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Cu-based shape memory alloy for thermostatic actuator device

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The functional characteristics (actuation force, movement) of an actuator based on a shape memory alloy (SMA) depend strongly on the specific properties (transition temperature, degree of shape recovery) of the used alloy in order to making the actuating element. Development of new SMA or improving of those becomes "classical" lead to the achievement of some more performant actuators based on SMA-s. The paper presents two polycrystalline alloys having shape memory effect (SME), belonging to the Cu-Al-Ni system, with compositional range between (12.2-13.5)% Al, (3.3-3.5)% Ni, balance Cu, modified by alloying with small quantities of Mn and Ti. The study of these alloys aims to carry out some thermal actuators designed to function in 20-80°C temperature range. The structure investigation of alloys was performed by optical methods, while mechanical characterization was performed by tensile tests. Direct and reverse martensitic transition temperatures were evidenced by thermal analysis: electrical resistivity dependence on temperature, and dilatometrical analyse in 20-200°C temperature range. The obtained results show that small Mn and Ti additions inserted in the composition of studied SMA lead to improving the alloy's structure and to an important modification of the critical temperatures to the functional thermal domain of proposed actuator.

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1. Introduction

The Cu-based SMAs (CuAlNi and CuZnAl) represent a good economical alternative, for the NiTi alloys due to their price of 100 times lower [1]. The CuAlNi alloys are the only commercials shape memory alloys that can be used at temperatures over 100°C. These SMAs are characterised by a good mechanical characteristics and about 5 % degree of shape recovery. The transition temperatures of cubic to orthorhombic fazes observed in CuAlNi SMAs are situated in a wide range, from 80 to 200 °C and are strongly influenced by Al content of alloys [2]. For some applications, in temperature range below 100°C, these transformation temperatures are too high for practical use. The addition of Mn (max. 3 %) in CuAlNi SMAs in detriment of Al content, reduces the transformation temperature, shifts the eutectoid to higher Al content and improves their ductility, while addition of small quantities of Ti (max. 1 %) contributes to finishing of grain structure [3].

The study of crystalline phase transformation behaviour involves many techniques, such as the differential scanning calorimetry, electrical resistivity, thermal expansion, internal friction measurement and thermoelectric power [2].

The electrical resistivity and thermal expansion are two very sensitively material parameters at crystal structure modification vs. temperature. In present work, for the determination of austenitic (As, Af) and martensitic (Ms, Mf) transformation temperatures of the studied CuAlNi SMAs, the authors used the variations of these parameters during heating and cooling processes. The mechanical characterization of the alloys was performed by tensile tests.

2. Experimental

CuAlNi SMAs usually contain 11-14.5 % Al and 3-5 % Ni, the balance being Cu. The martensitic transition temperatures can be adjusted by varying chemical composition. The following empirical relationship was useful for first estimate of the martensite-start (Ms) temperatures: [3]

$$Ms\ (^\circ C) = 2020 - 134\ (\text{wt}\ \%\ \text{Al}) - 45\ (\text{wt}\ \%\ \text{Ni}) \qquad (1)$$

The studied CuAlNi SMAs were obtained by melted in an induction heating furnace operating at 8000 Hz, in an Al_2O_3 crucible having a loading capacity of 1 kg, in vacuum atmosphere at 0,133N/m^2 pressure. The metallic load consisted of components with high purity (99.97 wt % - Cu, 99.80 wt % - Al, 99.95 wt % - Ni). The metallic bath was protected by a flux consisting in a mixture of CaF_2, Na_2CO_3, $Na_2B_4O_7$ and NaCl.

The samples, in wire and ribbon shapes, were obtained by remelting of small amounts of alloys in a high frequency induction furnace followed by rapid solidification in a copper mould.

The study of transition temperatures of experimentally SMAs was performed by using dilatometry and thermal resistivity analyses. For dilatometric analysis a Bauartt Weiss extensometer was used, the curves being plotted on an X-Y recorder. Electrical resistance measurements were performed using the four-point method by home-made setup. The measured voltage across two points was given by a constant current through the sample of 30 mA intensity. The dependence of electrical resistance vs. temperature was recorded by means of X-Y recorder.

The tensile tests have been performed on a Heckert - FPZ 100/1 type tensile testing machine.

The chemical analyses of prepared alloys were performed by gravimetric and volumetric chemical methods. For the samples which allowed, the chemical composition were determined and by means of DV6 Baird emission spectrometer.

3. Results and discussion

Eight alloys with compositions ranging between (12-14) wt % Al and (3-4) wt % Ni have been prepared, out of which two have been selected for this work having the chemical compositions given in Table 1.

