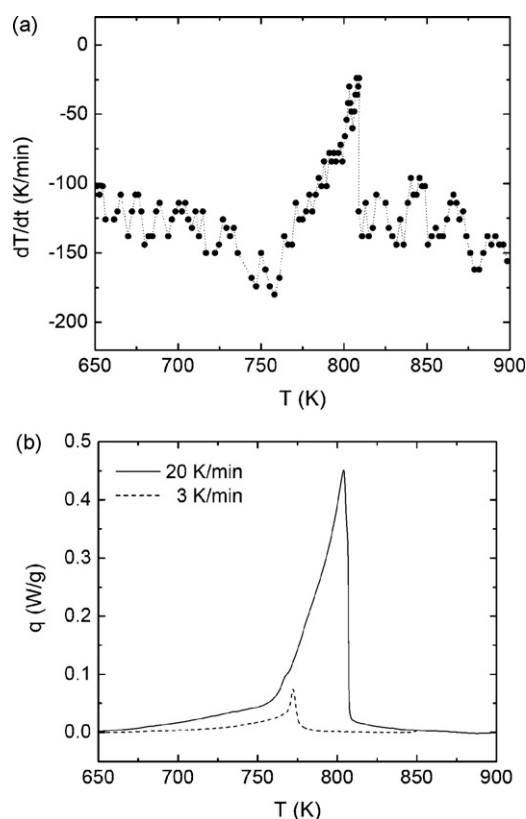
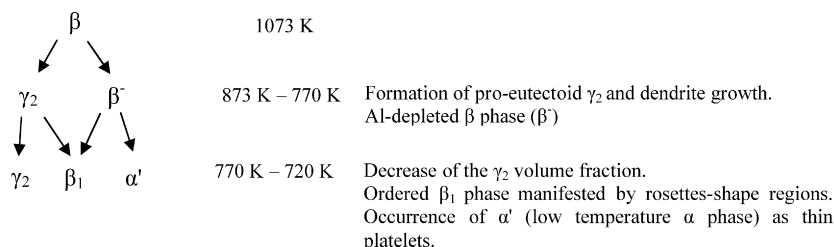


Fig. 3. Ordering peaks observed under cooling from 950 K by: (a)  $T-t$  measurements at 100 K/min; (b) calorimetric measurements at 20 and 3 K/min.

and each transformation influences those that follow. The sequence of transformations, when the sample is cooled at slow rate (3 K/min), are outlined in the diagram below for the Cu–22.60Al–3.26Be (at%) alloy:



In a Cu–22.6Al (at%) alloy, the first phase precipitated during continuous cooling at slow cooling rate is  $\alpha$  phase, and the alloy behaves as hypoeutectoid [1]. The sequence of transformations observed in the studied alloys is qualitatively similar to that of a hypereutectoid Cu–Al alloy, where the first phase precipitated is  $\gamma_2$ . It indicates the strong modifications introduced by Be on the Cu–Al phase diagram.

The disorder–order transition occurs around 800 K for the matrix of  $\beta$  phase with the initial composition, as seen in Fig. 3 for the sample with a high cooling rate. This result is in agreement with that previously reported by Jurado et al. [3]. They have found a single first order disorder–order transition in the Cu–Al–Be system, from a A2 to a DO<sub>3</sub> structure, at around 800 K for similar chemical composition. The current results show that ordering temperature is shifted to lower values, 770 K, when the

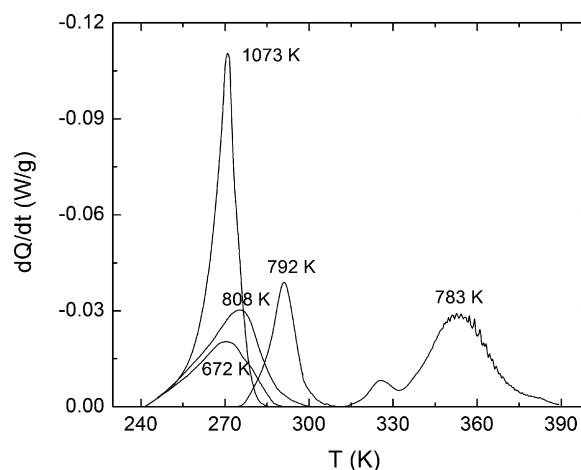


Fig. 4. Heating DSC cycles of quenched specimens from selected temperatures along the cooling curves. Quenching temperatures are indicated. The heating rate is 10 K/min.

