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Source / Izvornik: **Proceedings Book 19th International Foundrymen Conference, 2021, 362 - 371**

Conference paper / Rad u zborniku

Publication status / Verzija rada: **Published version / Objavljena verzija rada (izdavačev PDF)**

Permanent link / Trajna poveznica: https://urn.nsk.hr/urn:nbn:hr:115:141679

19th INTERNATIONAL FOUNDRYMEN CONFERENCE
Humans - Valuable Resource for Foundry Industry Development
Split, June 16th-18th, 2021
https://ifc.simet.hr/

MICROSTRUCTURE AND MICROHARDNESS OF Cu-Al-Mn-Zr ALLOYS BEFORE AND AFTER HEAT TREATMENT

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Poster presentation
Original scientific paper

Abstract

In this work preliminary results of the heat treatment effect on microstructure and microhardness of Cu-8.5Al-10Mn-(0.25-1.00)Zr alloys were presented. Ingots (8 mm in diameter and 15 mm in length) were produced by melting and casting process. Production of investigated alloys was performed in laboratory electric arc furnace. Melting was carried out using the heat produced by electric arc and by a water-cooled, specially constructed copper anode that also served as a casting mould. The samples were analysed in as-cast state and after heat treatment at 900 °C/15 min/water. Microstructural analysis was performed by optical microscopy (OM), scanning electron microscopy (SEM) equipped by device for energy dispersive spectroscopy (EDS). Preliminary optical microscopy analysis of investigated alloys confirmed that microstructure was consisted of martensite only in Cu-8.5Al-10Mn-0.25Zr alloy in as-cast and heat treated state. SEM analysis show the start of martensite formation in some places at all investigated alloys in both, as-cast and heat treated state. A microhardness measurement was performed by Vickers method. Microhardness values of Cu-8.5Al-10Mn-(0.25-1.00)Zr alloys were up to 215.8 HV1 after casting and up to 224.5 HV1 after heat treatment.

Keywords: *Cu-Al-Mn-Zr alloy, microstructure, heat treatment, microhardness*

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INTRODUCTION

Shape memory alloys (SMA) can be categorized in a group of functional and smart materials which characterized the property of remembering the shape they had before pseudoplastic deformation. Primarily, shape memory properties are functions of microstructures i.e. grain size, texture and presence of precipitates. The presence of martensitic phase as main microstructural constituent is absolutely necessary at shape memory alloys. The martensitic

transformation exhibited from β phase during the cooling process of shape memory alloys and this alloys can contained two types of thermal induced martensites, $\beta_1`$ and $\gamma_1`$ respectively. Martensites which will be formed depending on alloy composition and heat treatment [1].

Shape memory alloys on Cu-base are commercially attractive mainly for their low cost as compared with other family of shape memory alloys. Usually, Cu-based shape memory alloys can be grouped into three main categories: Cu-Zn, Cu-Al and Cu-Sn [2]. However, a third (e.g. Ni, Mn, Zn etc.) and fourth (e.g. Zr, Ag, Ti etc.) alloying elements can be added to improve upon the properties and remove drawbacks [3-5]. So, for improvement and achieving high ductility Cu-Al-Mn shape memory alloys are developed. In this alloys can be added zirconium as fourth microalloying element in order to refine the grain size. Chen at al. [6] have developed a new shape memory alloys with compositions Cu-11.91Al-2.48Mn-0.1Zr (wt.%) and concluded that this alloy exhibits a good resistance to irreversible martensite stabilization and has a high martensite start temperature of 210 °C.

In this work a Cu-SMA with composition of Cu-8.5Al-10-Mn-(0.25-1.00)Zr (wt.%) is investigated and the preliminary results of microstructure and microhardness analysis are included. This alloy was selected because it has potential to be used as high-temperature smart material for many applications, mostly sensors.