Table 1. The chemical compositions of the experimentally studied CuNiAl SMAs.

Symbol	Chemical composition, wt. %				
	Cu	Al	Ni	Mn	Ti
A	83.18	13.20	3.40	0.04	0.01
B	83.21	12.21	3.42	1.02	0.06

Reported to the chemical composition of the A alloy in B alloy we substituted 1 % Al with Mn in order to obtain a decrease of transition tempera-tures and to improve ductility of alloy. Small supplementation of Ti quantity has been done in order to finishing grain structure of B alloy.

The as-cast samples taken from each 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 both alloys presented similar values of the tensile strength, of about 240N/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 20ºC. Fig. 1 presents a tensile loading-unloading curve obtained on sample with 3 mm diameter made of the A alloy, showing that for a loading of 240 N/mm^2 applied to the alloy, a permanent strain, ε_p of about 1% have been obtained.

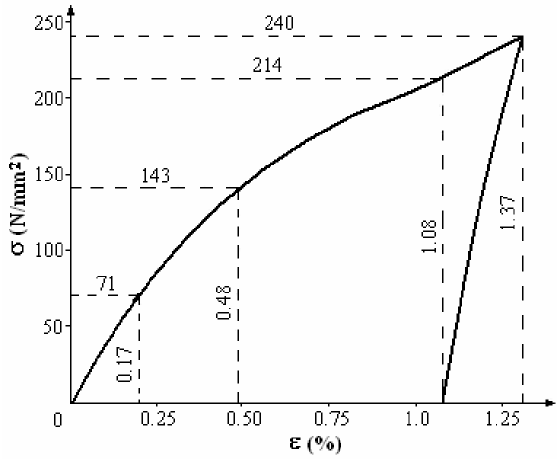

Fig. 1. Characteristic curve of the A alloy, subjected to the tensile loading-unloading test at room temperature.

After the first tensile loading-unloading cycle the A alloy sample have been subjected to dilatometric test within the temperature range 20-240°C. The obtained dilatometrical curve, which is presented in Fig. 2, revealed clear the austenite transition temperature: A_s = 150ºC and A_f = 195 ºC, and evidently, the presence of the shape memory effect. In according to relation (1) martensite-start temperature for the ternary A alloy is $Ms \approx 100$ °C.

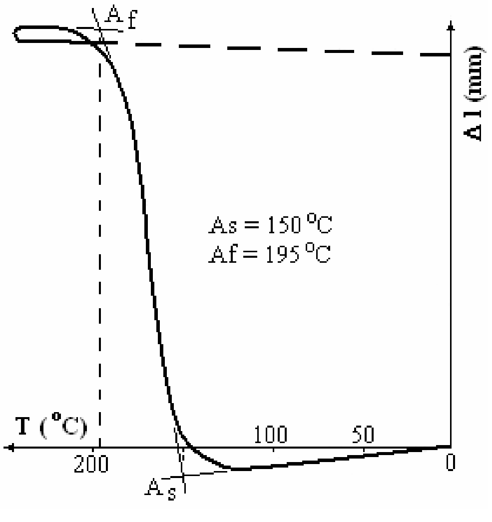

Fig. 2. Determination of austenite transition temperatures by dilatometrical analyse for A alloy.

Dilatometrical study on B alloy was performed from RT to 125 °C temperature range, on samples in two different states: after annealed at 750ºC and hot rolled (Fig. 3) and after hot rolled and quenched in water-ice from 750ºC (Fig. 4) at heating with 0.5 ºC/min heating rate.

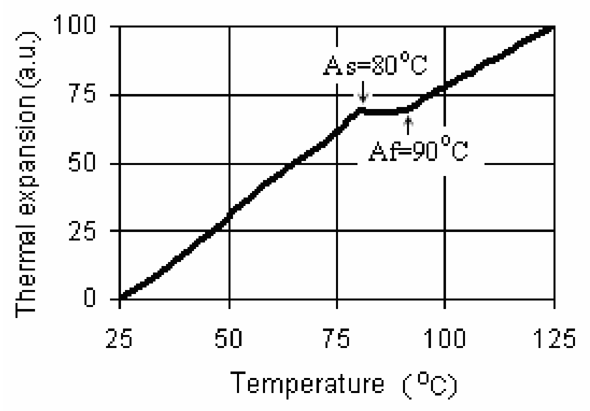

Fig. 3. Heating dilatation curve for B alloy in annealed and hot rolled state.

