

## COMPARATIVE STUDY OF CERTAIN Cu-Zn-Al-TYPE ALLOYS CONCERNING THEIR SUPERELASTIC BEHAVIOR AND SHAPE MEMORY

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Three alloys have been studied with the composition ranging between (22.0-22.5)% wt Zn, (5-6,5) % wt Al, balance Cu, obtained by melting in an induction furnace and gravitational casting. The samples cast from the three alloys have been subjected to loading - unloading trials by stressing. The papers presenting also the corresponding diagrams which give the pseudoelastic parameters. The shape memory effect (SME) and two way shape memory effects (TWSME) have been studied by dilatometric analysis and the effect of small variations in the Zn and Al compositions on the critical points has been revealed. At the same time, the tensile and dilatometric curves for the plastically deformed and annealed samples have proved a visible improvement in the shape memory effect..

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### 1. Introduction

At an international scale the shape memory alloys (SMA) used mainly for commercial belong to the Ni-Ti or copper-based (Cu-Zn-Al and Cu-Al-Ni) systems. The Cu-Zn-Al alloys stay on the second place due to the higher characteristics of the Ti based alloys in different application. Yet, taking into account the very high price (about 1\$/g) of the Ni-Ti alloys, the Cu-based alloys remain a good economical alternative, due to their price 100 times lower [1,2]. To the above economical arguments one must add those concerning their physical properties, such as the 6% shape memory effect (SME) or 2% two way shape memory effect (TWSME)[3,4], a 1J/g mechanical work developed by SME by heating, as well as the pseudoelastic

Effect (PSE) of 5% developed during the isothermal mechanical unloading [3,5].

The researches carried out with the view to obtain the Cu-Zn-Al alloys have focussed mainly on improving the above mentioned properties by manufacturing monocrystalline alloys or using high-purity components and complex technologies, often less economical for certain applications.

The Cu-Zn-Al shape memory alloys with the chemical composition ranging between (19-30)wt% Zn; (2-6)wt% Al - (0.04-1.3)wt% (Mn, B, Ce, Co, Fe, Ti, V, Zn) - balance Cu began to be industrially manufactured quite recently, around 1990 [3], and they have not been investigated enough with regard to the influence of the manufacturing technology and especially of their chemical composition, on the shape memory properties specific to this alloys. This work represents a continuation of the studies performed on the manufacturing and characterization of this alloys [6,7] and aims at revealing the influence of the chemical composition variation on the memory effect and the superelastic behaviour. At the same time, the researches were meant to lead to a Cu-Zn-Al shape memory alloy, useful in producing thermostats with temperature ranging between 0 °C - 100 °C.

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## 2. Experimental

The Cu-Zn-Al have been melted in an induction heating furnace operating at 8000 Hz, at a power of 60 kW with graphite crucible having a loading capacity of 20 Kg. The metallurgical load consisted of components with technical purity (99,97 wt% - Cu; 99,50 wt% - Al; 99,5 wt% - Zn), the flux for the metallic bath protection consisting of a mixture:  $\text{CaF}_2 + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{B}_4\text{O}_7 + \text{NaCl}$  [8]. The samples were obtained by remelting in a high frequency (20000 Hz) induction furnace and gravitational casting in metallic moulds. The as-cast samples of  $\phi 8 \times 75$  mm. were then shaped at a size of  $\phi 5 \times 75$  mm.

The pseudoelastic tests and tensile test have been performed on a „Heckert” - FPZ 100/1 type tensile testing machine.

For dilatometric analysis a BAUARTT WEISS extensometer was used, the curves being plotted on a X-Y recorder type HEWLETT – PACKARD.

The alloy chemical composition has been determined on the emission spectrometer DV6 BAIRD.

## 3. Results and discussion

Eleven alloys have been prepared with compositions ranging between Cu – (14 - 25) wt% Zn – (3 – 6.5) wt% Al out of which three have been selected for this work having the chemical compositions given in Table 1.

Table 1. Chemical compositions of the experimentally studied Cu-Zn-Al alloys.

Symbol	Chemical composition, % wt							
	Cu	Zn	Al	Ni	Fe	Ti	Mn	Sn
A	72.70	22.0	5.0	0.22	0.03	0.003	0.03	0.01
B	71.16	22.31	6.22	0.20	0.02	0.03	0.04	0.02
C	70.72	22.5	6.50	0.23	0.001	0.003	0.03	0.01

Three as-cast samples taken from each of the three alloys have been first subjected to tensile test in order to determine the maximum value of the unit loading, a value useful in the subsequent determination meant to render evident the shape memory effects and the pseudoelastic behaviour.