MATERIALS AND METHODS

The Cu-Al-Mn-Zr alloys were prepared from the pure metals with purity 99.99 % Cu (pellets 6x6 mm), 99.8 % Mn (flakes < 4 mm), 99.99 % Al (granules 2-10 mm) and 99.8 % Zr (granules 1-3 mm). The pure metallic components were smelted by laboratory vacuum electro-arc furnace at high current of 112 A (Fig. 1) used vacuuming and protection by argon. After vacuuming the argon was introduced in chamber in duration of 15 minutes. The alloys were smelted three times in protective argon atmosphere. The smelted alloys were poured into Cu-moulds with diameter of 8 mm and 12 mm high.

The target chemical compositions of produced alloys and marks of samples are shown in Table 1. Microstructure and hardness of investigated samples was examined after casting in Cu-moulds and after the heat treatment at 900 °C/15 min/water. Samples for microstructural analysis were prepared by mechanical grinding. Grinding was performed with paper No. 240-1200 and polishing with 0.3 μm Al_2O_3. After that, the samples are etcher in 2.5 g $FeCl_3$ + 48 ml methanol + 10 mL HCl solution during 5 s.

The microstructure characterization was carried out by optical microscope (OM) and scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS). Microhardness was tested by Vickers method at load 9.804 N for 10 s.

Figure 1. The laboratory electro-arc furnace used for smelting and casting in Cu-mould

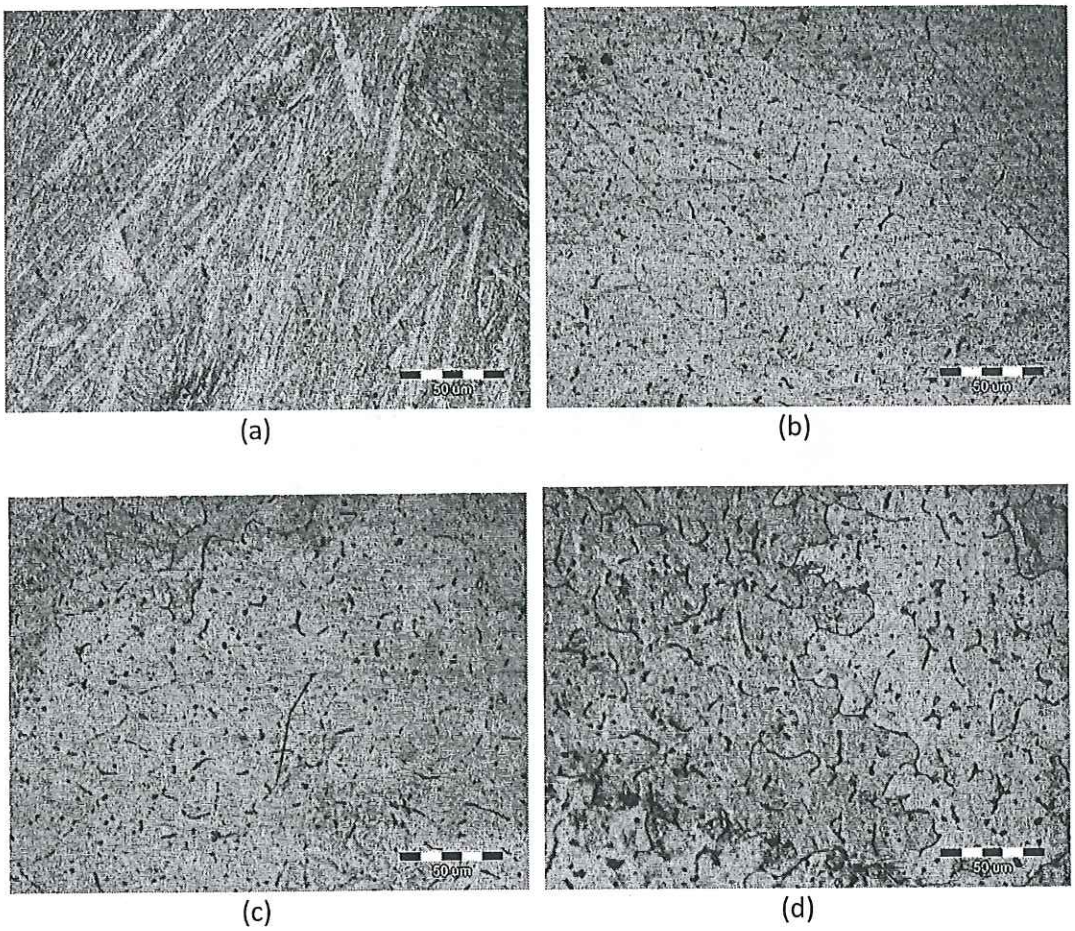
Table 1. List of marks and target chemical composition of investigated samples Cu-Al-Mn-Zr alloys

