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## MICROSCOPIC ANALYSIS OF THE Cu-Al-Mn-Ni SHAPE MEMORY ALLOY AFTER HEAT TREATMENT

**Abstract:** In this work, the microstructure of two nickel content (2.5 and 3.5 wt.%) Cu-Al-Mn-Ni shape memory alloy (SMA) after heat treatment was analyzed. The melting of technically pure was performed in specially designed copper anode which also was used as a casting mould. By this procedure, samples of cylindrical shape, ingots of 8 mm diameter and 15 mm length, were produced. The samples with various nickel content (2.5 and 3.5 wt.%) were subjected to heat treatment procedure. Selected samples were heat treated at 900 °C, held for 15 minutes on that temperature following water quenching. Optical and scanning electron microscopy revealed the presence of  $\beta'$  martensite in the microstructure. Microhardness of the samples increase drastically by increasing the nickel content from 2.5 to 3.5%, respectively.

**Key words:** Cu-Al-Mn-Ni alloy, shape memory alloys, martensite, microstructure, microhardness

## 1. INTRODUCTION

The technical importance of most engineering materials is based on their mechanical, electrical or magnetic properties, which should be independent from environmental influences. However, functional materials are not interesting so much for their properties under certain conditions, but much more for how they react on changes of these conditions. Shape memory materials belong to this group [1-3].

In recent years, Cu-Al-Ni shape memory alloys (SMA) have attracted attention due to their low cost, good electrical and thermal stability as well as higher operating temperature. However, the engineering application of the alloy has been restricted seriously because equiaxed polycrystalline Cu-Al-Ni alloy is prone to intergranular fracture during plastic deformation due to the large grain size and the existence of brittle  $\gamma_2$  phase [4-6].

Unfortunately, the ductility of CuAlNi SMA is generally found to be poor [7]. The certain steps for the improvement of ductility of CuAlNi alloys have been undertaken. The grain size refining has been achieved by rapid solidification techniques or by the addition of fourth and fifth alloying elements, such as titanium, manganese and boron [7-9].

The addition of the Mn to the binary Cu-Al system has resulted in enhanced ductility, which is very important for practical applications [10, 11]. In the Cu-Al-Mn SMAs, the low aluminum and the high manganese content showed good ductility and shape memory effect.

The objective of this research is to study the

microstructure of quaternary system (Cu-Al-Mn-Ni), and the effect of heat treatment on alloys microstructure at different nickel content.

## 2. EXPERIMENTAL

Cu-Al-Mn-Ni alloy is prepared by melting technically pure elements, 99.99% copper, 99.99% aluminum, 99.8% manganese and nickel 99.8%. The aim was to produce a shape memory alloy with the nominal chemical composition of Cu-13Al-2.5Mn-(2.5 and 3.5) Ni (wt.%). The melting furnace was used for melting and casting the ingots in a water-cooled, specially designed copper anode which also was served as a casting mold. The samples were remelted under argon protective atmosphere three times using an electrical arc to achieve homogeneity of the chemical composition. The weight of the ingot was about 6 g. After casting, the 8 mm in diameter and 15 mm in length ingots were obtained, Figure 1. Chemical composition and markings of the investigated samples are listed in Table 1.

Heat treatment of Cu-Al-Mn-Ni alloy was carried out by holding the samples at 900 °C for 15 minutes, followed by cooling in room temperature water. After heat treatment, the samples were metallographically prepared for examination on optical (OM) and scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS). For OM and SEM analysis, the samples were grounded (from 120 to 1000 grade paper), and polished in 0.3  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  solution. Afterwards, the samples were etched in a solution composed of 5 g  $\text{FeCl}_3$  and 96 ml methanol in 20 ml HCl. Microhardness

measurements were performed by Vickers method. The force applied to the tested samples was 9,804 N at the injecting time of 10 seconds.



Figure 1. Photograph of casted Cu-Al-Mn-Ni ingots

Table 1. Planned chemical composition of Cu-Al-Mn-Ni alloys, wt. %

Sample	Heat treatment	Chemical composition, wt. %			
		Cu	Al	Mn	Ni
A	900 °C/15'/H <sub>2</sub> O	82.0	13.0	2.5	2.5
B	900 °C/15'/H <sub>2</sub> O	81.0	13.0	2.5	3.5

### 3. RESULTS AND DISCUSSION

To determine the influence of heat treatment on the Cu-Al-Mn-Ni alloys microstructure samples were examined on an optical and scanning electron microscope, Figures 2-5.

