Effect of Mn content on the microstructure and phase transformation temperatures of the Cu-Al-Mn-Ag shape memory alloys

D. Manasijević¹*, T. Holjevac Grgurić², Lj. Balanović¹, U. Stamenković¹, M. Gorgievski¹, M. Gojić²

¹University of Belgrade, Technical Faculty in Bor, VJ12, 19210 Bor, Serbia
²University of Zagreb, Faculty of Metallurgy, Aleja Narodnih Heroja 3, 44103 Sisak, Croatia

Received 30 March 2020, received in revised form 2 June 2020, accepted 4 June 2020

Abstract

Two quaternary Cu-Al-Mn-Ag shape memory alloys with nearly constant Al and Ag contents and variable content of Mn were prepared by arc melting of pure metals. Experimentally determined overall compositions of the investigated alloys were Cu-9.4%Al-1.1%Mn-3.7%Ag (alloy 1) and Cu-9.5%Al-5.6%Mn-3.9%Ag (alloy 2) (in wt.%). Microstructures of the prepared samples were investigated in the as-prepared condition and after heat treatment, which included solution annealing at 850°C and quenching into the ice water.

The effects of alloy composition and heat treatment on the microstructure and transformation temperatures of the investigated shape memory alloys were investigated using scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) and differential scanning calorimetry (DSC). It was determined that alloy with low Mn content (alloy 1) exhibits martensite + α microstructure in the as-prepared state and the as-quenched state. The volume fraction of α-phase was much larger in the as-prepared condition. Ag was uniformly distributed between the co-existing phases. The microstructure of the alloy with a higher content of Mn (alloy 2) was fully martensitic in both investigated conditions. Martensite and austenite transformation temperatures were investigated using DSC.

Key words: shape memory alloy, Cu-Al-Mn-Ag alloy, microstructure, martensitic transformation

1. Introduction

Shape memory alloys (SMAs) are a group of alloys that can memorize or recover to its original shape under thermal changes or plastic deformation [1–3]. These functional alloys have a wide range of applications, as bioengineering, electro industry, automotive, and aircraft industry [1]. The most important groups of SMAs are the Ni-Ti-based alloys and the Cu-based SMAs [1, 2]. The Cu-based shape memory alloys are of less commercial use, but they are easier to produce and less expensive comparing to the Ni-Ti-based SMAs [1–3].

The shape memory effect is caused by the diffusion-less and reversible martensitic transformation (MT), which occurs between the high-temperature austenite phase and the low-temperature metastable martensite phase [4, 5].

Lately, Cu-Al-Mn alloys have been extensively studied because of their good shape memory properties, excellent ductility, and thermal conductivity, which makes them commercially attractive Cu-based SMAs [2, 6, 7]. Further improvement of the properties of Cu-Al-Mn SMAs by adding other elements such as Ni, Cr, Si, Ti, Mg, and Fe has been investigated in the literature [3, 7]. Additional alloying can affect their phase transformation temperatures, microstructure, grain size, and final shape memory properties. It is known that microstructure and transformation temperatures of Cu-based SMAs are also strongly dependent on their heat treatment [8]. The silver addition to Cu-Al-Mn alloys may improve its corrosion resis-
tance, microhardness, and characteristic phase transformation temperatures [9, 10].

In our previous work [11], the microstructure and thermal properties of the Cu-9.8%Al-7.6%Mn-4.4%Ag alloy were experimentally studied. In the present study, two Cu-Al-Mn-Ag alloys with low and medium Mn content and nearly constant contents of Al and Ag (Cu-9.4%Al-1.1%Mn-3.7%Ag and Cu-9.5%Al-5.6%Mn-3.9%Ag alloys) were investigated by using SEM-EDS and DSC techniques. Microstructures of the prepared alloys were analyzed after arc-melting and after heat treatment, which included solution annealing and quenching in the ice water. Transformation temperatures of the investigated alloys were investigated by the DSC technique.

Thus, the main goal of this study is to examine the effects of Mn content and heat treatment on the microstructure and phase transformation temperatures of the Cu-Al-Mn-Ag alloys prepared by arc-melting.