Mark of sample	Cu, wt.%	Al, wt.%	Mn, wt.%	Zr, wt.%
1	81.25	8.5	10	0.25
2	81.00	8.5	10	0.50
3	80.75	8.5	10	0.75
4	80.50	8.5	10	1.00

RESULTS AND DISCUSSION

This paper presents preliminary investigation results of the effect of zirconium additions on microstructure and microhardness of Cu-Al-Mn shape memory alloy. Figs. 2 and 3 shows micrographs obtained by optical microscopy of the investigated Cu-Al-Mn-Zr alloys after casting and after heat treatment at 900 °C/15 min/water. A more detailed analysis of micrographs obtained by optical microscopy in the as-cast state of Cu-Al-Mn-Zr alloys shows that only in case of the alloy that has 0.25 wt.% of Zr (sample 1) can be observed the martensite phase (Fig. 2). Other investigated alloys show dual-phase microstructure without martensite, probably β and γ_2. After heat treatment optical microscopy micrographs show similar behaviour (Fig. 3). According to the literature [4] the eutectic reaction takes place at 1037 °C and 8.5 % Al and at 565 °C and 11.8 % Al and β phase is transformed in the γ_2 phase.

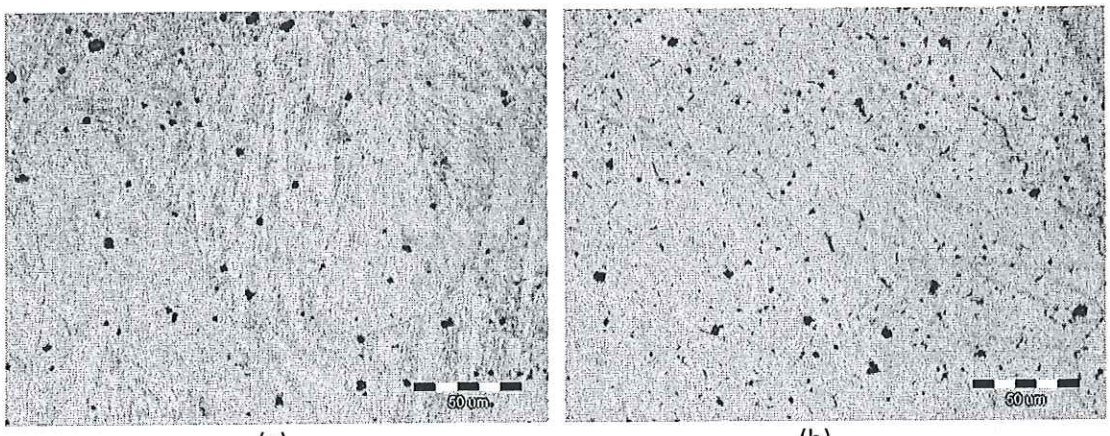
During cooling at non-equilibrium conditions β phase can be replaced by a martensite phase β_1'. The shape memory alloys can show the next ordering transitions: $\beta(A2) \rightarrow \beta_2(A2) \rightarrow \beta_1(L2_1)$ and after that the thermoelastic martensitic transformation has occurred as $\beta_1(L2_1) \rightarrow \beta_1$` (9R or 18R). The type $\beta_1$` martensite formed in the typical zig-zag morphology, while the γ_1` mainly appears as coarse variants.