The A, B and C alloys presented similar values of the tensile strength, ranging between  $220 \text{ N/mm}^2$  and  $250 \text{ N/mm}^2$ . After measuring the tensile strength, the samples from the A alloy were subjected to loading-unloading cycles on the tensile testing machine at a temperature of  $20^\circ\text{C}$ . The pseudoelastic twinning curves have been obtained, specific to the alloys in the austenitic state stressed at temperatures  $t > M_d$  [5]. Fig. 1 presents one of this tensile loading-unloading curves obtained on samples made of the A alloy, showing that for a unit loading of  $200 \text{ N/mm}^2$  close to the run-out limit on this alloy, permanent strains  $\epsilon_p$  of about 1% have been obtained. This strain is much lower than the value of 6% which can be obtained for a Ni-Ti-Fe alloy stressed under the same conditions [3], yet is close to the value specific to the Cu-Zn-Al alloys specified in the specialised literature [5].

Samples from the A alloy have been subjected to dilatometric analysis within the temperature range  $20 - 140^\circ\text{C}$ , after having previously been tensile strained up to values of the tensile unit loading lower than the breaking strain and to values corresponding to the permanent strain ( $\epsilon_p$ ) of about 1%. The dilatometric analysis has not revealed the presence of the shape memory effect, the sample behaving just like a usual metallic material. Obviously, it follows that this alloy shows no shape memory effect within the positive temperature range, but this effect might be present at negative temperatures, its critical transition points being placed below  $0^\circ\text{C}$ . This hypothesis is also backed up by the aspect of the loading-unloading curve presented in Figure 1, which shows a typical pseudoelastic twinning curve usually resulting within the austenitic temperature range exceeding the critical temperature  $M_d$  corresponding to the maximum temperature of stress induced martensite (SIM).

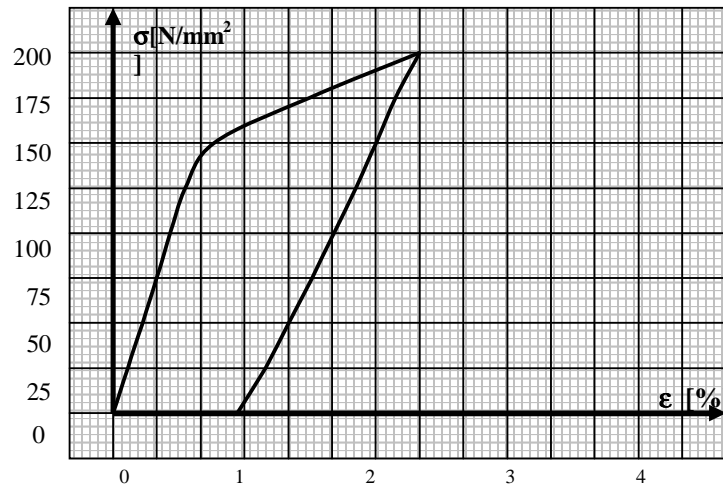


Fig. 1. Characteristic curve of the A alloy, subjected to one tensile loading-unloading cycle at the room temperature (20°C).

The as-cast samples from the B alloy have shown, after the first tensile loading-unloading cycle, a pseudoelastic curve with an total specific elongation of  $\epsilon_t=4\%$  and a pseudoelastic annealing with  $\epsilon_r=3.33\%$  and a plastic over strain  $\epsilon_p=0.77\%$ . As one can notice , a 0.31% increase of Zn and 1.22% increase of Al concentration as compared to the A alloy result in an improvement of the pseudoelastic parameters.

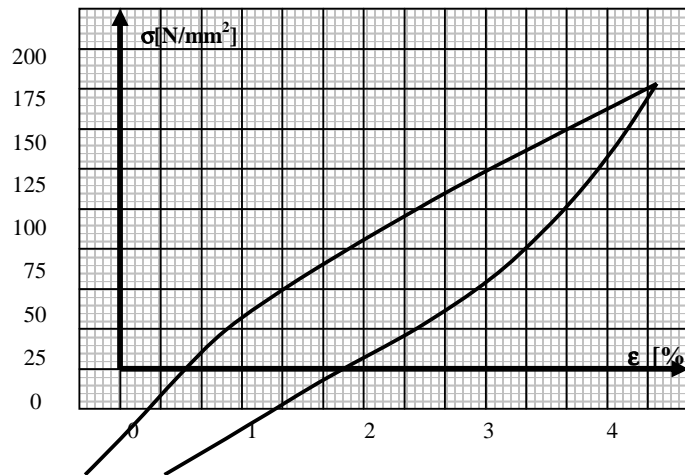


Fig. 2. Characteristic curve of the as-cast B alloy subjected to one tensile loading-unloading cycle at the room temperature ( $t=20^\circ\text{C}$ ).