At room temperature (RT) exists one single phase - the martensitic phase. On heating, austenitic (M→A) transformation, in both cases, is evidenced by a horizontal segment on dilatation curves. The two transformation temperatures *As* and *Af* are 80 and 90°C for hot rolled sample and 78 respective 94°C for quenched sample. The smaller austenitic transformation temperature range in case of hot rolled sample (10 reported to 16°C) can be explained by residual stresses generated in deformation process which accelerate the phase transformation process.

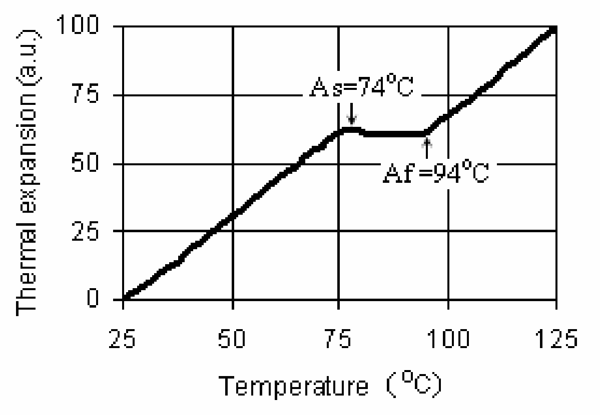

Fig. 4. Heating dilatation curve for B alloy quenched in water-ice from 750°C.

On cooling, due to a very small cooling rate (0.5°C/min), the β_1 metastable austenite, a solid solution based on Cu_3Al electronic compound, didn't transform integrally in γ_1' metastable martensite, it being partially decomposed in an eutectoid mechanical mixture [4] according to equilibrium eutectoid reaction:

$$\beta_1 \rightarrow \alpha + \gamma_2 , \tag{2}$$

where, α represents a complex solid solution based on Cu and γ_2 is a solid solution based on Cu_9Al_4 electronic compound with a complex cubic lattice. In this case, the martensitic start and finish transition temperatures *Ms* and *Mf* can not be determinate accurately by this method.

According to dilatometric curve registered at cooling (see Fig. 5) one can appreciate that the eutectoid transformation temperature have about the same value as austenitic finish transition temperature (93°C) occurred at heating.

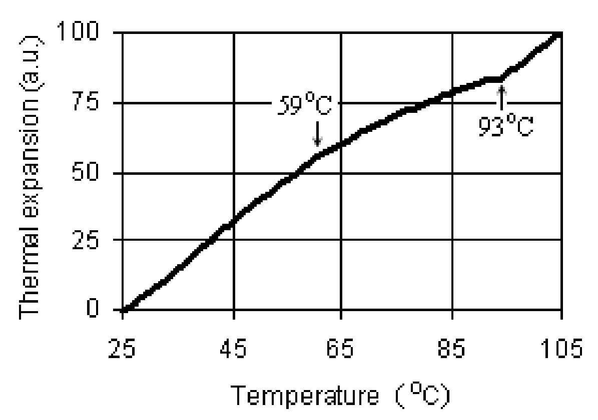

Fig. 5. Cooling contraction curve for B alloy in water-ice quenched from 750°C.

Further sample cooling do not produces jumps on contraction curve which should correspond to some critical temperatures. The contraction occurs continuously until it gets to initial value of sample length. At a subsequently heating in 25-125°C temperature range, a small increase of austenitic transformation temperature on dilatation curve was observed. This phenomenon may be caused by a long maintenance of the alloy in austenitic phase, when due to the appearance of some precipitates [5], austenitic phase changes lightly both its chemical composition and simultaneous martensitic transformation temperatures, which leads to shape memory behaviour degradation.

Direct and reverse martensitic transition temperatures for B alloy were evidenced and by study of dependence electrical resistivity vs. temperature. Electrical resistivity is a function of crystal structure. The CuAlNi SMAs have different crystal structures in different phases: bcc in high temperature austenitic phase, and orthorhombic in low temperature martensitic phase. Direct current resistivity measurements provide a simple and effective tool to detect structural (direct and reverse martensitic) transitions for these SMAs.

The sample chosen for the study of the effect of temperature on electric resistivity was heat treated for annealed at 750°C for 2 hours and then quenched in water-ice. The results of the resistivity measurements for a heating and cooling cycle are shown in Figure 6. The temperature dependence of the resistivity shows a sudden decrease while going from martensitic phase to austenitic phase and a sudden increase while going from austenitic phase to martensitic phase.

