

MICROSTRUCTURE AND PHASE TRANSFORMATIONS OF Cu-BASED SHAPE MEMORY ALLOYS

Assoc. prof. Tamara Holjevac Grgurić^{1*}, Prof. Dr Dragan Manasijević², Assistant prof. Ljubiša Balanović², Prof. Dr Duško Minić³, Assoc. prof. Stjepan Kožuh¹, Ivana Ivanić, PhD¹, Prof. Dr Mirko Gojić¹

University of Zagreb Faculty of Metallurgy, Croatia¹
University of Belgrade, Technical Faculty Bor, Serbia²
University of Pristina, Faculty of Technical Sciences, Kosovo³

tholjev@simet.hr

Abstract:

Cu-based shape memory alloys are increasingly used instead of nitinol alloys, due to their low price, good shape memory effect and superelasticity. In this work, Cu-Al-Mn alloys with different content of aluminium were investigated. Alloys were melted in the electric-arc furnace and casted in the cylindrical moulds as well as continuous casted. Microstructure of prepared samples was followed by scanning electron microscopy and phase transformations were determined by DSC analysis.

KEYWORDS: SHAPE MEMORY ALLOYS, CU-AL-MN ALLOYS, MICROSTRUCTURE, DSC ANALYSIS

Introduction:

Shape memory alloys (SMA) are smart, functional materials which have ability to memorize or recover to its original shape, under thermal changes or plastic deformation as well as magnetic variations [1-3]. Properties such as shape memory effect, superelasticity, good mechanical properties and damping properties makes them very interesting for a wide range of applications, as bioengineering, automotive and aircraft industry as well as electro-industry. Cu-based shape memory alloys recently more often replace the most important commercial SMA alloy, nitinol, due to easier production, low cost and good mechanical and electric properties. Addition of manganese to binary Cu-Al alloy significantly increases ductility and cold-workability of material, so Cu-Al-Mn ternary shape memory alloy has become a more significant commercial Cu-based SMA alloy than well-known Cu-Al-Zn and Cu-Al-Ni alloys [4]. Further addition of micro-alloying element to ternary Cu-Al-Mn alloy can influence on phase transformation temperatures, microstructure, grain size, shape memory effect (SE) and final properties. SE effect is a consequence of diffusionless martensitic transformation between high-temperature austenitic and low-temperature martensitic phase in material. Martensitic phase is metastable phase, formed under fast cooling or quenching in water, that can exist as 2M or 6M crystal structure.

Prerequisites and means for solving the problem:

The main aim of paper was investigate processing route for preparation of Cu-Al-Mn alloy with shape memory properties, by electric-arc furnace and continuous casting. Further, comparison of experimental results for transformation temperatures of Cu-Al-Mn alloys with different Al content, with calculated values by TCW5.

Materials and Methods:

Cu-Al-Mn ternary alloys were prepared by melting of pure metals of copper, with purity 99.9 %, aluminium, purity 99.5 % and manganese, purity 99.8 %. Cu-Al-Mn alloys with 9 wt.% of Mn and 1, 7, 8 and 11 wt.% of Al were prepared. Samples were melted in the electric-arc furnace under argon atmosphere, with current of 112 A. Furnace was vacuumed for 2 times during 15 minutes before each melting. Specimens were re-melted for 5 x due to better homogenization of material. Then, sample were casted in the

cylindrical mould with dimensions: diameter = 8 mm and length of 12 mm. Continuous casting of Cu-Al-Mn alloy was performed by melting of pure metals in the vacuum induction furnace at the temperature of 1250°C and casting of $\phi=8$ mm rod, with casting speed of 290 mm/min.

Further, samples were aged at 300 °C for 14 days for thermodynamic measurements. SMA compositions of Cu-Al-Mn alloys were heat-treated at 900 °C and quenched in the water. Cu-Al-Mn samples were prepared for microstructural investigations by inserting into the conductive paste by Automatic Mounting Press Buehler SimpliMet 1000. Grinding was performed by Buehler machine, with water-cooled SiC papers from 240 till 1200 grit, at force of 5 N and speed 150 rpm/min. Polishing of all specimens was done by microfiber felt with diluted alumina solution, at same force and speed. Specimens were then etched with solution of 2,5 g FeCl₃/48 mL CH₃OH/10mL H₂O.

