PROIZVODNJA I KARAKTERISTIKE LEGURA SA MEMORIJOM OBLIKA ZA NAMENU U ELEKTRONICI

MANUFACTURE AND CHARACTERISTICS OF SHAPE MEMORY ALLOYS FOR ELECTRONIC PURPOSES

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Među mnogim naprednim materijalima sa izuzetnim svojstvima i primenom, legure sa memorijom oblika (SMA) imaju jedinstvenu sposobnost da se vrate prethodno definisanim oblicima ili veličinama ako su podvrgnute odgovarajućoj termičkoj obradi. Memorijski efekat se može postići samo u prisustvu specifične fazne transformacije, reverzibilnog prelaza iz austenita u martenzit. Postoji nekoliko osnovnih tipova SMA, kao što su Ni-Ti (nitinol), legure na bazi Cu i legure na bazi Fe. Ekonomski efekat (niska cena) je glavna prednost SMA na bazi Cu u poređenju sa drugim SMA. Naime, ove Cu-Al-Ni legure mogu se primeniti u različitim industrijskim poljima, posebno kada su potrebne visoke temperature transformacije (blizu 200 ° C), zahvaljujući njihovoj odličnoj termičkoj stabilnosti i visokim temperaturama transformacije.

Ključne reči: *Cu-Al-Ni legure sa memorijom oblika; mikrostruktura; mikrotvrdoća*

Among the variety of advanced materials with exceptional properties and applications, shape memory alloys (SMAs) have a unique ability to return to previously defined shapes or sizes if subjected to the relevant thermal treatment. The memory effect can be reached only in the presence of specific phase transformation, reversible austenite to the martensite phase. There are several basic types of SMAs, such as Ni-Ti (nitinol), Cu-based, and Fe-based alloys. The economic effect (low price) is the main advantage of Cu-based SMAs compared with other SMAs. Namely, these Cu-Al-Ni alloys can be applied in various industrial fields, especially when high transformation temperatures are required (near 200 °C), thanks to their excellent thermal stability and high transformation temperatures.

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

1 Introduction

Shape memory alloys (SMAs) belong to a large group of smart materials that respond to the stimulus of the environment; they can memorize and recover their original shape, in other words, these alloys show the ability to return to some previously defined shape or size when subjected to the appropriate treatment. It is based on crystallographically reversible martensitic phase transformation. Such phase transformations can be obtained by mechanical (loading) or thermal treatment (both cooling and heating). SMAs are extremely sensitive to exact chemical composition, grain size, processing parameters, heat treatment, loading conditions, etc.

SMAs are interesting in numerous commercial engineering applications. There is a high demand for SMAs with high strength and shape memory effect in technical applications. During this century, shape memory alloys have been successfully introduced in a variety of technical areas. A very promising field for a high-volume application of SMAs is the actuator technology since, with a shape memory element, a pre-determined response can be obtained very easily by a thermal or electric stimulus. Especially the possibility to realize even complicated movements with an element of simple

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design and compact size makes shape memory actuators very attractive. Also these alloys can be used as sensors and connectors for microelectronic chips.

The main types of these alloys are nitinol (Ni-Ti), Cu-based, and Fe-based alloys. Considering all material characteristics, copper-based alloys are the most commercial from the group of SMA. The main advantages of Cu-based alloys are relatively simple fabrication procedure, high electrical and thermal conductivity compared to other shape memory alloys, and low price. Among Cu-based SMAs, the Cu-Al-Ni and Cu-Al-Zn alloys are extensively investigated.

Shape memory effect is a result of crystallographic reversible thermo-elastic martensitic transformation. There are two crystal phases in SMAs: the austenite phase (stable at high temperature) and the martensite phase (stable at low temperature). Austenite to martensite phase transformation can be obtained by mechanical loading and thermal methods (heating and cooling). During martensitic transformation, no diffusive process is involved, only inelastic deformation of the crystal structure. When the shape memory alloy passes through the phase transformation, the alloy transforms from high ordered phase (austenite) to low ordered phase (martensite). There are two types of martensite transformations: temperature-induced martensite, which is also called self-accommodating (twinned) martensite and stress-induced martensite, also called detwinned martensite. The austenite to martensite transformation cycle is characterized by four temperatures: M_s – martensite start temperature, M_f – martensite finish temperature, A_s – austenite start temperature, and A_f – austenite finish temperature. The main factors influencing transformation temperatures are chemical composition, heat treatment procedure, cooling speed, grain size, and number of transformation cycles. As a result of martensitic transformation in SMAs, several thermomechanical phenomena may occur: pseudoelasticity, shape memory effect (one-way and two-way) and rubber-like behavior. Pseudoelasticity occurs when the SMA is subjected to a mechanical loading at a constant temperature above A_f. Shape memory effect, mainly one-way, which is the most commonly used occurs when the sample is subjected to a mechanical loading. Then the stress reaches a critical value and the transformation of twinned martensite into detwinned begins; it terminates when the loading process is finished. When the loading-unloading process is finished, the SMA presents a residual strain recoverable by alloy heating, which induces the reverse phase transformation. As a result, the alloy recovers to its original shape [1,2].