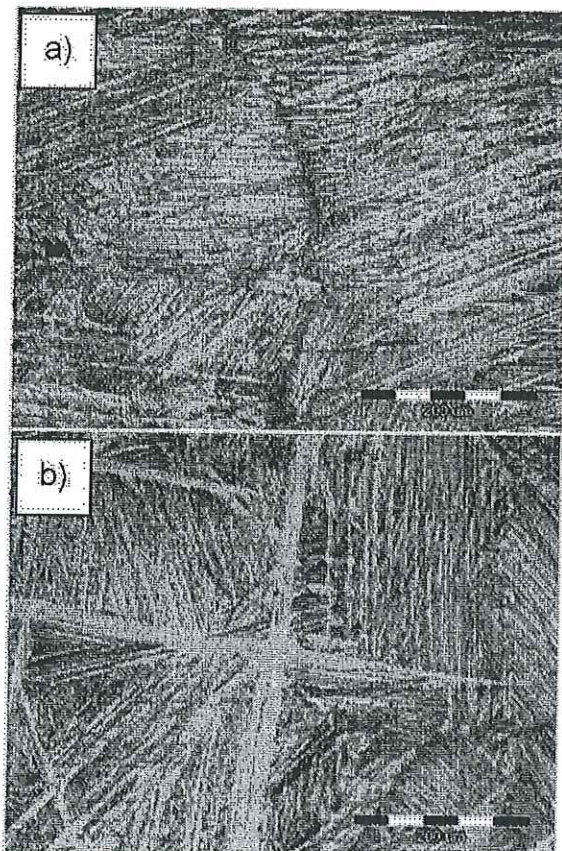


Fig. 2. Optical micrographs of the Cu-13Al-2.5Mn-2.5Ni (a) and Cu-13Al-2.5Mn-3.5Ni (b) SMA after quenching, magnification 200x

By analyzing obtained optical micrographs (Fig. 2) of the investigated alloys, it can be noticed no significant changes in the microstructure between the samples. A martensitic microstructure is visible and the martensitic needles have different orientation in particular grains. The SEM analysis (Figures 3-5) confirmed the martensite microstructure and revealed that the microstructure consisted probably from  $\beta'$ , martensite [8, 13]. The chemical composition of individual positions obtained by EDS was listed in Tables 2 and 3. EDS analysis showed very small differences in the chemical composition of individual positions for each sample. It can be noticed a decrease in aluminum content, which probably occurred due to aluminum oxidation during melting and casting.

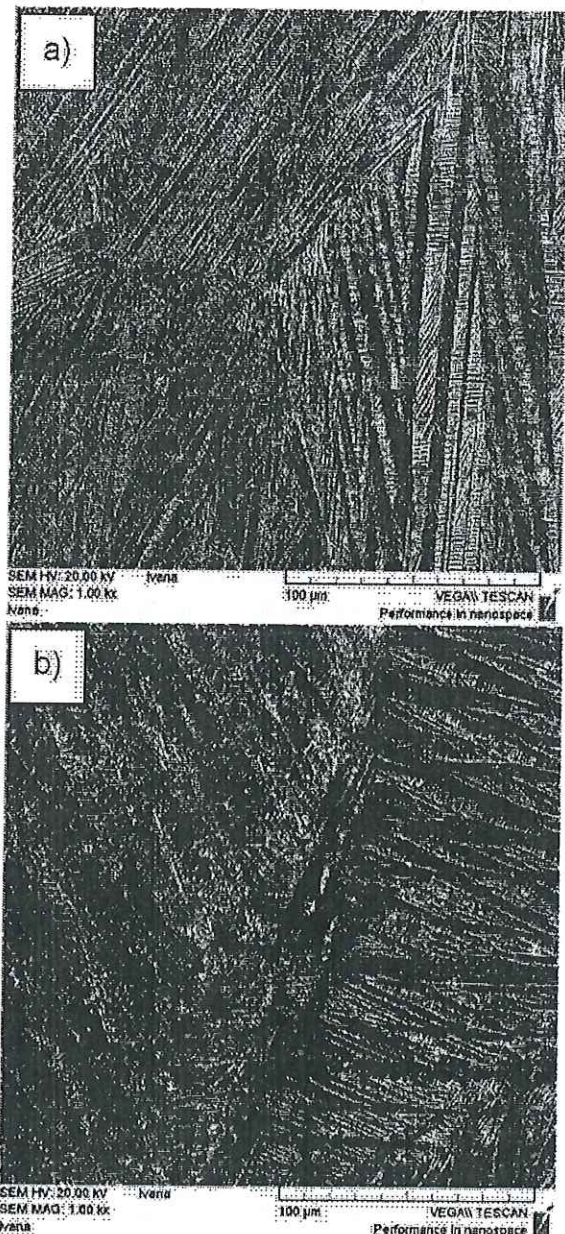


Fig. 3. SEM micrographs of the Cu-13Al-2.5Mn-2.5Ni (a) and Cu-13Al-2.5Mn-3.5Ni (b) SMA after quenching