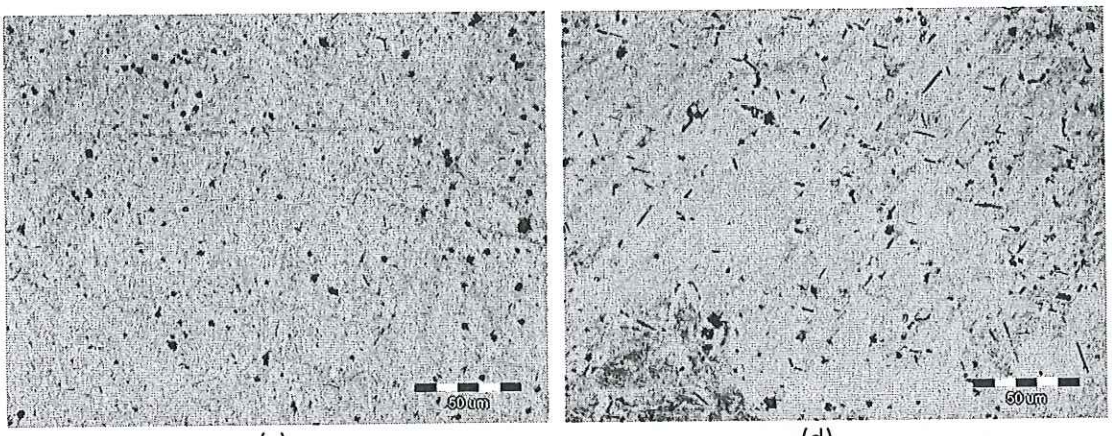
(a) (b)

(c) (d)

Figure 2. Optical micrographs of sample 1 (a), sample 2 (b), sample 3 (c) and sample 4 (d) after casting in Cu-mould; magnification 500X



(a) (b)

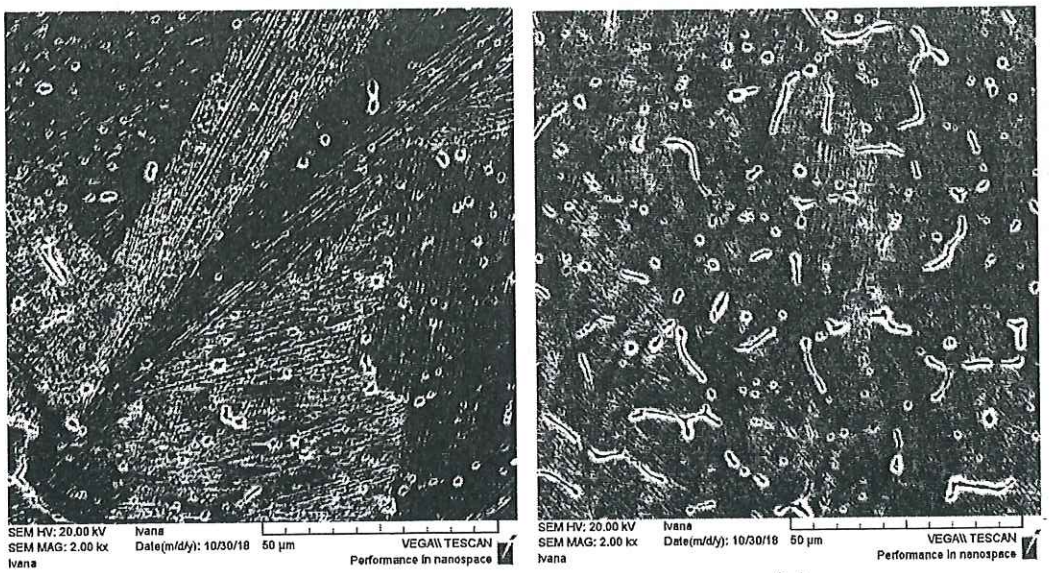


(c) (d)