Cavitation erosion is a phenomenon commonly encountered in hydraulic systems such as turbine blades, valves, propellers, and pipelines. It is typically caused by a rapid drop in the fluid pressure and the subsequent generation of steam bubbles which may collapse on the metal surface of the machinery. The energy released during this process can lead to local plastic deformation of the material and mass removal, while its extended action can result in malfunction or even failure of the component. Cavitation erosion includes not only properties of liquid, but also the properties of material, for example, hardness, microstructure, grain size of material, and so on. It is known [3] that the material with a homogeneous and fine-grained structure has good mechanical properties and high corrosion resistance. As there are no reported investigations regarding cavitation resistance testing of CuAlNi shape memory alloys, they are studied in terms of mass loss and microstructure in order to examine their potential use in relative applications.

2 Production of shape memory alloys

During the commercial production of shape memory alloys, several problems can occur, such as controlling the chemical composition of the alloy, achieving cold deformation conditions and heat or thermomechanical processing to achieve shape memory effect, etc.

Technologies for producing shape memory alloys are induction melting, vacuum induction melting, rapid solidification (melt spinning), vertical continuous casting, electron beam melting, plasma arc melting [4,5].

This is followed by processing of alloys by hot deformation (forging, rolling) and cold deformation (drawing and rolling), etc. The combination of these techniques and heat treatment creates the final product [6]. These methods are characterized by high cooling rates that allow very short time for diffusion processes and may lead to extremely fine microstructure, better homogeneity etc.

The advantages of induction melting are homogeneity and the ability to control the chemical composition of the ingot since alternating current mixes the melt. In this case the retort is made of graphite or CaO. In the case of graphite retort, contamination of the melt with oxygen and carbon is inevitable. The proportion of carbon in the melt depends on the temperature of the melt. In the case of NiTi alloy, the melt temperature must not be above 1450 °C, because then the graphite retort becomes inapplicable. The carbon content of the melt can be from 200 to 500 ppm and such small amounts do not affect the memory characteristics of the NiTi alloy [6].

Rapid solidification methods are acceptable although the process of producing shape memory alloys is very demanding. Solidification at cooling rates of 10^3 Ks^{-1} and higher is considered as rapid because at high cooling rates, during solidification and cooling, a very short time is available for diffusion processes to take place. Therefore, rapid solidification can lead to the formation of fine-grained microstructure, high solubility in the solid state, less segregation, better homogeneity with little or no secondary phases. Due to all the above, the alloys thus produced have better stability of mechanical properties at elevated temperatures, less pronounced grain growth during processing, better resistance to aging and reduced brittleness, and may improve electrical and magnetic properties and corrosion resistance [4].

The vertical continuous casting of the CuAlNi alloy is schematically presented in Figure 1. It can be seen that the alloy solidifies in the water-cooled crystallizer and a rod of a certain diameter emerges between the rollers which rotate in the direction of the melt flow.

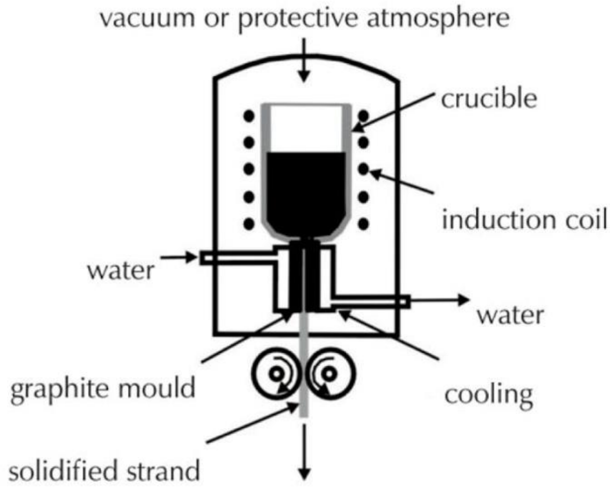


Figure 1. Casting of CuAlNi alloy by vertical continuous casting technique [7]