After the first tensile loading-unloading cycle the B alloy samples have been subjected to dilatometric tests within the temperature range  $20^\circ\text{-}140^\circ\text{C}$ . Even though the B alloy has shown a superior pseudoelastic behaviour the dilatometric analysis has not revealed the presence of the shape memory effect within the specified temperature range.

The as-cast C alloy subjected to tensile loading-unloading tests showed a characteristic curve (Fig.3) with a plastic overstrain  $\epsilon_p=1.52\%$  (which is higher than the values obtained for the A and B alloys), as well as a non-linear elastic recoverable strain  $\epsilon_r=1.48\%$ , which is smaller than the one for the B alloy, get higher than the one for the A alloy.

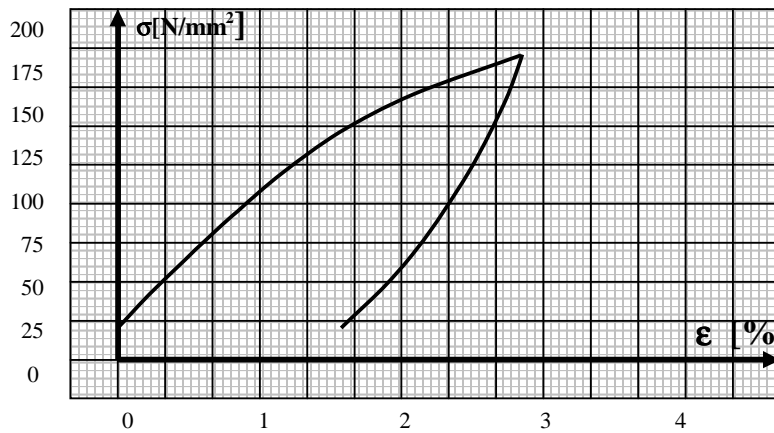


Fig. 3. The characteristic curve of the as-cast C alloy subjected of one tensile loading-unloading cycle at  $t=20^\circ\text{C}$ .

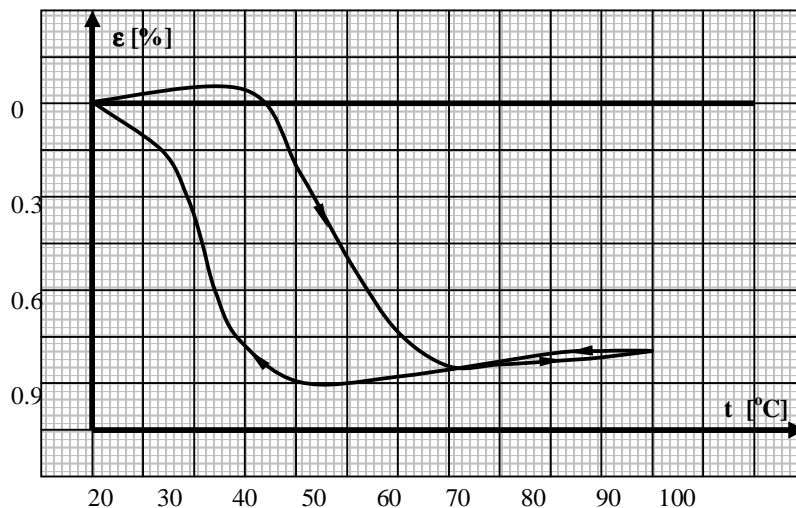


Fig. 4. The dilatometric curve illustrating the presence of a two-way shape memory effect stabilized after 10 heating/cooling cycles.

After the first tensile loading-unloading cycle, the C alloy samples has been subjected to dilatometric tests revealing a shape memory effect of about 2%. Going on with the dilatometric measurements after 10 heating/cooling cycles a stabilized two-way shape memory effect of about 1% was obtained, as presented in Fig. 4.

As far as the C alloy is concerned, light increases by 0.19%wt of Zn concentration and by 0.28%wt of Al concentration as compared to the B alloy lead to the drift of the critical transition points within the positive temperature range, and therefore to the occurrence of a shape memory effect. The higher plastical strain of the C alloy illustrated on the tensile diagram in Fig.3 can be explained by the fact that the alloy is in a martensite state (for these alloys the martensite is more plastic than the austenite [9]) at testing temperatures lower than the critical temperature  $M_s$  which, according to the dilatometric diagram (Fig. 4) is placed around  $42^\circ\text{C}$ .

After plastic processing by hot hammer forging at  $t \approx 820^\circ\text{C}$  and a water hardening treatment, the C alloy has registered an improvement of its tensile strength ranging between 260 –280  $\text{N/mm}^2$ . During the first tensile loading-unloading cycle on the forged and hardened samples the characteristic curve from Fig. 5 was obtained, which shows a visible increase of the total strain  $\epsilon_p = 4.2\%$ , an

increase of the pseudoplastic strain recoverable strain  $\epsilon_r = 1.66\%$  and a much higher permanent strain ( $\epsilon_p = 2.3\%$ ) than the values for the same as-cast alloy.

