

Thermal Stability of Beta Phase in a Cu-Al-Be Shape Memory Alloy

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ABSTRACT.

Thermal stability of the beta Cu-Al-Be phase with an eutectoid composition was studied by thermoelectric power measurements. Depending on the aging temperature, precipitates of the α_2 and γ_2 phases were identified by optical and electron microscopies. From these results, C curves were deduced in a TTT diagram and a peritectic $\beta \rightarrow \alpha_2$ transition temperature was deduced to be close to 275°C.

1. INTRODUCTION.

In spite of the good shape memory behavior shown by Cu-Al-Be alloys [1,2,3,4,5], not enough studies have been performed about the effect of Be in the low temperature region of the Cu-Al phase diagram. In earlier work an M_s temperature dependence with composition was defined as $M_s = 638 - 43\%Al - 302\%Be$ (wt.%) [1,2]. Recently, Belkahla found an alternative M_s relationship using a greater number of samples: $M_s = 1245 - 71\%Al - 893\%Be$ (wt.%). Moreover, he found that 0,5 wt% Be addition decreases the eutectoid line in about 50°C in Cu-Al alloys [3,4].

We know that shape memory properties in Copper based alloys depend on the martensitic transformation stability, and therefore they also depend on the β phase stability. This information is then important for applications. Some of the authors have reported a preliminary study on the β phase stability made by calorimetric techniques [5]; a TTT diagram was deduced, but no information about the precipitates formed was presented. The aim of this work is to identify the precipitated phases during isothermal aging treatments, and to learn about the effect of Be additions in the low temperature region of the phase diagram. Thermo-electric power (TEP) measurements and transmission electron microscopy were used in order to obtain this information.

2. EXPERIMENTAL.

The alloy with chemical composition: Cu-11,5wt.%Al-0,5wt.%Be was provided by the Trefimétaux Society, as a 3 mm. thickness plate ribbon. After quenching from about 650°C the measured M_s temperature was between -45 and -50°C.

A step quenching was applied to avoid M_s variations caused by ordering [6]. The aging treatments were carried out in salt baths from 200°C to 500°C and in oil baths for lower temperatures. After each aging treatment, the samples were quenched to 100°C and left for 15 minutes at this temperature before performing TEP measurements at room temperature. TEP measurements were made on samples of 50x3x1 mm³, by applying a temperature gradient (ΔT) of 10°C.

The microscopic observations were made in a Jeol 200-CX transmission electron microscope (TEM), and in an optical microscope. Disk shaped samples ($\phi=3$ mm) for TEM studies were cut by using a low speed diamond saw. Electrochemical thinning of the disks was performed by the twin jet method, until perforation of the samples. For electron microscopy, the chemical solution was: 25 vol% HPO₃ + 25 vol.% CH₃OH + H₂O. The polishing solution used in optical microscopy was: 100 ml of acetic acid (75%aq.) + 20 ml of HNO₃ + 30 ml of acetone; another etching solution was 95 ml of ethanol + 2gr of FeCl₃ + 2 ml of HCl.

3. RESULTS.

3.1 Thermoelectric power measurements.

Figure 1 shows the thermoelectric power (TEP) evolution with time for agings at several temperatures. Two different stages can be clearly identified: The former is an increase of the TEP values, and the second corresponds to a decrease of the same. The first stage does not correspond to any change detected by calorimetric measurements. In contrast, the second stage occurs at times when clear variations in the calorimetric response are detected due to precipitation.

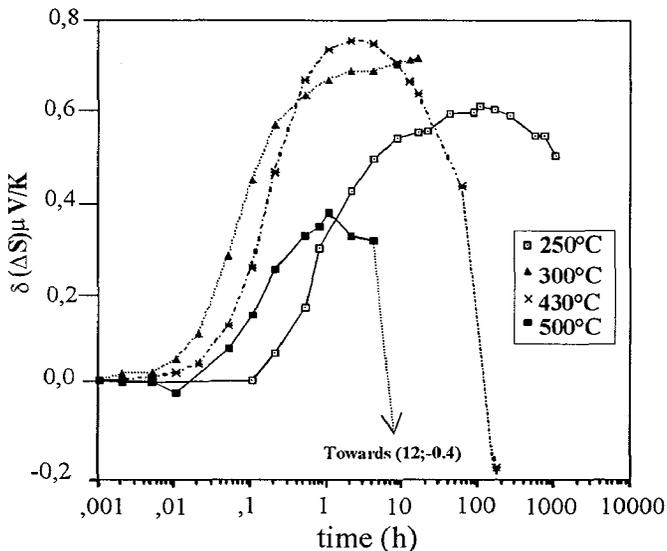


Figure 1 : Thermoelectric power during aging.

the precipitates have a polyhedral shape, these precipitates are very similar to the γ_2 precipitates found in Cu-Al-Ni alloys [9,10], and also similar to the γ_2 precipitates in Cu-Zn-Al alloys [11]. These precipitates were identified as a γ_2 phase.

