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

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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 diffusionless 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-

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Table 1. Experimentally determined overall compositions of the investigated samples

Sample	Experimentally determined composition with calculated standard uncertainties (wt.%)			
	Cu	Al	Mn	Ag
1	85.8 ± 0.4	9.4 ± 0.3	1.1 ± 0.1	3.7 ± 0.2
2	81.0 ± 0.4	9.5 ± 0.2	5.6 ± 0.2	3.9 ± 0.2

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 $FeCl_3 \cdot 6H_2O$ 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 (M_s, M_f, A_s, and A_f) 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 γ'_1 (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, γ'_1 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

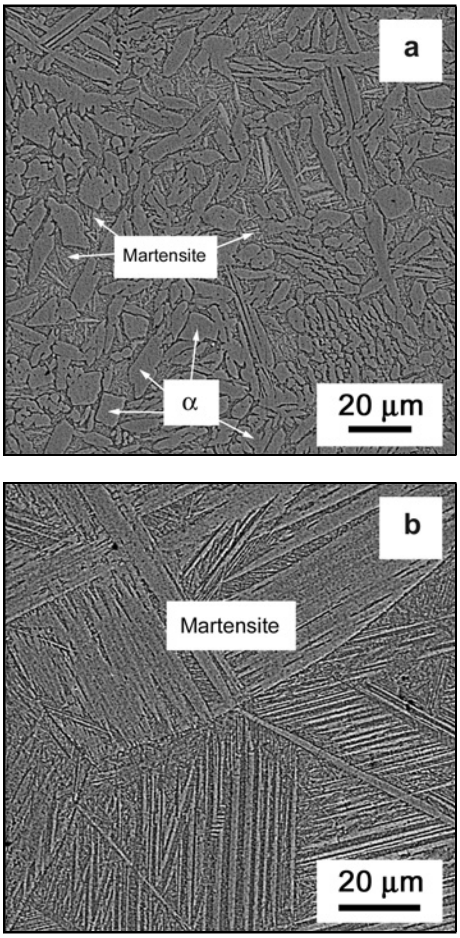

Fig. 1. SEM micrographs of investigated bulk alloys after arc melting: (a) Cu-9.4%Al-1.1%Mn-3.7%Ag alloy and (b) Cu-9.5%Al-5.6%Mn-3.9%Ag alloy.

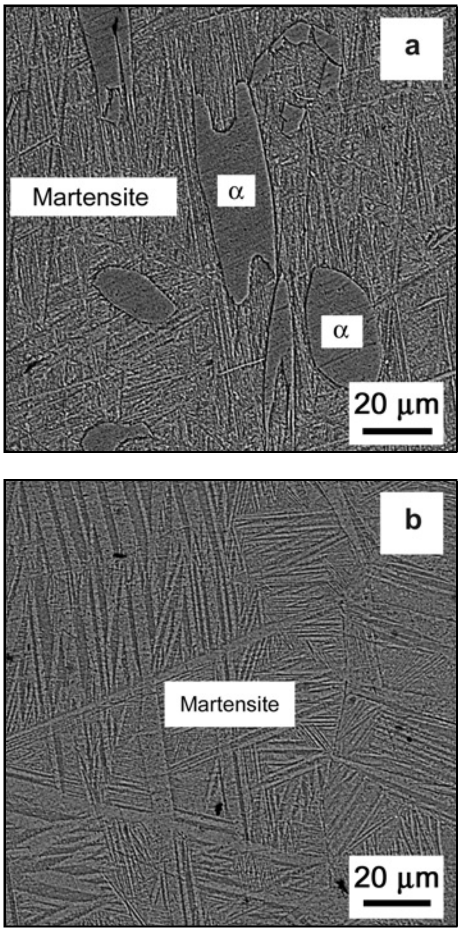

Fig. 2. SEM micrograph of the investigated bulk alloys after solution annealing at 850 °C for 30 minutes and quenching in the ice water: (a) Cu-9.4%Al-1.1%Mn-3.7%Ag and (b) Cu-9.5%Al-5.6%Mn-3.9%Ag.

is formed. In the intermediate concentration interval, both β_1' and γ_1' martensites co-exist [16].

