Preliminary Results of Copper Based Shape Memory Alloys Analysis used for MEMS Applications

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Abstract. Shape memory alloys (SMAs) are commonly used in micro-electro-mechanical systems (MEMS). Having the unique shape memory, super-elastic affects and now damping capacity SMAs have become an important smart material for a broad range of engineering applications in last year's. Copper based SMAs are promising alloys, based on the obtaining price and good characteristic properties. Shape memory alloys as thin films are used for fast actuation in applications due to their high surface to volume ratio comparing to bulk SMAs. In this paper two shape memory alloys based on copper, proposed as targets in different deposition processes to obtain MEMS and with different chemical composition, are analyzed through scanning electrons microscope (SEM), XRD and EDAX considerations after water quenching and recovery heat treatments. The martensite variants are dimensioned and 3D aspects are also analyzed for both metallic materials. The metallic phases obtained after heat treatment are determined and compare in both thermal influenced cases.

Introduction

Shape memory alloys (SMAs) are materials (metallic, polymers, ceramiques etc.) that possess usually, two (or in special cases several) crystallographic phases so-named "reversible martensitic transformations" a diffusion-less transition [1]. Related to M↔A transformation there are two special effects. The shape memory effect (SME) refers to the ability of the metallic alloy (in our case) first deformed in its low-temperature phases (called "martensite" in analogy with classic steel phase) to remind and recover its original shape upon heating to its high temperature phase [2]. This effect considered at macroscopic scale represents a thermally induced crystallographic phase change. On cooling stage the material transforms to the martensitic phase. This phase is characterized by a lower symmetry than parent phase and has different possible crystallographic orientations (usually named variants). In this paper the influenced of two heat treatments on the martensitic structure of two shape memory alloys is analyzed using 2D and 3D investigations at macro and micro scale. XRD results in both cases follow the chemical characterization of the phases after heat treatments apply. New thermal processes to obtain TWSME (two-way shape memory effect) in copper based SMA are

searched as new "thermal training processes" so the material will be able to "memorize" progressively a new shape [3, 4].

Experimental details

On two cast alloys that might exhibit shape memory effect (SME) two heat treatments were applied, water quenching (w.q.) and thermal recovery (t.r.), in order to highlight and analyze the martensite variants. These heat treatments consist in hardening by water immersion and recovery treatment performed in a laboratory oven, Vulcan A130 model, by heating the samples at 850° C and 900 seconds and cooled in water at room temperature (25° C) and secondly heating at 250° C and free air cooling to room temperature. XRD analyzes were performed immediately after the heat treatments of the samples that were "cold" polished in order to remove surface oxides formed during heat treatment. Alloys microstructure was determined by scanning electron microscopy (SEM Vega-Tescan LMH II) on cold mechanically polished samples and chemically attacked with $ClFe_3$ solution. The 3D analysis, using scanning electron microscopy, was performed using the software VegaTescan/Image operations/3-D view using a 45°, rotation angle and 50° elevation at the Z-scale at 10%.

Experimental results

Two CuZnAl shape memory alloys were obtained in a classical melting oven keeping the mass percentages of chemical elements mixture in proper ranges to exhibit shape memory effect. These alloys were poured in lamella shape and differentially heat treated to highlight the martensitic state of the material. These alloys were named as alloy 1, the quenched material and alloy 2 respectivelly the recovered one. By chemical considerations point of view the new obtained materials were analyzed through mass spectroscopy and X-ray energy dispersive analyze and the elements percentages are shown in Table 1.

Table 1. The chemical compositions of Cu-based shape memory alloys

Alloy number	Mass percentages %			Atomic percentages %		
	Cu	Zn	Al	Cu	Zn	Al
Alloy 1 (spectrometer)	72.1	21.2	6.41	66.7	19.1	14.17
Alloy 1 (EDAX)	71.9	20.6	7.5	66.5	18.6	15.2
Alloy 2 (spectrometer)	75.1	18.1	6.63	67.8	19.1	14.7
Alloy 2 (EDAX)	74.6	17.9	7.5	67.6	18.40	15.8

The materials present a good chemical homogeneity at macro and micro scale with reduce differences between the results of two different investigation methods.

For samples cooled from the β phase region of high temperature it can be observed a martensitic transformation L21 → M18R type. Using the XRD technique, the network parameters of 9 or 18R orthorhombic structure type and the changes that occur due the heat treatment can be followed and analyzed. Alloy no.1 shows predominant β phase with empirical formula $Cu_{0.61}Zn_{0.39}$ and lower rates of Al_3Cu_2 and $CuZn_5$ phases.