sample is cooled at slow rates, allowing the precipitation of  $\gamma_2$ . In comparison with  $\beta$  phase,  $\gamma_2$  is richer in Al and Be, with a composition Cu–27.9Al–4.6Be (at%) [11], and consequently its precipitation depletes the matrix of these elements. According to the studies of Jurado et al. [3,12], the ordering temperature decreases with the decrease in the Al content, while Be content does not have significant effect. The decrease of Al in  $\beta$  phase owing to  $\gamma_2$  precipitation could then account for the modification in the ordering temperature. At low temperatures,  $\alpha'$  crystals in the form of thin platelets grow in the matrix. Similar to the Cu–Al alloy [8], these platelets initially precipitate in the aluminum deficient region between the rosettes of ordered  $\beta$  phase,  $\beta_1$ . They would be formed by a bainitic mechanism, i.e. the plates nucleate by a shear mechanism in the same way

as the growth of martensite plates, but subsequently grew by diffusion-controlled processes, as have been observed in Cu–Al [8] and Cu–Zn–Al alloys [13].

The evolution of the microstructures and the critical temperatures determined in the studied alloys were compared to those reported for polycrystals Cu–23.26Al (at%) [8,2], Cu–22.7Al–2.8Be (at%) [7], and a Cu–23.23Al–3.54Be (at%) monocrystalline alloy [9]. A quasi-binary Cu–Al–Be phase diagram, for approximately 23 at% Al, was built based on continuous cooling data (Fig. 5). The ordering temperature for each alloy was estimated as the temperature at which rosettes of  $\beta_1$  phase appear during continuous cooling at a rate slower than 5 K/min. The Cu–23Al at% alloy presents a hypoeutectoid behaviour. As the beryllium content increases, the pro-eutectoid  $\alpha$  phase formation temperature shows a marked decrease, while

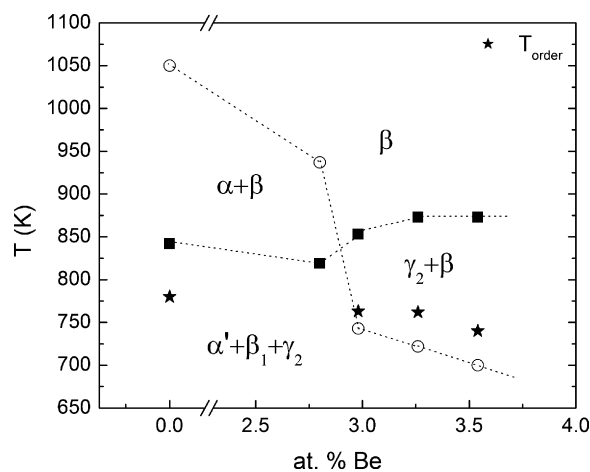


Fig. 5. Phase diagram of the Cu–Al–Be alloy with  $\approx 23$  at% Al. See text.

the  $\gamma_2$  formation temperature remains practically unchanged. As the content of Be reaches and exceeds 2.9 at%,  $\gamma_2$  is the first observed phase and the alloy presents a hypereutectoid behaviour. This shows that small modifications in the beryllium content produce effective changes in the ranges of phase stability. According to Belkahlia et al. [7], upon cooling of a Cu–Al–Be alloys with 2.8 at% Be, the beginning of the  $(\gamma_2 + \beta)$  field occurs at higher temperatures as the aluminum content increases, while the temperature of the beginning of the ternary domain  $(\alpha' + \beta_1 + \gamma_2)$  decreases. In this aspect, the beryllium effect is qualitatively similar to that of aluminum.

DSC cycles show that the precipitates have a marked effect on the  $\beta$ -martensite transformation. The temperature of the calorimetric peak for the martensite to austenite transformation,  $A_p$ , could be well determined, and it gives a quantification of this effect. Fig. 6 shows the  $A_p$  dependence on the quenching temperature,  $T_q$ , for samples Cu–22.60Al–3.26Be (at%), as well as the  $\gamma_2$  volume fraction,  $f_{\gamma_2}$ . The  $\gamma_2$  volume fraction could not be measured when martensite is present at RT because the martensite needles mask the precipitation. The transformation peak temperature is markedly changed by  $\gamma_2$  precipitation, with