2. Experimental procedure

The Cu-Al-Mn-Ag alloys were prepared by arc-melting of calculated quantities of pure copper (99.99 %), aluminium (99.97 %), manganese (99.95 %) and silver (99.99 %) in the vacuum and with a current of 112 A. Alloys were re-melted several times for better homogenization and cast in the mould with dimensions: diameter 8 mm and length 12 mm. Heat treatment of the prepared Cu-Al-Mn-Ag alloy samples included solution annealing at 850 °C for 30 min and direct quenching into the ice water.

The samples used for the scanning electron microscopy (SEM) observations were mechanically ground and polished. The solution containing 2.5 g FeCl₃·6H₂O and 1 ml HCl in 48 ml methanol was used as an etchant.

Scanning electron microscope (TESCAN VEGA3) with energy dispersive spectroscopy (EDS) (Oxford Instruments X-act) was used for microstructure investigation of prepared alloys, and the measurements were carried out with accelerating voltage 20 kV. The quantitative EDS analysis, using high purity copper as the standard metal, was performed for the determination of chemical compositions of the samples and identification of co-existing phases. The overall compositions of the alloys were determined by EDS analysis of as large as possible surface of the samples. The compositions of the co-existing phases within the studied samples were determined by examining the surface of the same phase at different regions of the sample (at least five measurements were examined per phase).

The average overall chemical compositions of the investigated samples obtained by EDS analysis with calculated standard uncertainties are given in Table 1.

Martensite and reverse martensite (austenite) transformation temperatures (Ms, Mf, As, and Af) were studied on DSC analyzer Mettler Toledo 822e. The temperature and heat flow calibration were carried out by using indium metal (purity 99.999 %) as a standard. Measurements were performed in an argon atmosphere, using two heating/cooling cycles from −50 to 250°C with heating/cooling rate 10°C min⁻¹.

3. Results and discussion

3.1. Microstructures of alloys after arc-melting

Microstructures and phase compositions of the Cu-9.4%Al-1.1%Mn-3.7%Ag and Cu-9.5%Al-5.6%Mn-3.9%Ag bulk alloys after arc melting were investigated using SEM-EDS.

Characteristic SEM images of the investigated bulk alloys are presented in Fig. 1. The microstructure of the Cu-9.4%Al-1.1%Mn-3.7%Ag alloy consists of many, irregularly distributed precipitates of Cu-based α-phase in the martensite matrix (Fig. 1a). Because of the low content of Mn (1.1 wt.%), it can be anticipated that the shape memory properties of this alloy are similar to those of the Cu-Al alloys [12, 13]. Thus, martensite observed could be disordered β′ martensite, identified in the Cu-Al alloys containing less than 11 wt.% of Al [12].

The Cu-9.5%Al-5.6%Mn-3.9%Ag alloy has a fully martensitic microstructure without any α precipitates (Fig. 1b). The spear-like and zig-zag martensite morphologies suggest the formation of ordered β′₁ martensite [6, 14–16]. It is known that in the Cu-Al-Mn alloys, depending on the amount of Al and Mn, three types of martensite (β′ (3R), β′₁ (18R), and γ₁ (2H)) can be formed during fast cooling from the β-phase region [16]. At lower Al contents, β′₁ martensite is predominant, while at higher amounts of Al, γ₁ martensite...
Table 2. Chemical compositions of co-existing phases within the Cu-9.4%Al-1.1%Mn-3.7%Ag alloy after arc melting determined by EDS analysis (wt.%)

| Alloy Phase | Cu  | Al  | Mn  | Ag  |
|-------------|-----|-----|-----|-----|
| Cu-9.4%Al-1.1%Mn-3.7%Ag | α-phase | 88.6 | 8.1 | 1.0 | 2.3 |
|              | martensite | 84.9 | 9.8 | 1.2 | 4.1 |