Microstructure of as-cast and heat-treated samples were determined by optical microscopy at Olympus GX 71s with digital camera DP70 and software for automatically imaging processing AnalySIS Materials Research Lab, Japan. Scanning electron microscopy was performed by Tescan Vega TS 5136 MM, equipped with EDS Bruker. Differential scanning calorimetry was conducted by NETSZCH STA Jupiter 449. Dynamic measurements were done in 2 heating/cooling cycles, in temperature range from 25 °C till 1250 °C, with heating/cooling rate 10 K/min in the inert atmosphere. Transitions at lower temperatures were determined by MDSC Mettler-Toledo 822e, in temperature range from -50°C till 250 °C.

Results and discussion:

Phase diagram calculation of Cu-Al-Mn system under equilibrium conditions was performed by software Thermo-Calc 5, based on the CALPHAD method and minimisation of free Gibbs energy for all phases and components in ternary system. Thermodynamic database was prepared with thermodynamic parameters for pure elements taken from SGTE database, parameters for binary sub-systems Cu-Al, Al-Mn and Cu-Mn as well as optimized parameters for ternary Cu-Al-Mn system, for Cu-rich corner, according to Miettinen [5].

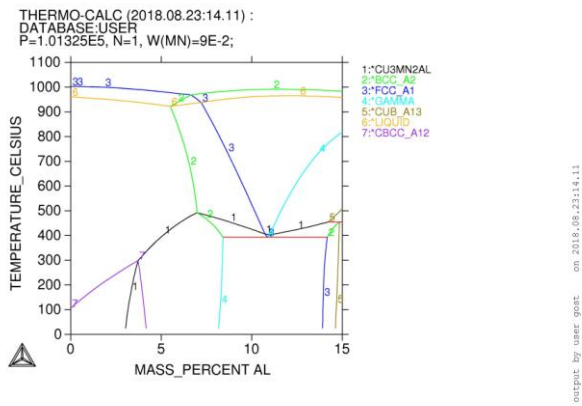
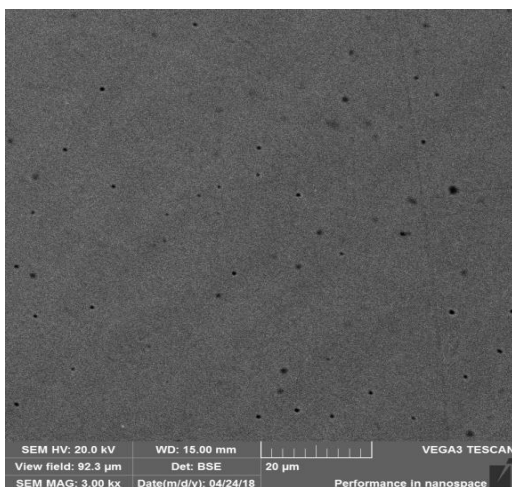


Figure 1. Calculated vertical section for Cu-9wt.%Mn by TCW 5

Calculated vertical section for Cu-9wt.%Mn with different aluminium content is given in Fig. 1. It can be seen that in system Cu-1wt.%Al-9wt.%Mn solidification mechanism, under equilibrium, starts with precipitation of α -phase (Cu-rich phase) at 1001 °C and then at 177 °C precipitates also manganese, as α -Mn (Fig. 1). Fig. 2a shows two-phase microstructure of Cu-1 wt.%Al-9wt.%Mn alloy in the as-cast state, with α -phase as matrix and existence of manganese precipitates. After aging at 300 °C for 14 days, morphology was changed and it is observed mostly α - (Cu-rich) phase with fcc structure, what is in correlation with calculated phase diagram (Fig.2b).



a)



b)

Figure 2. SEM micrographs for Cu-1 wt.%Al-9wt.%Mn alloy: a) as-cast state, b) after aging at 300 °C for 14 days

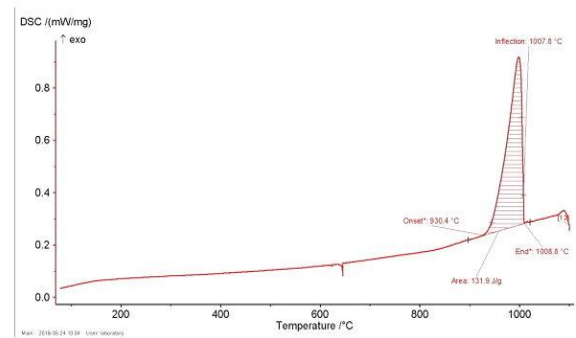


Figure 3. DSC cooling curve for Cu-1 wt.%Al-9wt.%Mn alloy after aging at 300 °C for 14 days