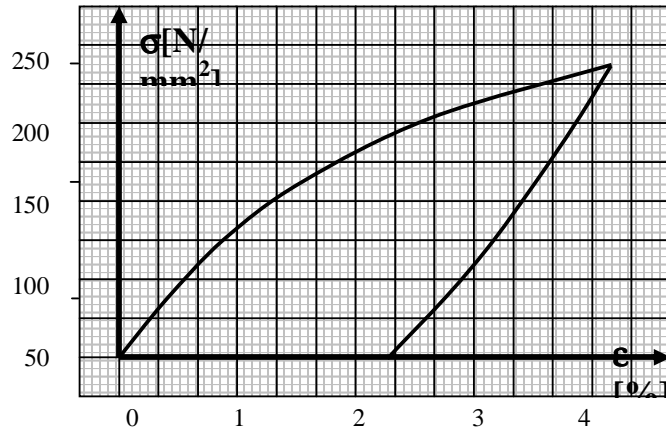


Fig. 5. The characteristic tensile curve of the forged and hardened C alloy at  $t=20^\circ\text{C}$ .

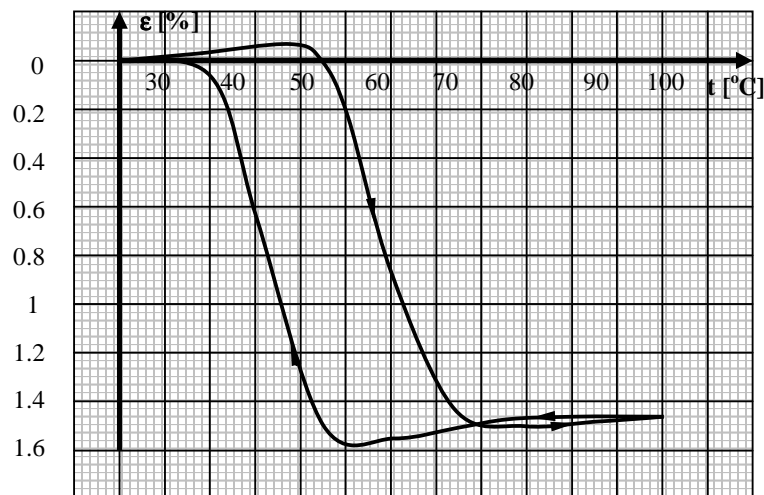


Fig. 6. The dilatometric curve stabilized after 10 cycles obtained on C alloy samples forged and hardened.

At the same time, the dilatometric analysis has revealed that the shape memory effect is higher for the strained and hardened C alloy, as compared to the same as – cast alloy.

Fig. 6 shows a two-way shape memory effect stabilized after 10 heating/cooling cycles, with an amplitude of about 1.5%, which is higher than in the as-cast alloy. One can notice that the plastic deformation and the thermal treatment did not result in significant alteration of the transition critical points.

#### 4. Conclusions

For the studied Cu-Zn-Al alloys, a narrow-range modification of the chemical composition does not result in important alteration of the unit tensile loading, but it leads to significant differences with respect to the pseudoelastic properties and shape memory effect.

The modification of the composition of the A alloy as compared to the B alloy by increasing the Al concentration by 1.22%wt and the Zn concentration by 0.31% results in the following

modifications of the pseudoelastic parameter: the overall elongation  $\epsilon_t$  increases from 2.3% to 4%; the pseudoelastic recoverable strain  $\epsilon_r$  increases from 1% to 3.33% and the permanent plastic  $\epsilon_p$  decreases from 1% to about 0.6%.

Both the A and B alloys present a pseudoelastic austenitic twinning curve at the room temperature and do not show a shape memory effect at positive temperatures.

The composition modification of the B alloy by increasing the Zn concentration by 0.19%wt and Al concentration by 0.28%wt results in the shape memory alloy C within the positive temperature range (0-140°C) effect backed-up by the dilatometric analysis.

The plastic deformation and the hardening treatment did not result in a significant modification of the critical points as compared to the as-cast state, but the shape memory effect increased.

Considering the above, one can draw the conclusion that the chemical composition has a deciding influence on the position of the critical temperatures and the shape memory effect. Taking into account the usual accepted variations of the industrial alloy chemical composition, in the case of the shape memory alloys with prescribed characteristics, it is necessary to elaborate a series of alloys with close compositions and to make a selection based on dilatometric analysis.

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