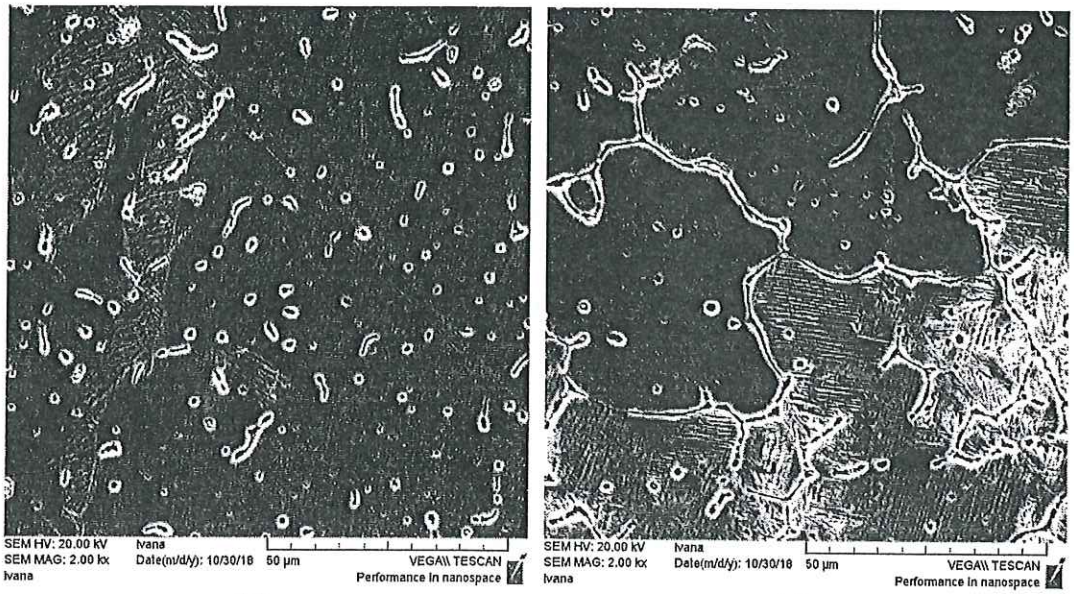
Figure 3. Optical micrographs of sample 1 (a), sample 2 (b), sample 3 (c) and sample 4 (d) after heat treatment 900 °C/15 min/water; magnification 500X

SEM micrographs of as-cast state sample 1 (alloy with 0.25 wt. % Zr) show presence of martensite, which was also observed on optical micrographs. However, at the higher magnifications by SEM analysis can be observed the start of martensite formation in some places in the other investigated alloys (Figs. 4 and 5). From the results of EDS analysis (Table 2) it can be seen that there is no significant difference in chemical composition in all investigated positions. Only at some places incompletely dissolved particles of zirconium were observed. After the heat treatment SEM micrographs show the presence of martensite but with more particles of γ_2 phase precipitates (Figs. 5 and 6). Results of EDX analysis performed after heat treatment (Table 3) show similar content of Cu, Al, Mn and Zr as in investigated position on sample after casting (Table 2).

Chen et al. [6] mentioned that parent phase of the Cu-11.9Al-2.48Mn-0.1Zr alloy is stable and does not decompose easily during aging. This can be caused by Mn addition to Cu-Al system which stabilizes the β phase and makes β phase region wider. Also, they concluded that as results of this process can be present a small quantity of γ_2 precipitates.