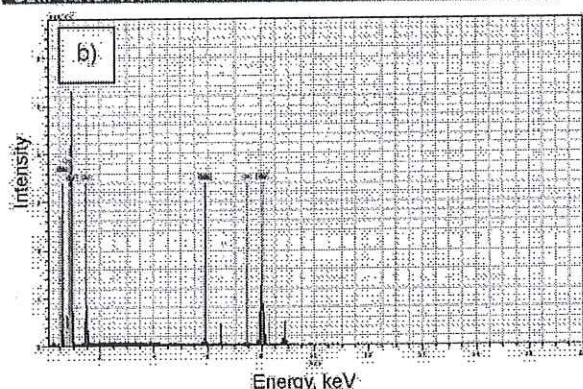
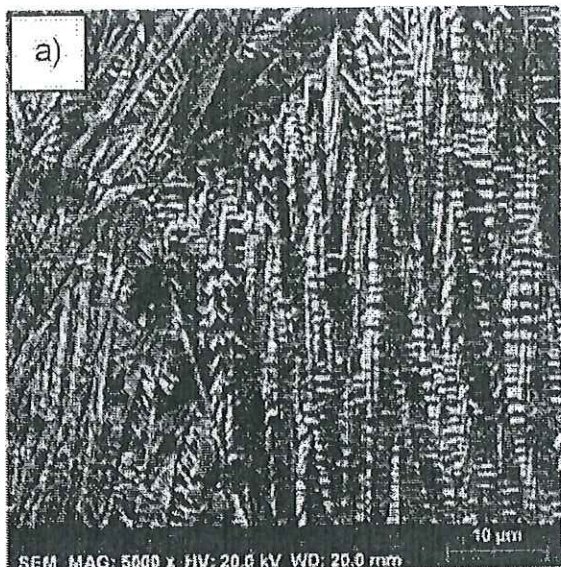


Fig. 4. SEM micrograph (a) and EDS spectrum of position 1 (b) of the Cu-13Al-2.5Mn-2.5Ni SMA

Table 2. The results of EDS analysis of the shape memory alloy

Position	Chemical composition, wt. %			
	Cu	Al	Mn	Ni
1	83.88	10.36	2.77	2.99
2	84.01	10.20	2.66	3.13

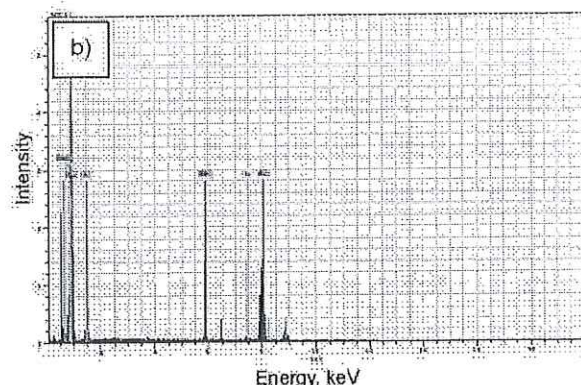


Fig. 5. SEM micrograph (a) and EDS spectrum of position 1 (b) of the Cu-13Al-2.5Mn-3.5Ni SMA

Table 3. The results of EDS analysis of the shape memory alloy

Position	Chemical composition, wt. %			
	Cu	Al	Mn	Ni
1	82.90	10.42	2.70	3.98
2	84.10	9.29	2.66	3.94

The Vickers microhardness test results for the Cu-Al-Mn-Ni alloy are shown in Table 4. It is visible that the alloy with higher nickel content has drastically higher mean value of microhardness. The increase of 1 wt.% of nickel increase microhardness from 229.9 HV1 to 446.7 HV1, respectively.

