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MARTENSITIC TRANSFORMATION AND METALLURGICAL STUDY OF LOW TEMPERATURE Cu-Al-Be TERNARY ALLOY

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Abstract: The present study on a Cu-Al-Be alloy has given the following characteristics: the addition of small concentration of beryllium to the eutectoïdal alloy close to Cu_3Al leads to a sharp decrease of the martensitic transformation temperatures. At the same time the composition corresponding to the maximum stability of the beta phase does not change significantly. The eutectoïdal temperature is lowered, but the temperature of beta solution treatment remains the same. Moreover there is no change in the nature of the martensitic transformation ($DO_3 \leftrightarrow$ 18R). All these properties are very interesting from the industrial point of view: whatever is the M_s temperature chosen, the beta phase stability will be approximately the same since the alloy is always close to the "eutectoïdal" composition. This alloy will be the complement of Cu-Al-Ni alloy towards low transformation temperatures (from -200 °C to +60 °C) with approximately the same stability at high temperature.

INTRODUCTION

Many investigations for application uses have been reported on Cu-base shape memory alloys such as Cu-Zn-Al, Cu-Al-Ni, etc..., but the first one is very sensitive to aging (1-2) and martensitic stabilization (3) and therefore cannot be used above 100 °C, and the second alloy becomes fragil when its martensitic transformation temperature domain is below about 50°C; moreover this martensitic transformation changes from $\beta_1 \rightarrow$ 18R to $\beta_1 \rightarrow$ 2H and becomes less reversible (4). A gap is therefore present corresponding to alloys transforming below 50 °C and resisting to aging at about 200 °C. Fragmentary results on Cu-Al-Be alloy (5-7) allow to hope that this alloy can fill this gap. The purpose of this work is to explore this alloy from metallurgical point of view (phase diagram) and martensitic transformation (control of transformation temperature).

EXPERIMENTAL

The alloys are prepared by induction melting of Cu-4% Be commercial alloy, pure aluminium (99,99 %) and electrolytic copper, into an evacuated chamber under a nitrogen rich atmosphere. Cylindrical ingots are obtained by in-situ pouring of the

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liquid alloy into bulk copper molds. The polycrystals are then homogenized at 850 °C for 5 hours and quenched into water at room temperature. Chips are collected for analyse by Plasma Emission Spectroscopy and the resulting compositions are obtained with 0,02 % accuracy.
Samples of 100-150 mg are cut out from the ingots for the measurements of Differential Scanning Calorimetry (DSC). Conventionally the M_s temperature is chosen for 10 % of martensite transformation and DSC curves are measured at a rate of 5°C/min (unless otherwise stated). Samples of size (4 x 4 x 40 mm^3) are cut for dilatometry measurements. Dilatometry and DSC curves which allow to determine the variations of the eutectoïdal temperature are made at a rate of 0,5 °C/mn.

RESULTS and DISCUSSION

The compositions and eutectoïdal temperatures for fifteen alloys used to determine the beryllium content influence on the eutectoïdal temperature are given in table 1. For these alloys the transformation cycles are accomplished from 0 to 600 °C at a rate of 0.5 °C/min. The eutectoïdal temperature as a fonction of beryllium content is displayed on figure 1.
Figure 1a shows that the eutectoïdal temperature first decrease until about 0.7 wt% beryllium then increases to be stable above 1 % Be. Figure 1b exhibits the same evolution focussed on beryllium percentages used in the following. Indeed alloys with more than 0.7 wt% beryllium have an M_s temperature below -210 °C as will be seen later and are not industrially very useful. In the studied domain a linear decrease of the eutectoïdal temperature with beryllium content is observed. The eutectoïdal temperature, considered here, is the average value between eutectoïdal temperature obtained at increasing temperature and the one determined at decreasing temperature. The DSC apparatus being limited to 600 °C, dilatometry measurements have been used to bring more informations on the phase diagram at higher temperatures (up to 900 °C). Concerning the eutectoïdal temperature the two experimental techniques are in good agreement.