Besides the commercial rod or wire material, thin ribbons, wire and / or fibers of CuAlNi can be produced using a melt-spinning method in order to miniaturize shape memory elements for possible applications in the field of microsensors and microactuators. The term melt-spinning denotes various techniques in which a thin stream of melt solidifies in a cooled gas, liquid or on a solid substrate to produce thin ribbons. The most used method for the production of rapidly solidified ribbons is free jet melt spinning (also known as chill block melt spinning), Figure 2.

The melt-spinning process starts with induction melting of the alloy in a graphite crucible. It is well known that Cu melts do not show any reaction with graphite and the solubility of graphite also is negligibly low. When an overpressure is applied within the crucible the melt will flow through a sprayer onto a rotating copper wheel where it hardens. The solidified ribbons are gathered subsequently in a collection tray. The process is carried out under protective gas.

This process is influenced by several parameters such are the circumferential velocity of the wheel, the overheating of the melt during the casting procedure, the overpressure in the crucible, the shape of the nozzle and its distance from the wheel. Varying these parameters permits to produce ribbons of different geometries. The width of the ribbon can be wider than the size of the nozzle, and the thickness of the ribbon is usually 10 to 100 μm. The surface finish, microstructure, and mechanical and functional properties as well, are also dependent on the parameters set. Typical cooling speed is 10^5– 10^7 Ks^{-1}.

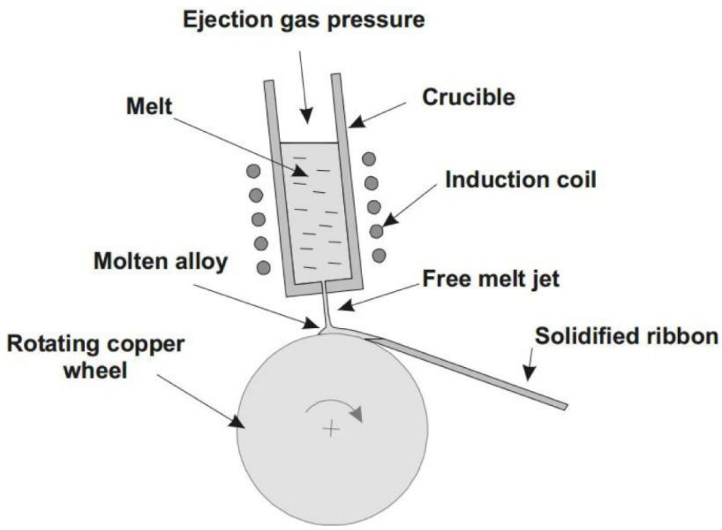


Figure 2. Free jet melt spinner technique [4]

As the cooling rate increases, the grain size decreases, and the concentration of structure defects increases, which results in improved mechanical properties and lower transformation temperatures. The concentration of structural defects (free spaces, dislocations, etc.) has a very large influence on the martensitic transformation temperatures. Lattice defects prevent the growth of martensite and lower the temperatures of phase transformations.

Homogeneous copper-based alloys can also be produced by mechanical alloying and powder metallurgy, for example CuAlNi and CuAlNiMn. According to that procedure, a mixture of powders is obtained by grinding metals in rotating drums with steel balls balls of different diameters. Afterward the mixture is purged with argon to prevent its oxidation. The resulting mixture of powders is hot compacted for in a mold in a vacuum. The alloy is then hot-extruded. However, it was concluded that the obtained alloys still do not have defined systematic and suitable production conditions for obtaining a satisfactory shape memory effect [8,9].

3 Application of shape memory alloys

Alloys with the shape memory effect as relatively new functional materials have a wide range of applications. Due to their exceptional properties, they are used in many industrial sectors:

- electrical industry- antennas of mobile devices, sensors, actuators, electrical connectors and switches, safety valves;
- mechanical industry- pipe couplings, bridge bars, vibration damping elements;
- medicine- cardiovascular surgery (blood vessel filters), orthopedic surgery (implants - stents, screws, spinal fixators), orthodontic appliances, spectacle frames;
- fashion and decoration, etc.