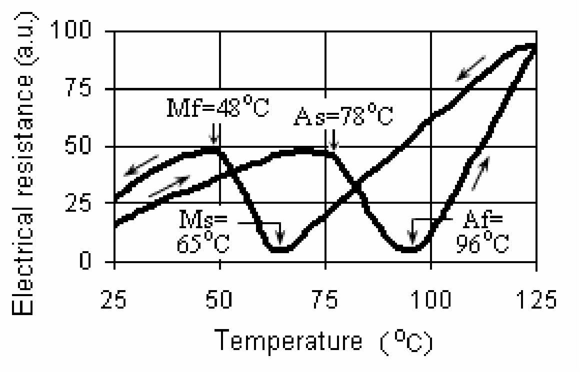

Fig. 6. Temperature dependence of electrical resistance of B alloy in water-ice quenched state.

Electrical resistivity plots show a clear peaks and determination of all transformation temperatures *A*s, *Af*, *Ms* and *Mf* is possible without ambiguity. Austenitic start (*As*) and finish (*Af*) transformation temperatures determined at heating are 78 and 96°C respectively. At cooling, the martensitic transformation start at 65°C (*Ms*) and finish at 48°C (*Mf*). It is obviously that austenitic and martensitic transformations which occur in heating-cooling cycle are delayed by about 30°C which represent the thermal hysteresis of transformation for B alloy.

The Mn was added into B alloy in order to reduce the transition temperatures and to suppression of the eutectoid reaction (2), but Ti was added to control grain size and to eliminate of intergranular cracking. Titanium is effective in reducing the tendency for grain growth. The addition of Ti leads to the formation of Ti-rich second phases. But the grain refinement is attributed to the grain-growth-inhibiting effect of Ti in solid solution [6]. In order to overcome the brittleness of the B alloy, Mn and Ti were added to them.

The A alloy (without grain-refining additions) shows very coarse grains (~1500 μm). But on addition of Mn and Ti as grain refiners in B alloy, we observed a considerable reduction in the grain size (~55%). This is attributed to the formation of fine precipitates that precluded the nucleation and growth of grains by the pinning effect [7].

The microstructure of alloys was investigated by means of optical microscope Neophot 21 doted with an electronic system for image acquisition. The microstructures of the base alloy (A) and the grains refined (B) are shown in Figures 7 and 8. The alloys show plate or needle-like martensites with a self-accommodating morphology [8].

The parent phase, austenite (β) from A alloy, gets converted to β_1' martensite. But in B alloy, the formed martensite has two different morphologies: acicular morphology - β_1' and self-accommodating morphology - γ_1'.

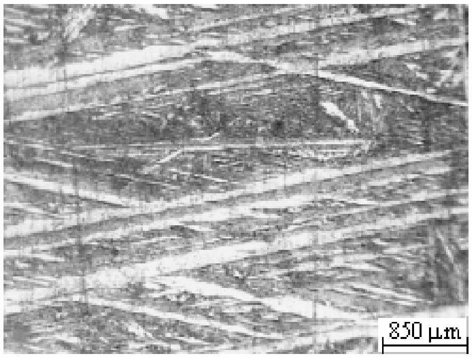

Fig. 7. Microstructure of A alloy after annealed 2 hours at 750°C followed by water-ice quenched.

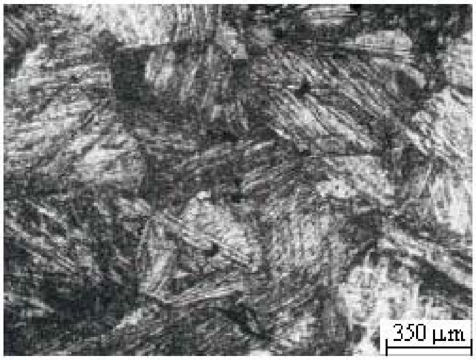

Fig. 8. Microstructure of B alloy after annealed 2 hours at 750°C followed by water-ice quenched.

4. Conclusions

By substituting one percent from Al content of the Cu13.2Al3.4Ni with Mn, an important decrease of transformation temperatures of about 40 °C was obtained. In the same time, it was observed a reduction of thermal hysteresis of transformation from about 40°C for Cu13.2Al3.4Ni SMA to about 30°C for new Cu12.2Al3.4Ni1MnTi SMA and can be usable for a thermostatic actuator device designed to function in 20-80°C temperature range.

The cooling with very small cooling rate or long maintenance in austenitic phase lead to the degradation of shape memory characteristics of CuAlNi SMAs because of the eutectoid transition appearance or the modification of chemical composition of the β_1 austenitic phase.

If the intermediate heat treatments (annealed) are correct made, the plastic deformation (cold and hot forged or rolled) did not resulted in a significant modification of the critical points as compared to the as-cast state, but the shape memory effect was improved.

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 CuAlNi 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 thermal analysis.

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