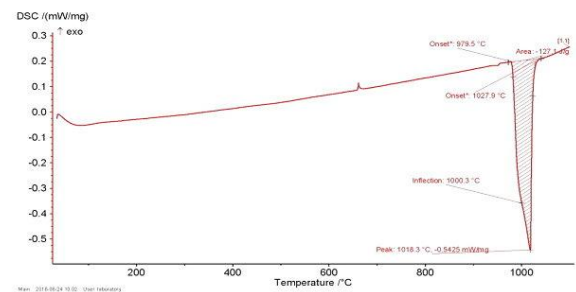
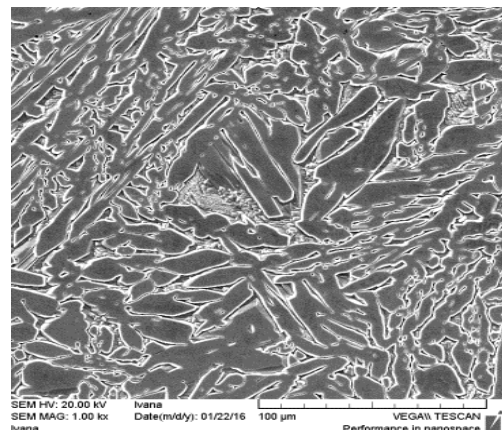


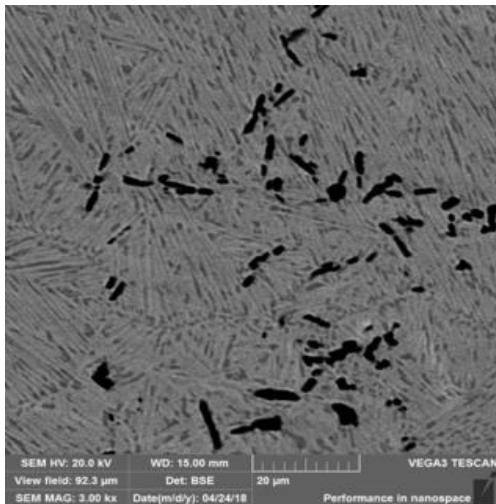
Figure 4. DSC heating curve for Cu-1 wt.%Al-9wt.%Mn alloy after aging at 300 °C for 14 days

DSC cooling curve for investigated sample presents precipitation of α -phase at temperature of 1008 °C, what is in good agreement with predicted theoretical value (Fig. 3), as well as DSC heating results (Fig. 4).

Sample with higher content of aluminum, Cu-7wt.%Al-9wt.%Mn, under equilibrate conditions, solidifies with precipitation of β -phase at 972 °C and at 944 °C precipitation of α -phase. Solidus temperature is calculated at 936 °C and reiciation of ternary phase, Cu₃Mn₂Al (τ_3 -phase) at 490 °C (Fig. 1).



a)



b)

Figure 4. SEM micrographs for Cu-7 wt.%Al-9wt.%Mn alloy: a) as-cast state, b) after aging at 300 °C for 14 days

Microstructure of Cu-7wt.%Al-9wt.%Mn alloy in the as-cast state show two-phase morphology, but not $\alpha+\tau_3$, as it can be expected due to Thermo-Calc calculation, but $\alpha+\beta$ morphology, what indicates that high-temperature β -phase remains in microstructure during casting due to faster cooling (Fig. 4a). After aging at 300 °C for 14 days, it can be observed new precipitates in α -matrix, probably τ_3 -phase (Fig. 4b).

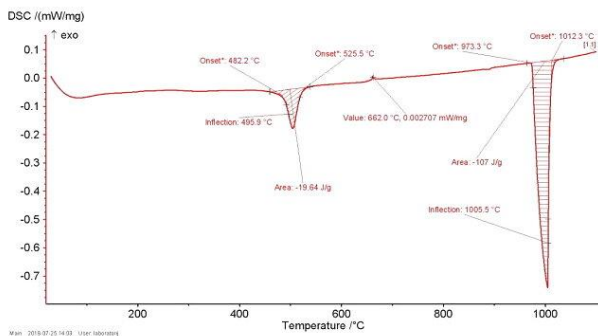


Figure 5. DSC heating curve for Cu-7wt.%Al-9wt.%Mn alloy after aging at 300 °C for 14 days