3.2. Microstructures of the heat-treated alloys

Microstructures of the Cu-9.4%Al-1.1%Mn-3.7%Ag and Cu-9.5%Al-5.6%Mn-3.9%Ag heat-treated bulk alloys are shown in Fig. 2. A considerable amount of martensitic phase can be observed in the microstructure of the Cu-9.4%Al-1.1%Mn-3.7%Ag alloy after quenching together with the several grains of the Cu-rich α-phase (Fig. 2a). Based on the results of phase fractions image analysis, the phase fraction of α-phase after heat treatment is considerably smaller compared to the as-prepared state of the alloy (Fig. 1a).
Table 3. Chemical compositions of co-existing phases in Cu-9.4%Al-1.1%Mn-3.7%Ag alloy after solution annealing at 850 ºC for 30 minutes and quenching determined by EDS analysis (wt.%)  

| Alloy                | Phase    | Cu     | Al     | Mn     | Ag     |
|----------------------|----------|--------|--------|--------|--------|
| Cu-9.4%Al-1.1%Mn-3.7%Ag | α-phase  | 88.1   | 8.1    | 1.0    | 2.8    |
|                       | martensite | 85.2   | 9.8    | 1.1    | 3.8    |

Phase transformation temperatures in the temperature range from –50 to 250 ºC for the two investigated Cu-Al-Mn-Ag alloys in the as-quenched condition were measured using the DSC method. Martensite and reverse martensite (austenite) transformation temperatures for the Cu-9.4%Al-1.1%Mn-3.7%Ag and Cu-9.5%Al-5.6%Mn-3.9%Ag as-quenched alloys were studied using two DSC heating/cooling cycle in the temperature range from –50 to 250 ºC. Figure 4 presents DSC curves for the Cu-9.4%Al-1.1%Mn-3.7%Ag and Cu-9.5%Al-5.6%Mn-3.9%Ag alloys obtained in the second cycle. It can be seen that DSC cooling curves for both investigated alloys are characterized by the appearance of three successive exothermic peaks at low temperatures, which are related to the formation of different martensitic phases. The manifestation of consecutive peaks suggests the formation of different martensitic structures during the cooling of the alloys [11]. For the Cu-9.4%Al-1.1%Mn-3.7%Ag alloy, the onset temperature of the first identified DSC peak on cooling was 105.0 ºC and the endset temperature was 63.2 ºC (Fig. 4a). The onset and endset temperatures of the second detected peak were 46.4 and 7.7 ºC. For the third detected peak, onset and endset temperatures were 0.2 and –41.2 ºC. For the Cu-9.5%Al-5.6%Mn-3.9%Ag alloy, characteristic onset and endset temperatures of the first, second, and third DSC peaks were 61.8 and 36.2 ºC (first peak), 22.8 and 8.6 ºC (second peak), 2.8 and –16.5 ºC (third peak) (Fig. 4b).

Based on the obtained results, it can be concluded that Cu-9.4%Al-1.1%Mn-3.7%Ag alloy has higher martensite start (Ms) temperature (105.0 ºC) than Cu-9.5%Al-5.6%Mn-3.9%Ag alloy (61.8 ºC). Both in-
investigated alloys have higher $M_s$ temperatures than Cu-10%Al-8%Mn-4%Ag alloy (29.5°C) [11] and Cu-7.0%Al-10.0%Mn-3.0%Ag alloy (-50°C) [9]. This is in line with the literature results [3] on the basis of which the martensite transformation temperatures decrease with increasing contents of manganese and aluminium.

However, as in the case of Cu-10%Al-8%Mn-4%Ag alloy investigated in [11], endothermic DSC peaks related to the reverse martensite (austenite) transformation were not identified in the investigated temperature range. This could be explained by the effect of martensite stabilization in directly quenched alloys, which is caused by the presence of excess quenched-in vacancies in the as-quenched alloy [11, 22–24].

4. Conclusions

Based on the results of the microstructural and thermal analysis performed in the present study, the
following conclusions can be made:

1. The microstructure of the as-prepared low-manganese Cu-9.4%Al-1.1%Mn-3.7%Ag alloy included a large phase fraction of irregularly distributed grains of stable α- and martensite phase in the base. The microstructure of the Cu-9.5%Al-5.6%Mn-3.9%Ag alloy included only martensite in the as-prepared condition.

2. After solution annealing at 850 °C and quenching in the ice water microstructure of Cu-9.4%Al-1.1%Mn-3.7%Ag alloy was primarily composed of martensite and a smaller fraction of α-phase precipitates. The fully martensitic structure was observed in the case of Cu-9.5%Al-5.6%Mn-3.9%Ag alloy.