The results obtained by these measurements (calorimetry, dilatometry) on alloys of tables 1 and 2 allow to draw a section of the Cu-Al-Be ternary diagram for 0.47 wt% beryllium (see figure 2). It can be stated that the minimum temperature of β phase stability (600 °C) is close to 11.8 wt% aluminium composition, that is to say at almost the same place than for the binary Cu-Al alloy. Moreover the eutectoïdal temperature exhibits a decrease of 50 °C in relation to the one of the binary alloy. A new ternary domain ($\alpha + \beta + \gamma_2$) occurs for this composition domain between the minimum temperature of β phase stability and the eutectoïdal temperature.

Table 2 gives the compositions and M_s temperatures for eight alloys elabored with constant beryllium content in order to determine aluminium influence on transformation temperatures. The linear variation of M_s temperature with aluminium content (see figure 3a) allows to deduce an influence coefficient of 71 ± 8 °C by weight percent for aluminium.
Table 3 gives the compositions and M_s temperatures for twenty-one alloys elabored with aluminium content close to the "eutectoïdal" composition. The linear variation of M_s transformation temperature with beryllium content (see figure 3b) allows to determine an influence coefficient of 893 ± 20 °C by weight percent for beryllium.

From these results, the following relation can be written which is valid for aluminium and beryllium contents included between 10–12,5 % and 0,3–0,65 % respectively:

$$M_S\ (°C) = 1245 - 71\ \%\ Al - 893\ \%\ Be$$

The first striking feature that can be deduced is the very high sensitivity of the transformation temperature to the alloy composition especially for beryllium.

Figure 4 shows typical DSC curves at cooling for a specimen of alloy (CAB 5) aged at 220 and 260 °C for various times. As can be seen from the curves the martensitic transformation is not appreciably affected by 220 °C or 260 °C aging as long 100 h. A small shift toward high temperatures is noticed above 200 h aging. whereas some degradation of the shape of the DSC curve is observed correlated with an increase of the hysteresis of the transformation. The degradation is probably due to the partial decomposition of the β_1 phase into products close to α and γ_2 which acts on the transformation temperatures (modification of the remaining $\beta 1$ phase) and the hysteresis (obstacles to interfaces movements).

CONCLUSION

From the present study the following conclusions can be given:

— An addition of small concentrations of Beryllium to Cu-Al alloys close to the eutectoïdal composition leads to a sharp decrease of the martensitic transformation temperatures.

— The aluminium composition corresponding to the maximum stability of the β phase does not change significantly.

— The eutectoïdal temperature is lowered, but the temperature of β solution treatment remains the same.

From other measurements not shown here it has been proved that the nature of the martensitic transformation is not affected ($DO_3 \leftrightarrow 18R$). All these properties are interesting: whatever is the M_s temperature chosen (between -200 °C and 50 °C) by addition of Be to the eutectoïdal Cu-Al alloy, the β phase stability will be approximately the same since the alloy stays always close to the eutectoïdal composition. This alloy is therefore the good complement of Cu-Al-Ni alloy towards low transformation temperatures with approximately the same resistance to ageing.

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Référence	% Al (wt)	% Be (wt)	T. eut. (°C)
CAB 94	11,53	0	558
CAB 3	11,42	0,31	520
CAB 12	11,67	0,33	513
CAB 10	11,57	0,37	512
CAB 15	11,66	0,42	511
CAB 4	11,50	0,43	510
CAB 14	11,79	0,47	509
CAB 64	11,91	0,47	508
CAB 19	11,67	0,51	508
CAB 13	11,72	0,52	508
CAB 17	11,79	0,54	508
CAB 2	11,40	0,65	505
CAB 90	11,74	0,95	515
CAB 91	11,73	1,42	517
CAB 92	11,79	1,90	517

Table 1: Beryllium content influence on eutectoïdal temperature.

Référence	% Al (wt)	% Be (wt)	M_s (°C)
CAB 52	10,37	0,47	95
CAB 53	10,88	0,47	50
CAB 54	11,35	0,47	13
CAB 55	11,65	0,47	- 6
CAB 56*	11,65	0,47	0
CAB 57	12,27	0,47	- 36
CAB 64	11,91	0,47	- 25
CAB 60	12,45	0,47	- 61

Table 2: Aluminium content influence on transformation temperature (* single crystal).