Average chemical compositions of identified phases for the Cu-9.4%Al-1.1%Mn-3.7%Ag alloy were determined using EDS analysis and shown in Table 2. The α-phase has a higher amount of copper and a lower amount of aluminium than the matrix martensitic phase. The manganese amount is nearly the same in both identified phases, and silver content is to some extent higher in the martensite phase than in the α-phase (4.1 % in the martensite phase and 2.3 % in the precipitate α-phase). It can be concluded that the precipitate phase represents Cu-rich α-phase.

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 °C 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

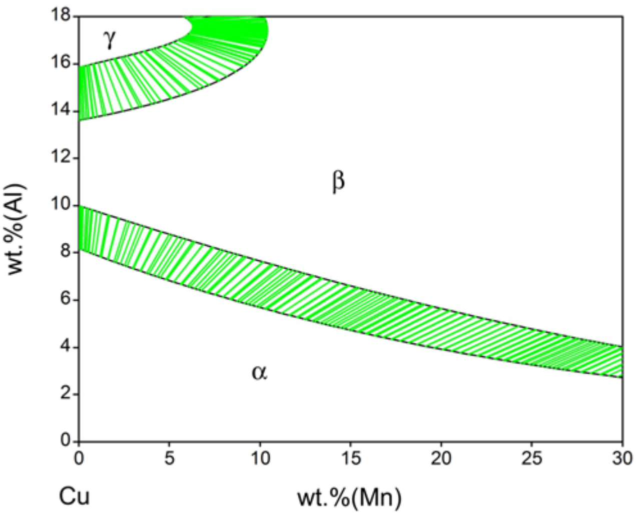

Fig. 3. Calculated phase diagram of the Cu-Al-Mn ternary system at 850 °C.

Average chemical compositions of identified phases for the Cu-9.4%Al-1.1%Mn-3.7%Ag alloy were determined using EDS analysis and shown in Table 3. The grains of the dark α-phase have a higher amount of Cu and a lower amount of Al than the brighter martensitic phase in the base. Mn and Ag are distributed within both co-existing phases.

The microstructure of the Cu-9.5%Al-5.6%Mn-3.9%Ag alloy after quenching (Fig. 2b) was fully martensitic, similar to the observed microstructure in the as-prepared condition (Fig. 1b).

Figure 3 shows the calculated Cu-rich part of the phase diagram of the Cu-Al-Mn ternary system at 850 °C using the optimized thermodynamic parameters from Miettinen [17] and Pandat software [18]. It is known that precondition for the martensite formation is the rapid cooling of the alloy from the high-temperature phase stability region of the β-phase, which is the parent phase for the martensite phase.

According to the calculated phase diagram at 850 °C shown in Fig. 3, ternary Cu-Al-Mn alloy with the Al content of about 9.5 % and a very small content of Mn is in the $\alpha + \beta$ two-phase region. The increase of Mn content in the ternary Cu-Al-Mn alloys extends the phase stability region of β-phase, makes the β-phase more stable to diffusional decomposition and improves conditions for the formation of martensite phase upon rapid alloy cooling. Thus, it can be anticipated that martensite would be easily formed in the alloy with a higher content of Mn, which is in agreement with the experimental results from the present study. It can be concluded that the increase of manganese content in the Cu-Al-Mn-Ag alloy hinders the formation of stable α-phase during cooling and improves conditions for martensitic transformation. This result is in agreement with the findings of Matsushita et al. [19], Obrado et al. [20], and Zhang et al. [21] for ternary Cu-Al-Mn alloys.

3.3. Transformation temperatures of the as-quenched Cu-Al-Mn-Ag alloys

Phase transformation temperatures in the temperature range from –50 to 250 °C 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 °C. 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 martensite 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 °C and the endset temperature was 63.2 °C (Fig. 4a). The onset and endset temperatures of the second detected peak were 46.4 and 7.7 °C. For the third detected peak, onset and endset temperatures were 0.2 and –41.2 °C. 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 °C (first peak), 22.8 and 8.6 °C (second peak), 2.8 and –16.5 °C (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 °C) than Cu-9.5%Al-5.6%Mn-3.9%Ag alloy (61.8 °C). Both in-