The shape memory effect observed in many alloys systems represents a thermoelastic martensitic transformation direct result [5, 6]. This transformation is crystallographic reversible and represents the base of the shape recovery mechanism. The bcc phase presents on cooling two ordering transitions. The first cooling transition represents an ordering reaction of the closest phases (near neighbor - nn) that leads to a B2 type matrix (CsCl type) called β2. A further cooling induces another ordering of the following phases from the crystalline structure

and it will become the DO3 (Fe3Al type) also called β1 or L21. Atoms sizes have an important effect on the formation of ordered structures [7]. However, some researchers [8] affirm the fact that DO3 perfect matrices will never be found in CuZnAl alloys and the resulting structure by the above described mechanism could be a $L2_1$ matrix. A2 disordered phase transformations in the basic phase B2 occurs during quenching in water [7] because the transition from B2 to L2 phase can be suppressed by quenching in water after a preliminary homogenization treatment. Fig. 1 presents the alloys diffractograms 1 in a) and 2 in b) for both heat treated samples.
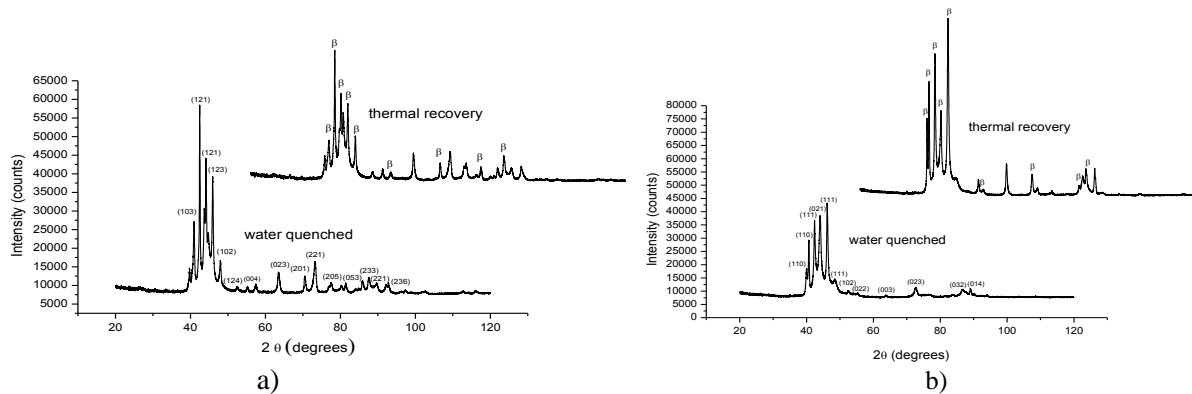

Fig. 1. X-ray shape memory alloys diffractograms of the samples of alloys one and two for different heat treatments

The lines observed in diffractograms were identified as M18R martensite superlattice reflections and attributed on the orthorhombic system. Plane spacing of diffraction planes in CuZnAl alloys shown in figure 1 processed with two various conditions can be observed. The structure of β martensite in copper based materials is based on one of the {110} basal planes in which the atoms are shifted or adjusted slightly in accord with the tetragonal distortion of martensite [4]. If the atoms are randomly distributed in the basal plane the ratio a/b of the lattice parameters should be equal to sqrt3/2 for 18R martensites. In our case, the lattice parameters presented in Table 2, the ratio is 0.861 and this deviation from ideal values of a/b results in splitting of certain diffraction lines in the orthorhombic martensite phase.

Table 2 Lattice parameters of β phase of the copper based shape memory specimens

Alloy	Lattice parameters for β phase			
	a (Å)	b (Å)	c (Å)	β
Alloy 1/ t.r.	4.27	4.46	38.678	90°
Alloy 1/ w.q.	4.27	4.46	38.674	90°
Alloy 2/ t.r.	4.273	4.963	38.675	90°
Alloy 2/ w.q.	4.271	4.961	38.672	90°

For alloys 1 and 2, especially for the second one, recovery treated residual austenite peaks can be also observed on the XRD diffractograms. The shape memory alloy 1 present a martensitic structure after both cooling methods. The variants dimensions, orientation and homogeneity are analyzed using scanning electrons microscope and atomic force microscope. Micro-structural considerations of shape memory alloy 1 are presented in Fig. 2 for 500x and 5000x amplifications of structure. Macroscopic the alloy 1 structure presented in both cases (thermal recovered, a) and quenched at room temperature, d)) a homogeneous structure with well defined grains. In the thermal recovered sample case the martensite variants are especially as arrowhead with the same orientation but also as diamond shapes and as plates with different orientations.