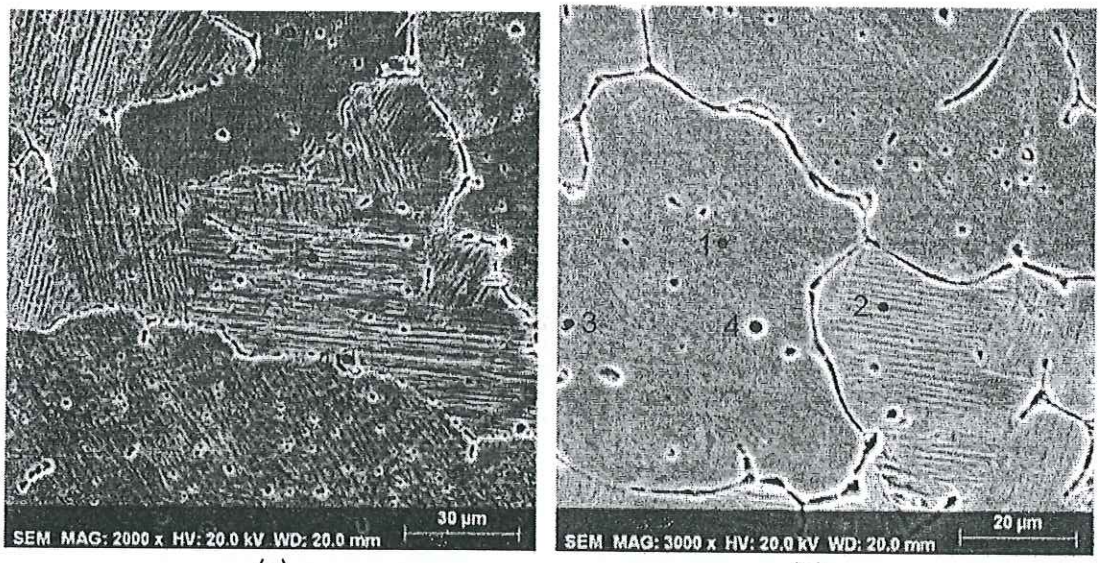


(a) (b)



(c) (d)

Figure 4. SEM micrographs of sample 1 (a), sample 2 (b), sample 3 (c) and sample 4 (d) after casting in Cu-mould



(a) (b)

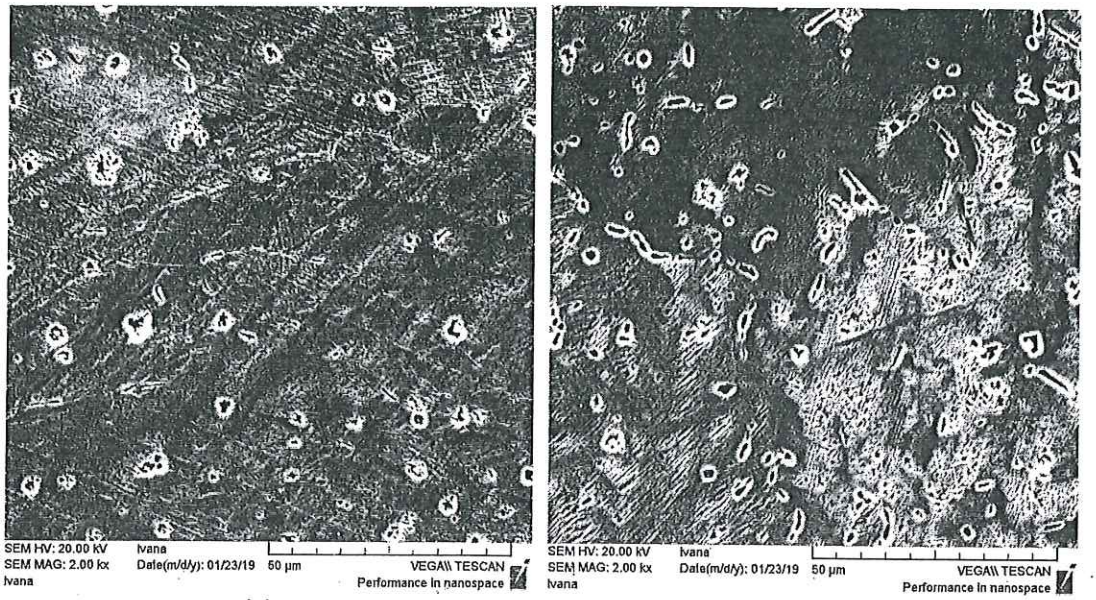
Figure 4. SEM micrographs of sample 1 (a) and sample 4 (b) after casting with marked positions for EDS analysis