3.2 Transmission Electron Microscope Observations.

TEM observations showed two different types of precipitates, immersed in the β phase matrix with a well defined DO₃ ordered structure, as reported before [4]. The first type of precipitates appeared after aging at low temperatures, between 200°C and 275°C, and they were plate shaped with edges parallel to the cubic {100} planes of the β phase. The crystallographic analysis of these precipitates shows a structure similar to that of the α_2 phase of Cu-Al alloy [7,8].

For aging at higher temperatures, from 300 to 350°C, the

4. DISCUSSION.

The TEP results shows that for low temperatures, the first evolution stage has an activation energy of $E_A = 0,63 \pm 0,03$ eV. It is interesting to note that a comparable energy value was reported by Van Humbeeck for vacancies diffusion in β Cu-Zn-Al alloys, measured by positron annihilation [12]. The first stage could then be attributed to a diffusion mechanism of quenching vacancies in the β phase. On the other hand, the activation energy for ordering has been reported as $0,3 \pm 0,05$ eV [6], it is therefore possible that an ordering process occurs during vacancy migration.

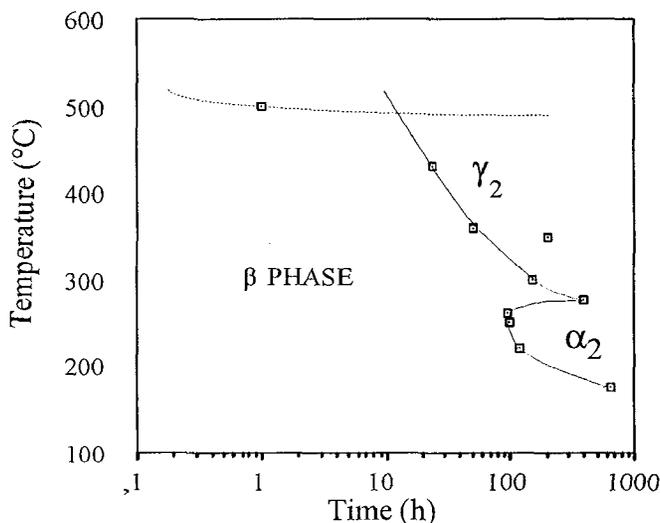


Figure 2. TTT diagram.

temperature of the characteristic transformations, with no shifts in composition. Therefore, the Cu-Al-Be phase diagram could be deduced from the Cu-Al one by a simple displacement toward the lower temperatures. The eutectoid temperature is decreased in about 50°C (i.e., to 500°C). The peritectoid temperature could be lowered too in about 50°C , which locates this temperature close to 300°C .

From the results presented here, the peritectoid temperature can be located more precisely at 275°C , because the α_2 phase was identified under this temperature.

This diagram is helpful to know the stability of the β phase, and in consequence that of the martensitic transformation and the one way shape memory applications. However, when the important transformation characteristic is the hysteresis, a more limited stability domain must be taken into account.

5. CONCLUSIONS.

The main conclusions of this work are:

1. The Thermoelectric power results show a strong evolution before precipitation, this process was attributed to a vacancy diffusion with an activation energy of $0,63 \pm 0,03$ eV. The DO_3 ordering occurs probably during vacancy diffusion.

From our results we can construct a TTT diagram as shown in figure 2. C curves in this diagram correspond to the formation of the equilibrium phases. For the low temperature domain (from 175 to 275°C) the proposed reaction is $\beta \rightarrow \alpha_2 + \beta$. In the middle domain (from 275°C to 350°C) the precipitation is proposed to be $\beta \rightarrow \gamma_2 + \alpha$. For the higher temperature region (higher than 500°C) the reaction $\beta \rightarrow \alpha + \beta + \gamma_2$ has been proposed by Belkahla et al. [3].

Close to the stoichiometric composition (Cu_3Al) of the equilibrium phase diagram, Belkahla et al. reported that Be adjunction produces a general decrease in

2. Two types of precipitation were identified in β Cu-Al-Be for agings at low temperatures, below 275°C the precipitates were of α_2 phase, and for higher temperatures the γ_2 phase was found.
3. The equilibrium phase diagram reported by Belkahla can be improved by adding a peritectoid reaction close to 275°C.

Acknowledgments:

H. Flores Zúñiga acknowledges the Tréfinmétaux society for the alloy provided, and the GEMPPM - INSA de Lyon, FRA.

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