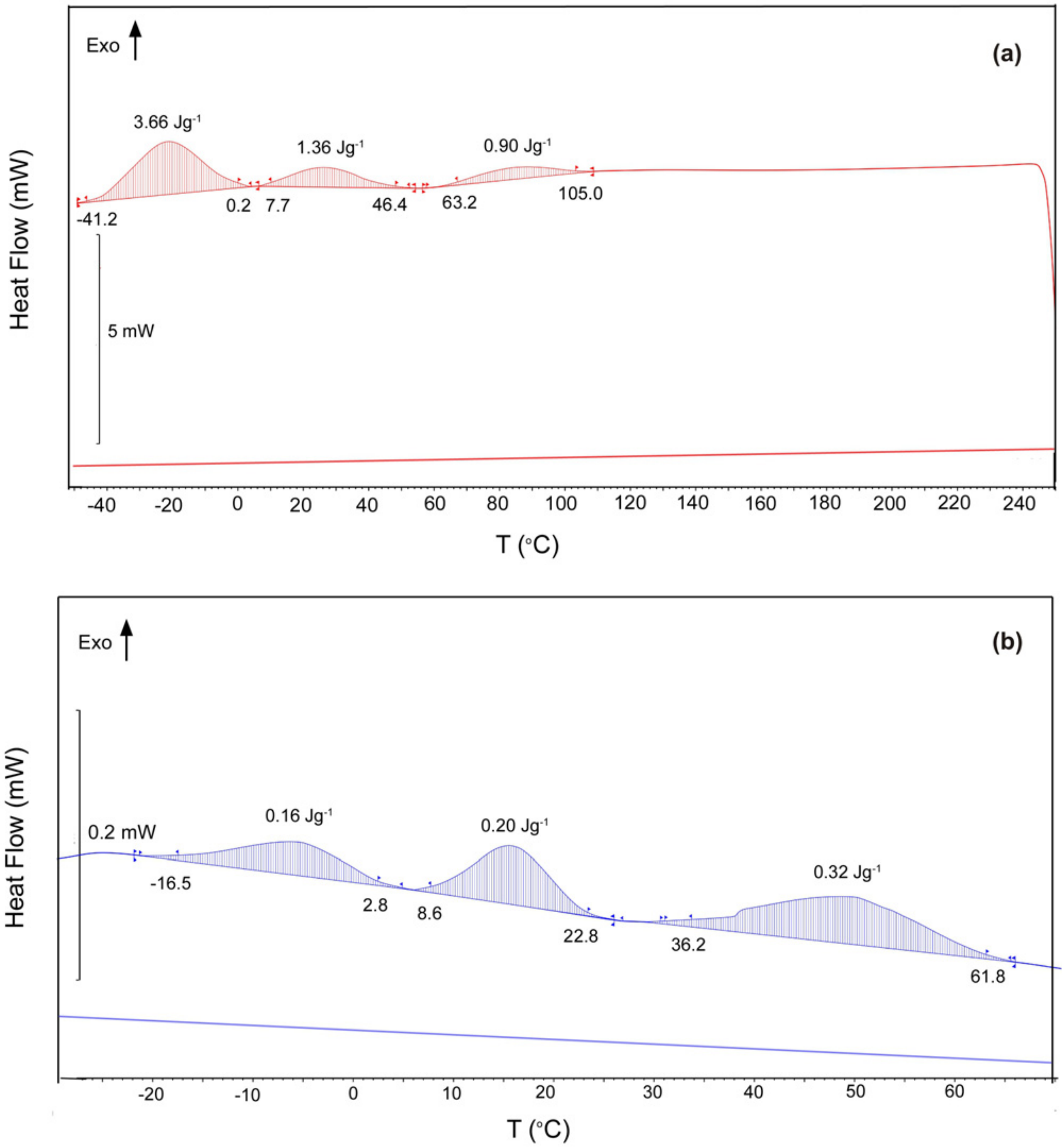

Fig. 4. DSC curve: (a) Cu-9.4%Al-1.1%Mn-3.7%Ag alloy and (b) Cu-9.5%Al-5.6%Mn-3.9%Ag alloy.

vestigated alloys have higher Ms temperatures than Cu-10%Al-8%Mn-4%Ag alloy (29.5 ℃) [11] and Cu-7.0%Al-10.0%Mn-3.0%Ag alloy (–50 ℃) [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-phase 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-Ag 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.

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