3. Similarly to the Cu-Al-Mn alloys, the increase of Mn content in the Cu-Al-Mn-Al alloys widens the region of stability of β-phase, hinders precipitation of stable α-phase and improves conditions for martensite formation.

4. Phase transformation temperatures of Cu-9.4%Al-1.1%Mn-3.7%Ag and Cu-9.5%Al-5.6%Mn-3.9%Ag alloys in the as-quenched condition were measured using the DSC technique. Characteristic three-step martensitic transformations were observed during cooling DSC cycles in the temperature interval from −50 to 250 °C for both investigated alloys. The appearance of three successive endothermic peaks is caused by the formation of different martensitic phases. Martensite start temperature for the Cu-9.4%Al-1.1%Mn-3.7%Ag alloy was 105.0 °C, and for the Cu-9.5%Al-5.6%Mn-3.9%Ag alloy was 61.8 °C. Direct quenching of alloys into the ice water has resulted in the stabilization of the obtained martensitic structure, and reverse martensite transformation temperatures were not identified in the investigated temperature range.

Acknowledgements

This work has been supported by the Croatian Science Foundation under the project IP-2014-09-3405 and by the Ministry of Education, Science and Technological Development of the Republic of Serbia, within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor, according to the contract with registration number 451-03-68/2020-14/200131.

References

[1] R. Dasgupta, A look into Cu-based shape memory alloys: Present scenario and future prospects, J. Mater. Res. 29 (2014) 1681–1698. doi:10.1557/jmr.2014.189.

[2] Y. Sutou, T. Omori, R. Kaihuma, K. Ishida, Ductile Cu-Al-Mn based shape memory alloys: General properties and applications, Mater. Sci. Technol. 24 (2008) 896–901. doi:10.1179/174328408X302567.

[3] U. S. Malik, V. Sampath, Influence of aluminum and manganese concentration on the shape memory characteristics of Cu-Al-Mn shape memory alloys, J. Alloy Compd. 459 (2008) 142–147. doi:10.1016/j.jallcom.2007.04.254.

[4] M. Blanco, J. T. C. Barragan, N. Barelli, R. D. Noce, C. S. Fugivara, J. Fernandez, A. V. Benedetti, On the electrochemical behavior of Cu-Al-Mn-Al alloy containing the β′-phase (martensite) in borate buffer, Electrochim. Acta 107 (2013) 238–247. doi:10.1016/j.electacta.2013.05.147.

[5] Z. Stošić, D. Manasijević, Lj. Balanović, T. Holjevac-Grgurić, U. Stamenković, M. Premović, D. Minić, M. Gorgievski, R. Todorović, Effects of composition and thermal treatment of Cu-Al-Zn Alloys with low content of Al on their shape-memory properties, Mater. Res.-Ibero-Am. J. 20 (2017) 1425–1431. doi:10.1590/2179-80992017-0152.

[6] G. Lojen, M. Gojić, I. Anžel, Continuously cast Cu-Al-Ni shape memory alloy – Properties in as-cast condition, J. Alloy Compd. 580 (2013) 497–505. doi:10.1016/j.jallcom.2013.06.136.

[7] T. Holjevac Grgurić, D. Manasijević, S. Kozuhi, I. Ivanić, Lj. Balanović, I. Anžel, B. Kossec, M. Bizjak, M. Knežević, M. Gojić, Phase transformation and microstructure study of the as-cast Cu-rich Cu-Al-Mn ternary alloys, J. Min. Metall. B 53 (2017) 413–422. doi:10.1029.179509032.

[8] P. Dagdelen, M. Sait Kana, M. Boyrazli, Cooling condition effects on transformation temperature and microstructure of Cu₅₆Al₅₄Ni₃₄Ti₂ SMA, J. Chem. Technol. Metall. 54 (2019) 204–208.

[9] C. M. A. Santos, A. T. Adorno, N. Y. Oda, B. O. Sales, L. S. Silva, R. A. G. Silva, Phase transformations and aging of the Cu₉₂.₉Al₄.₅Mn₃.₉Ni₅.₆ alloy, J. Alloy Compd. 685 (2016) 587–592. doi:10.1016/j.jallcom.2016.05.303.