Référence	% Al (wt)	% Be (wt)	M_s (°C)
CAB 3	11,42	0,31	159
CAB 12	11,67	0,33	121
CAB 10	11,57	0,37	83
CAB 15	11,66	0,42	42
CAB 4	11,50	0,43	42
CAB 6	11,45	0,47	1
CAB 14	11,79	0,47	- 10
CAB 18	11,76	0,47	- 7
CAB 24	12,04	0,47	- 20
CAB 19	11,67	0,51	- 48
CAB 23	12,04	0,51	- 55
CAB 13	11,72	0,52	- 41
CAB 7	11,41	0,52	- 34
CAB 56	11,63	0,52	- 47
CAB 5	11,65	0,52	- 50
CAB 22	11,69	0,54	- 64
CAB 17	11,79	0,54	- 64
CAB 8	11,46	0,55	- 70
CAB 21	11,70	0,56	- 84
CAB 20	11,78	0,57	- 95
CAB 2	11,40	0,65	-147

Table 3: Beryllium content influence on M_s temprature.

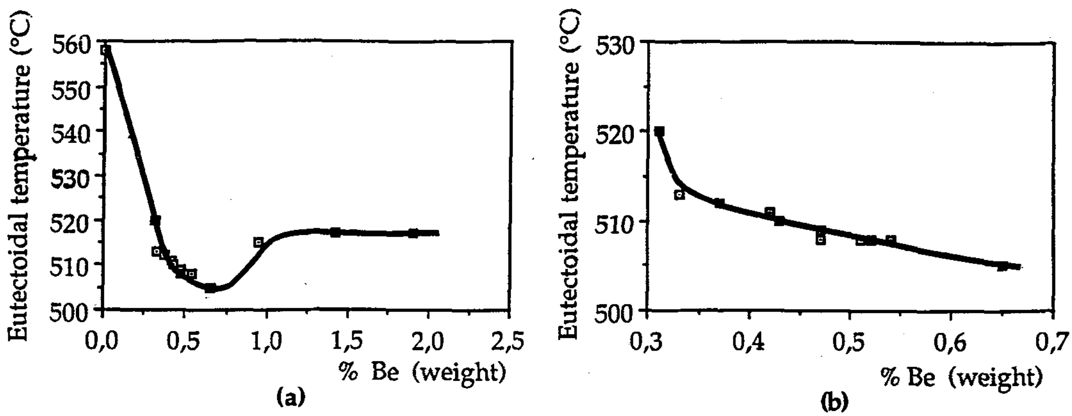

Figure 1: Beryllium content influence on eutectoïdal temperature.

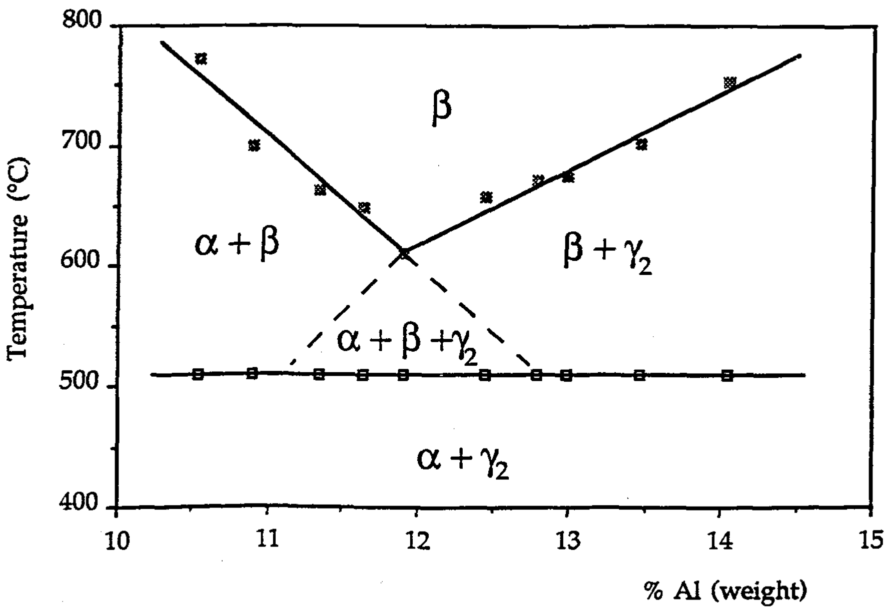

Figure 2: Section at 0.47 % Be of Cu-Al-Be ternary alloy.