Table 4. Results of the microhardness of Cu-Al-Mn-Ni alloys, HV1

Sample	HV1	Mean value, HV1
Cu-13Al-2.5Mn-2.5Ni	229.1	229.9
	230.5	
	230.0	
Cu-13Al-2.5Mn-3.5Ni	449.7	446.7
	450.4	
	440.0	

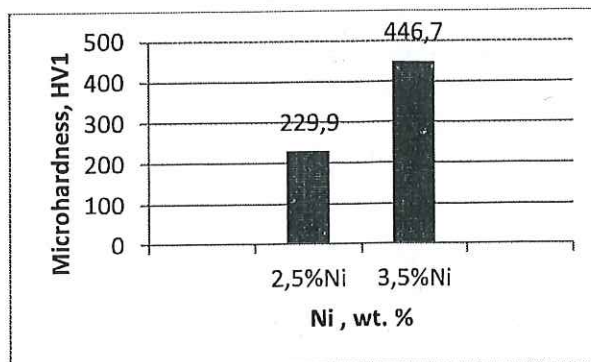


Fig. 6. Mean value of microhardness of the Cu-Al-Mn-Ni after quenching

## 5. CONCLUSIONS

From the microstructural and microhardness analysis of the Cu-13Al-2.5Mn-(2.5 and 3.5) Ni (wt.%) shape memory alloy after quenching can be withdrawn following conclusions:

- Optical micrographs of the investigated Cu-Al-Mn-Ni alloys in both samples show martensitic microstructure after quenching.
- Scanning electron microscopy confirmed the presence of martensite in the microstructure. Martensite has a different orientation in different grains and the shape of martensitic needles is characteristic for  $\beta'$  martensite.
- EDS analysis confirmed small differences in the chemical composition of all analyzed positions. It is observed a lower aluminum content than it was planned, which can be associated with oxidation of aluminum during melting and casting.
- Microhardness values increase drastically from 229.9 HV1 to 446.7 HV1 with increase of nickel content from 2.5 to 3.5 wt.%, respectively.

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## 6. REFERENCES

- [1] Ivanić, I., Gojić, M., Kožuh, S., *Slitine s prisjetljivosti oblika (I. dio): najznačajnija svojstva*, Kemija u industriji 63 (2014) 9 - 10, 323 - 239.
- [2] Lexcellent, C., *Shape-memory Alloys Handbook*, John Wiley&Sons Inc., Hobogen, 2013.
- [3] Lojen, G., Anžel, I., Kneissl, A., Krizman, A., Unterweger, E., Kosec, B., Bizjak, M., *Microstructure of rapidly solidified Cu-Al-Ni shape memory alloy ribbons*, Journal of Materials Processing Technology 162-163 (2005) 220-229.
- [4] Ivanić, I., Gojić, M., Kožuh, S., *Slitine s prisjetljivosti oblika (II. dio): podjela, proizvodnja i primjena*, Kemija u industriji 63 (2014) 9 - 10, 331 - 344.
- [5] Lagoudas, D. C., *Shape Memory Alloys Modeling and Engineering Applications*, Springer, Texas, USA, 2008.
- [6] Wang, Z., Liu, X.F., Xie, J.X., *Effect of  $\gamma_2$  phase evaluation on mechanical properties of continuous columnar-grained Cu-Al-Ni alloy*, Materials Science and Engineering A 532 (2012) 536-542.
- [7] Gao, Y., Zhu, M., Lai, J.K.L., *Microstructure characterization and effect of thermal cycling and ageing on vanadium-doped Cu-Al-Ni-Mn high-temperature shape memory Alloy*, Journal of Materials Science 33 (1998) 3579 - 3584.
- [8] Sari, U., *Influence of 2.5 wt% Mn addition on the microstructure and mechanical properties of Cu-Al-Ni shape memory alloys*, International Journal of Minerals, Metallurgy and Materials 17 (2010) 2, 192-198.
- [9] Sutou, Y., Kainuma, R., Ishida, K., *Effect of alloying elements on the shape memory properties of ductile Cu - Al - Mn alloys*, Materials Science Engineering A237 - 275 (1999), 375 - 379.
- [10] Kainuma, R., Takahashi, S., Ishida, K., *Thermoelastic martensite and shape memory effect in ductile Cu - Al - Mn alloys*, Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science 27 (1996) 8, 2187 - 2195.
- [11] Saud, S., Hamzah, N. E., Abubakar, T., Bakhsheshi-Rad, H. R., Zamri, M., Tanemura, M., *Effects of Mn additions on the structure, mechanical properties, and corrosion behavior of Cu-Al-Ni shape memory alloys*, Journal of Materials Engineering and Performance 23 (2014) 10, 3620-3629.
- [12] Mallik, U. S., Sampath, V., *Influence of aluminum and manganese concentration on the shape memory characteristics of Cu - Al - Mn shape memory alloys*, Journal of Alloys and Compounds 459 (2008) 1 - 2, 142 - 147.
- [13] Aksu Canbay, C., Karagoz Genc, Z., Sekerci, M., *Thermal and structural characterization of Cu-Al-Mn-X (Ti, Ni) shape memory alloys*, Applied Physics A 115 (2014), 371 - 377.

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