[10] R. A. G. Silva, S. Gama, A. Pagunotti, A. T. Adorno, T. M. Carvalho, C. M. A. Santos, Effect of Ag addition on phase transitions of the Cu-22.26at.%Al-9.93at.%Mn alloy, Thermochim. Acta 554 (2013) 71–75. doi:10.1016/j.tca.2012.12.014.

[11] D. Manasijević, Lj. Balanović, T. Holjevac Grgurić, U. Stamenković, D. Minić, M. Premović, R. Todorović, N. Štrbac, M. Gorgievski, M. Gojić, E. Govorčin Bajšić, The effect of silver addition on microstructure and thermal properties of the Cu-10%Al-8%Mn shape memory alloy, Metall. Mater. Eng. 23 (2017) 255–266. doi:10.30544/321.

[12] P. R. Swann, H. Warlimont, The electron-metallography and crystallography of copper-aluminium martensites, Acta Metall. 11 (1963) 511–527. doi:10.1016/0001-6160(63)90086-5.

[13] J. Marcos, L. Mañosa, A. Planes, R. Romero, M. Luñán Castro, Kinetics of the phase separation in Cu-Al-Mn alloys and the influence on martensitic transformations, Philos. Mag. 84 (2004) 45–90. doi:10.1080/14786430310001604994.

[14] U. Sari, I. Aksoy, Electron microscopy study of 2H and 18R martensites in Cu-11.92wt.%Al-3.78wt.%Ni shape memory alloy, J. Alloy Compd. 417 (2006) 138–142. doi:10.1016/j.jallcom.2005.09.049.

[15] R. Dasgupta, A. K. Jain, P. Kumar, S. Hussein, A. Pandey, Effect of alloying constituents on the martensitic phase formation in some Cu-based SMAs, J.
[16] E. Aldirmaz, I. Aksoy, Effects of heat treatment and deformation on 2H and 18R martensites in Cu-9.97%Al-4.62%Mn alloy, Arab. J. Sci. Eng. 39 (2014) 575–580. doi:10.1007/s13369-013-0871-z

[17] J. Miettinen, Thermodynamic description of the Cu-Al-Mn system in the copper-rich corner, Calphad 27 (2003) 103–114. doi:10.1016/S0364-5916(03)00035-X

[18] W. Cao, S. L. Chen, F. Zhang, K. Wu, Y. Yang, Y. A. Chang, R. Schmid-Fetzer, W. A. Oates, PANDAT software with PanEngine, PanOptimizer and PanPrecipitation for multi-component phase diagram calculation and materials property simulation, Calphad 33 (2009) 328–342. doi:10.1016/j.calphad.2008.08.004

[19] K. Matsushita, T. Okamoto, Effects of manganese and ageing on martensitic transformation of Cu-Al-Mn alloys, J. Mater. Sci. 20 (1985) 689–699. doi:10.1007/BF01026544

[20] E. Obrado, C. Frontera, L. Manosa, A. Planes, Order-disorder transitions of Cu-Al-Mn shape-memory alloys, Phys Rev. B 58 (1998) 14245. doi:10.1103/PhysRevB.58.14245

[21] G. Zhang, H. Yin, C. Zhang, Z. Deng, R. Zhang, X. Jiang, X. Qu, Effect of Mn on microstructure and properties of Cu-12Al powder metallurgy alloy, Mater. Res. Express. 7 (2020) 016546. doi:10.1088/2053-1591/ab63f8

[22] S. Kustov, J. Pons, E. Cesari, J. van Humbeeck, Chemical and mechanical stabilization of martensite, Acta Mater. 52 (2004) 4547–4559. doi:10.1016/j.actamat.2004.06.012

[23] T. Suzuki, R. Kojima, Y. Fujii, A. Nagasawa, Reverse transformation behaviour of the stabilized martensite in Cu-Zn-Al alloy, Acta Metall. 37 (1989) 163–168. doi:10.1016/0001-6160(89)90275-7

[24] C. L. del Castillo, M. L. Blázquez, C. Gómez, G. Mellor, N. de Diego, J. del Río, The stabilization of martensite in Cu-Al-Mn alloys, J. Mater. Sci. 23 (1988) 3379–3382. doi:10.1007/BF00551322