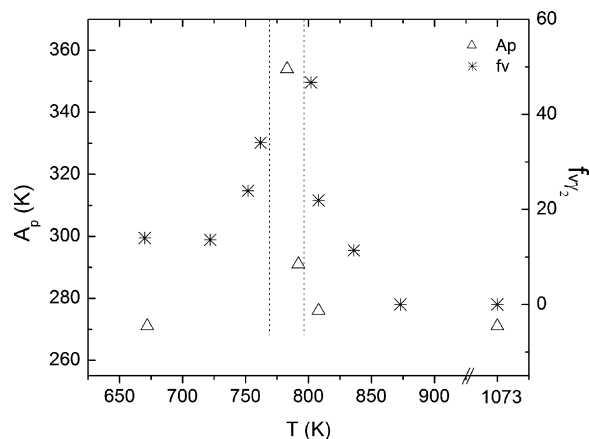


Fig. 6. Peak temperature of the calorimetric signal for the martensite to austenite transformation,  $A_p$ , and  $\gamma_2$  volume fraction as a function of the quenching temperature.

the highest shift of  $A_p$  by around 80 K for  $T_q \approx 783$  K relative to the reference sample, in  $T_q = 1073$  K condition. A similar alloy without precipitation quenched from almost the same  $T_q$  shows an  $A_p$  increase around 10 K [14].

Different possible contributions have to be considered in order to explain the influence of  $T_q$  on the critical transformation temperatures. The depletion in Al and Be content of  $\beta$  phase owing to the  $\gamma_2$  precipitation could lead to an effective change in the transformation temperatures due to the strong dependence of these temperatures with the composition. A decrease in 1% of Be results in an increase of around 100 K in Ms; while a decrease in 1% of Al causes an increase of around 40 K [3,7]. This chemical effect becomes important where a maximum in  $f_{\gamma_2}$  can be expected to exist. The compositional changes caused by  $\gamma_2$  precipitation, and the consequent shifts in the transformation temperatures, have been observed in other CuAl alloys with addition of Ni [15]. Another contribution to be discussed is the influence of the quenched-in vacancies on the transformation critical temperatures. Romero et al. [14] have reported a maximum of retained vacancy concentration after quenching from 775 K. According to their results, the maximum shift in the transformation temperatures is around 10 K, and it is attributed to the relative depletion of Be concentration related to vacancy excess. The shift of the martensitic transformation temperatures measured in the current study is significantly larger. This supports the hypothesis that the shifts observed are mainly related to the compositional change in the  $\beta$  phase owing to  $\gamma_2$  precipitation, and in a lower extent to the quenched-in vacancies. The transformation peak temperature for  $T_q = 670$  K, is almost the same as that for the reference sample. For this  $T_q$ ,  $\alpha'$  phase is also present, but it does not seem to affect the  $\beta$ -martensite transformation.

## 5. Conclusions

The continuous cooling transformation behaviour and its effect on the thermoelastic behaviour of two Cu–Al–Be shape memory alloys have been studied by electrical resistometry, microscopy and differential calorimetry. With a slow cooling rate (3 K/min), the alloys show a hypereutectoid behaviour as a result of Be addition, and the sequence of  $\gamma_2$  and  $\alpha'$  precipitation plus  $\beta$  phase ordering was properly characterized. The progression of phase transformations is characterized by the nucleation and dendritic growth of pro-eutectoid  $\gamma_2$ ; followed by  $\beta$  phase ordering ( $\beta_1$ ), a decrease of the  $\gamma_2$  volume fraction, and the precipitation of  $\alpha'$  phase. A quasi-binary phase diagram in the range of approximately 0.0–4.0 at% Be with around 23 at% Al was estimated from continuous cooling data. As Be content increases, the  $\gamma_2$  formation temperature slightly increases, while the  $\alpha$  formation temperature decreases. The transition from a hypoeutectoid to a hypereutectoid behaviour occurs for a Be content of around 2.9 at%. The precipitation of  $\gamma_2$  phase depletes the  $\beta$  matrix of Al and Be, leading to a decrease of the ordering temperature. A shift of the martensite–austenite critical temperatures above RT is observed for the higher  $\gamma_2$  volume fraction. This can be mainly attributed to the  $\beta$  phase compositional changes owing to  $\gamma_2$  precipitation.

## Acknowledgements

The authors acknowledge the financial support of the CONICET, the ANPCYT, the Secretaría de Ciencia y Técnica of the Universidad Nacional del Centro, and the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires, Argentina.

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