For thermal recovered sample the grains dimensions vary between 110 and 145 μm length, around 50 areas of the same sample were investigated and measured and an average of 25 grains for recovered sample and 15 grains for water quenched on a 0.25 mm^2 surface, comparing with the water cooled sample that present reduced areas with small grains, around 50 μm in length, and areas with long martensitic variants with lengths bigger than 200 μm being a favorable structure for shape memory effect.
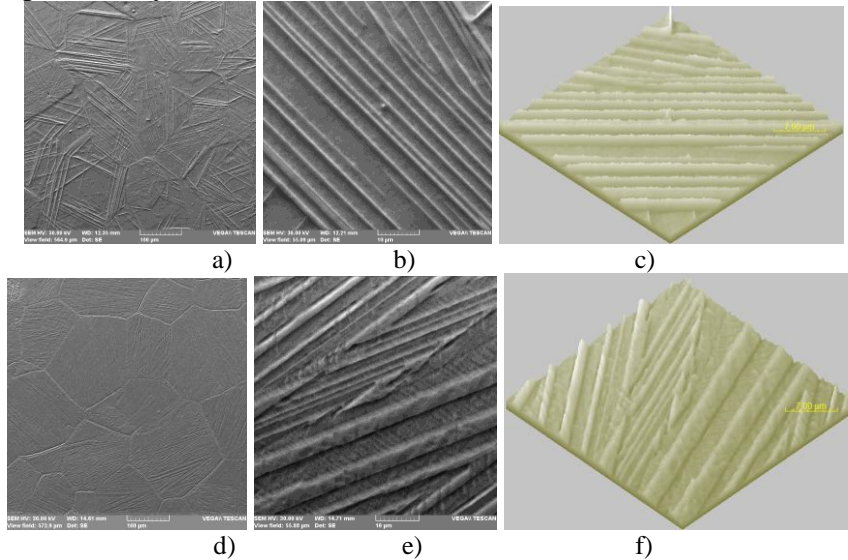

Fig. 2 SEM and AFM investigations of shape memory alloy 1 structure after thermal recovery, a), b) and c) and after a hardening heat treatment in d), e) and f)

At micro-scale primer and secondary variants can be observed in both cases with 2-5 μm width and an average of 2.2 μm in air cold cooled sample and 1.8 μm for sample quenched in water (the average was obtained after 100 measurements of martensite variants). The angle orientation between martensite variants is usually at 45° and the plates have an approximate height of 400 nm for primary plates and 200 nm for secondary variants determined from 3D acquisitions with SEM.
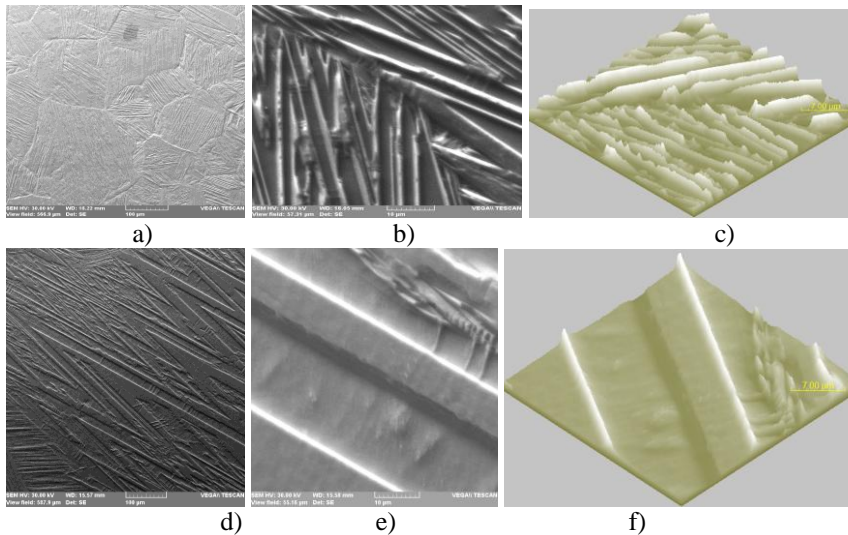

Fig. 3 SEM and AFM investigations of shape memory alloy 2 structure after the the thermal recovery in a), b) and c) and hardening heat treatment in d), e) and f)

The results with SEM of second alloy analysis are presented in Fig. 3 for both heat treatments conditions. In the first case, the hardened alloy, macro-structural aspects presented

martensitic grains with lengths between 50 and 150 μm, around 50 areas of the same sample were investigated and measured and an average of 28 grains for thermal recovered sample and 2 grains for quenching heat treated on a 0.25 mm^2 surface, compared with the quenched sample that presents big areas with martensitic variants, around 500 μm in length, favorable for shape memory effect. At micro-scale primer, in both cases, and secondary, only in water cooled case, variants can be observed with a 0.5-0.75 μm width and an average of 0.68 μm in air cold cooled sample and 2-3 μm width and an average of 2.8 μm for sample quenched in water (the average was obtained after 100 measurements of martensite variants).The secondary variants are about 100 nm for sample treated in water. The angle orientation between martensite variants is usually at 45° and the plates have an approximate height of 400 nm for primary plates and 100 nm for secondary variants determined from 3D acquisitions with SEM equipment.

Conclusions

Two shape memory copper based shape memory alloys were obtained through classical method. The transformation from β phase to martensitic phase is L2$_1$ for both cooling conditions of the alloys studied in this paper. It has been found that M18R orthorhombic martensitic structure transformed from β phase is ordered in all cases. The conditions applied for 3D analysis with scanning electron microscopy satisfy the values recorded by atomic force microscopy thus obtaining a new method for analyzing surface condition. Advantages of 3D analysis using the SEM are given by the investigated surface sizes (at the AFM equipment these are limited by the sensor model to 10x10 or 100x100 μm^2), in many cases the material surface roughness, speed of obtaining the results and the possibility of pieces and samples analysis with a complex geometry without damaging the structure.

Acknowledgement

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