DSC results show first transformation at heating curve at 482 °C and the second transition at 495 °C, related to dissolution of τ_3 -phase and order-disorder transition of β -phase (Fig. 5). Two more transitions are determined at 973 °C and 1005°C at heating curve. Calculated solidification mechanism for Cu-11wt.%Al-9wt.%Mn alloy is given as:

- 991 °C: L → β phase
- 964 °C: solidus
- 467 °C: → $\beta + \gamma_2$
- 408 °C: → $\beta + \gamma_2 + \tau_3$
- 393 °C: → $\alpha + \gamma_2 + \tau_3$

SEM micrograph after homogenization at 300 °C shows existence of three-phase morphology (Fig. 6), and DSC results presents two transitions at heating curve, with temperatures at 450 °C and 511 °C. Solidus temperature is experimentally obtained at 968 °C, what is in very good agreement with calculated value (Fig. 7). Temperature of 999 °C at heating curve, as well as 986 °C at cooling curve is related to β -phase. (Figs. 7,8).

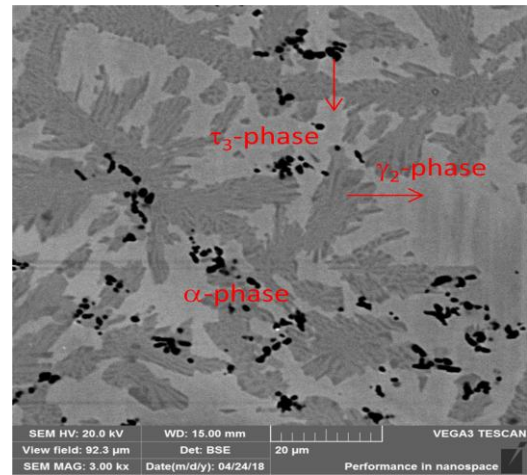


Figure 6. SEM micrographs for Cu-11 wt.%Al-9wt.%Mn alloy after aging at 300 °C for 14 days

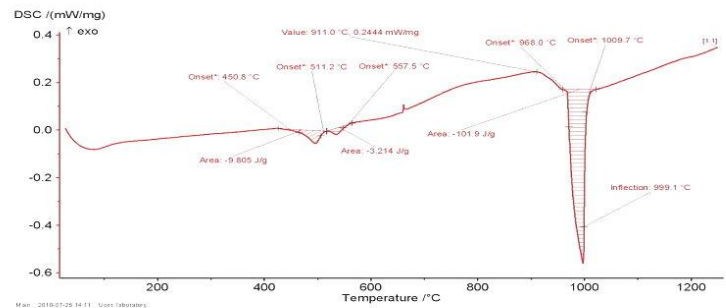


Figure 7. DSC heating curve for Cu-11wt.%Al-9wt.%Mn alloy after aging at 300 °C for 14 days

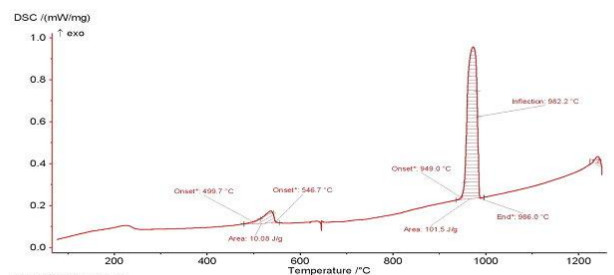


Figure 8. DSC cooling curve for Cu-11wt.%Al-9wt.%Mn alloy after aging at 300 °C for 14 days

Cu-8wt.%Al-9wt.%Mn shape memory alloy prepared by electric arc furnace, in the as-cast state after homogenization at 900 °C and quenching in water, show also two-phase microstructure, $\alpha+\beta$ (Figs. 9,10).

After continuous casting, in the as-cast state it can be observed martensitic needles inside grains, what indicates partially formation of metastable, β -phase (Fig. 11). Figure 12. shows completely formed martensitic structure after homogenization and quenching. Based on DSC results, start martensitic temperature in the as-cast state is at $M_s=37^\circ\text{C}$ and finish $M_f=13^\circ\text{C}$. After homogenization, two exothermic peaks at cooling curve indicate formation of different martensitic structures, with $M_s=42^\circ\text{C}$ and $M_f=5^\circ\text{C}$.