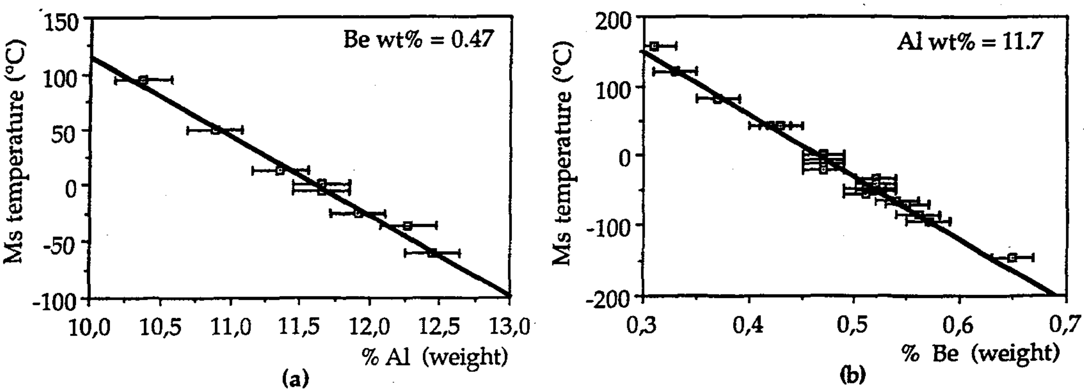

Figure 3: Correlation between aluminium (a) and beryllium (b) contents and M_S transformation temperatures in Cu-Al-Be ternary alloy.

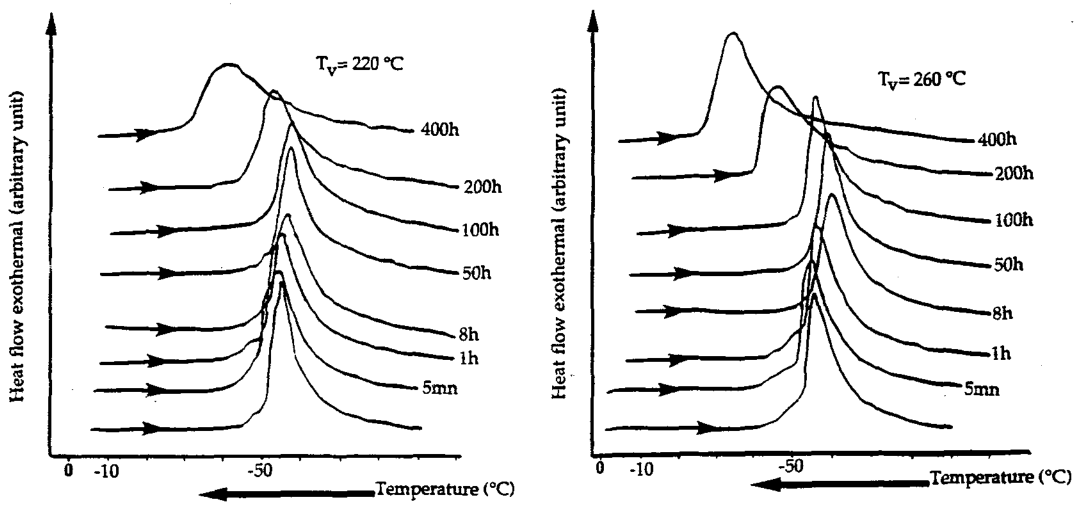

Figure 4: DSC curves after aging at 220 and 260 °C for various times in alloy CAB 5 on cooling.