Table 2. Results of EDS analysis of sample 1 (a) and sample 4 (b) after casting; positions marked at the Fig. 4

Sample	Position	Chemical composition, wt.%			
		Cu	Al	Mn	Zr
1	1	82.53	7.70	9.23	0.54
	2	82.34	8.04	9.01	0.61
	3	82.75	7.58	9.28	0.39
	4	80.75	7.61	9.17	2.47
	5	84.02	6.22	9.34	0.42
4	1	82.79	7.31	9.43	0.47
	2	83.07	6.87	9.75	0.31
	3	80.74	9.05	9.44	0.77
	4	82.87	7.22	9.38	0.53

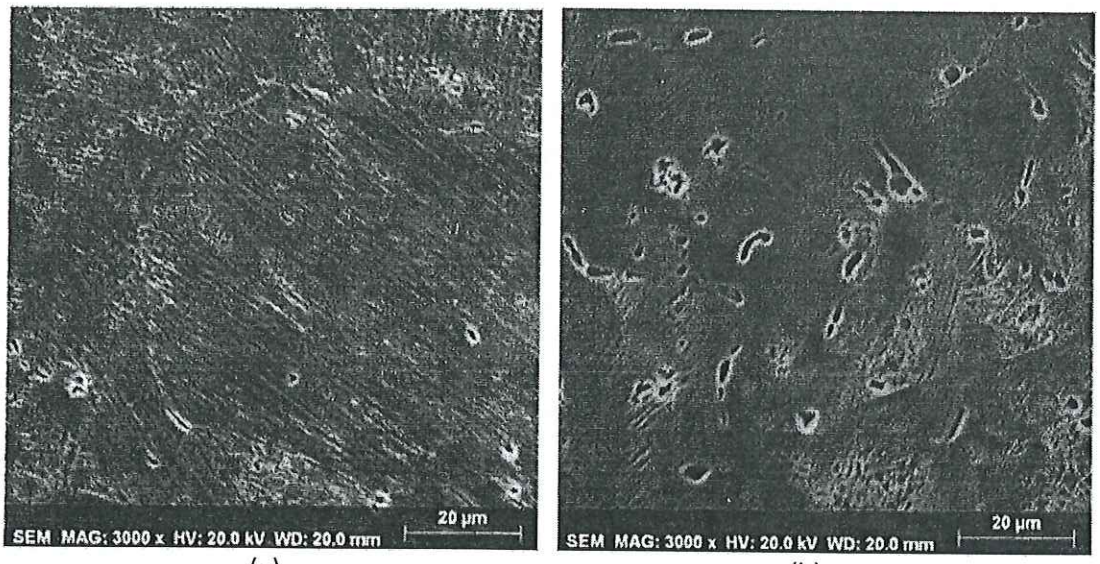
(a)

(b)



(c) (d)

Figure 5. SEM micrographs of sample 1 (a), sample 2 (b), sample 3 (c) and sample 4 (d) after heat treatment 900 °C/15 min/water



(a) (b)

Figure 6. SEM micrographs of sample 1 (a) and sample 4 (b) after heat treatment 900 °C/15 min/water with marked positions for EDS analysis

Table 3. Results of EDS analysis of sample 1 (a) and sample 4 (b) after heat treatment 900 °C/15 min/water; positions marked at the Fig. 6

Sample	Position	Chemical composition, wt. %			
		Cu	Al	Mn	Zr
1	1	82.71	7.14	9.68	0.47
	2	82.56	7.51	9.50	0.43
	3	82.68	6.92	9.90	0.50
4	1	82.97	6.89	9.78	0.36
	2	82.63	7.40	9.34	0.63
	3	82.75	7.03	9.82	0.40

In Fig. 7 it can be seen that the as-cast state of the investigated Cu-Al-Mn-Zr alloys has the lowest microhardness values (188.4-215.8 HV1), in comparison with microhardness values of samples after heat treatment (212-224.5 HV1). However, these differences are negligible and can be related to small changes in microstructure and to the error of the measurement.