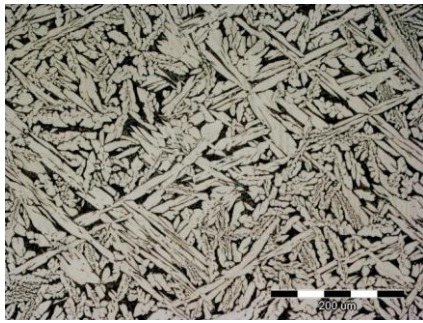


Figure 9. Optical microscopy of Cu-8wt.%Al-9wt.%Mn SMA alloy in the as-cast state

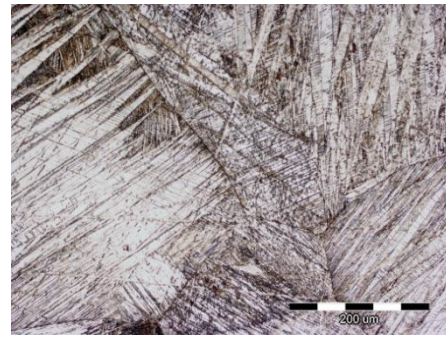


Figure 12. OM micrograph of continuously casted Cu-8wt.%Al-9wt.%Mn SMA alloy after homogenization at 900°C/30 minutes/H₂O

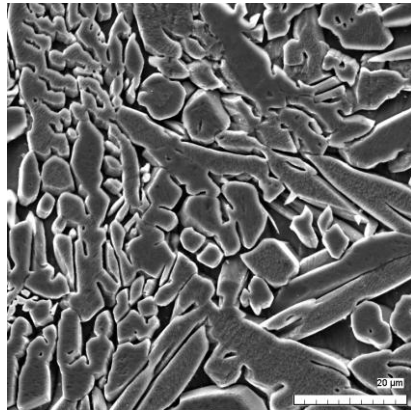


Figure 10. SEM micrograph of Cu-8wt.%Al-9wt.%Mn SMA alloy in the as-cast state

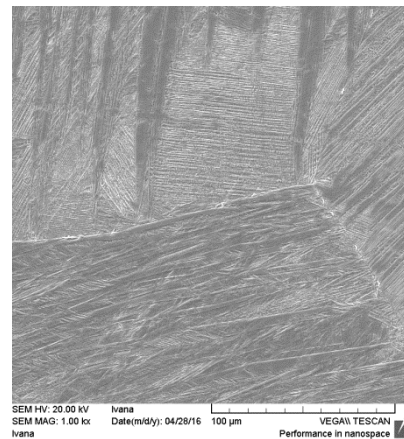


Figure 13. SEM micrograph of continuously casted Cu-8wt.%Al-9wt.%Mn SMA alloy after homogenization at 900°C/30 minutes/H₂O

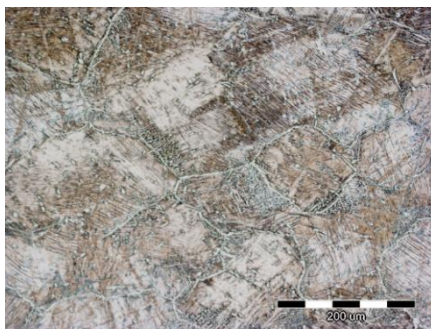


Figure 11. OM micrograph of continuously casted Cu-8wt.%Al-9wt.%Mn SMA alloy in the as-cast state

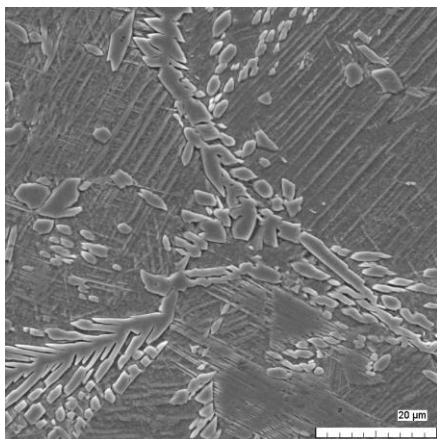


Figure 12. SEM micrograph of continuously casted Cu-8wt.%Al-9wt.%Mn SMA alloy in the as-cast state

Conclusion:

Experimental results of Cu-Al-Mn samples with different content of aluminium show good agreement with theoretical calculations for investigated ternary system. Cu-8wt.%Al-9wt.%Mn was successfully prepared by continuous casting and homogenization at 900 °C and quenching in water, with intensively formed martensitic structure through the sample. Start martensitic temperature was determined at 42°C and finish martensitic temperature at 5°C.

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