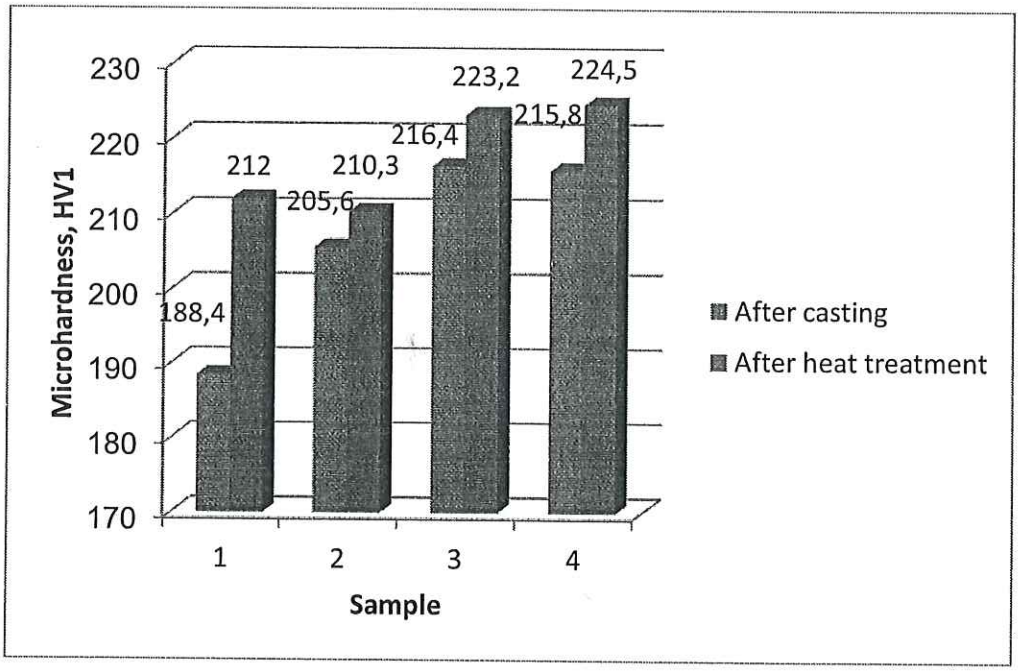


Figure 7. Microhardness values after casting and heat treatment 900 °C/15 min/water

CONCLUSIONS

The microstructural analysis with microhardness testing were carried out on laboratory produced ingots (ϕ8 x 12 mm) of Cu-Al-Mn-Zr alloys before and after heat treatment (900

°C/15min/water). From the obtained preliminary results, we can draw the following conclusions:

- Optical microscopy in the as-cast state of investigated alloys shows that only in sample 1 (alloy with 0.25 wt.% Zr) can be clearly observed the martensite phase. Other investigated alloys show dual-phase microstructure without martensite, probably β and γ2. After heat treatment optical microscopy micrographs show similar behaviour.
- SEM micrographs before and after heat treatment of the sample 1 (alloy with 0.25 wt.% Zr) show clear presence of martensite, but because possibility of scanning at the higher magnifications by SEM analysis it is visible the start of martensite formation in some places in the other investigated alloys.
- EDS analysis shows that before and after heat treatment there is no significant difference in chemical composition in all investigated positions.
- Microhardness values before heat treatment were slightly lower (188.4-215.8 HV1), in comparison with microhardness values of samples after the heat treatment (212.0-224.5 HV1).

Acknowledgements

This work was supported by the institutional project of University of Zagreb Faculty of Metallurgy "Properties of metallic materials" (FPI-124-2020-MG).

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