Alloys such as nitinol dominate the commercial market (biomedicine, aviation industry, car industry, etc.), due to their pronounced shape memory effect, good pseudoelasticity and superior properties such as ductility, favorable mechanical properties, corrosion resistance, biocompatibility, biofunctionality, and shape recovery.

There is also interest in incorporating alloy wires with shape memory effect into composite matrices to change the vibration frequency of the structure or to control the shape of the structural elements. Very thin ribbons of NiTi shape memory alloy can serve as a material for use in the manufacture of microdevices for microsystems such as micropumps, microwrappers, micro-grippers, micromirrors, microcages, etc.

CuAlNi alloys are significantly cheaper than NiTi alloys. They are considered an important functional material for actuators and sensors, the so-called smart or intelligent materials. Also these alloys can be used as connectors for microelectronic chips.

Ferromagnetic shape memory alloys can be used as sensors or magnetic actuators due to their unique property - magnetically induced deformations [10].

4 Experimental

4.1 Sample fabrication

The polycrystalline Cu-12.8Al-4.1Ni (wt. %) shape memory alloy was prepared from pure raw materials of copper, aluminum, and nickel in a vacuum induction furnace. The heating temperature was 1240 °C. A solid bar of 8 mm was produced directly from the melt by means of a device for the vertical continuous casting connected with a vacuum induction furnace. Continuous casting of the bar was carried out with a speed of 320 mm/min (as-cast state, sample L). After the casting, the heat treatment procedure was performed by the solution annealing at 885 °C for 60 min followed by water quenching (quenched state, sample K-2).

4.2 Cavitation testing

The cavitation erosion tests were implemented using a vibratory apparatus as presented in Figure 3 according to the ASTM G32 [11]. The experimental set-up consisted of a 360 W generator of high frequency, an electrostrictive transducer, a mechanical vibration transformer and a bath of distilled water where the samples were placed. The frequency of the vibrations was set at 20 kHz and their amplitude at the top of the ultrasonic transformer at 50 μm. The gap between the surface of the sample and the transformer probe was 0.5 mm. Three replicate specimens were used for the measurements, while each presented result is the mean value of the obtained results [12].

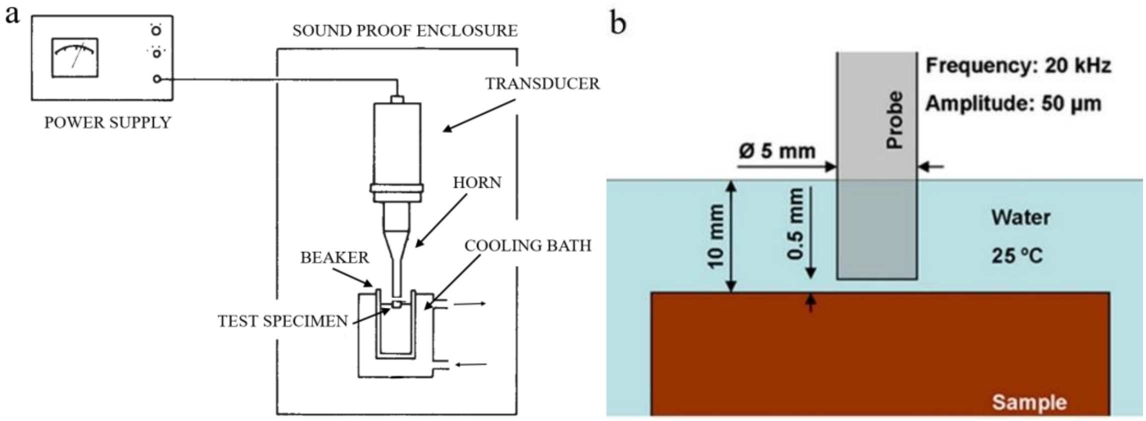


Figure 3. a) Schematic representation of the cavitation test set-up (modified from ASTM G32), b) experimental details of the cavitation erosion experiment

The mass loss and the degradation level were measured during the testing at preselected time intervals i.e. 15, 30, 60, 90, 120, 180, 300, and 420 minutes. A weighing scale with 0.1 mg resolution was used to record the mass loss versus time. Prior to each measurement, the samples were cleaned with ethanol and dried with compressed air. A final evaluation of the erosion characteristics was employed by means of mass loss and scanning electron microscopy.

5 Results and Discussion

5.1 Characterization of fabricated samples

SEM images of the manufactured CuAlNi shape memory alloy samples after both continuous casting and quenching are presented in Figure 4.

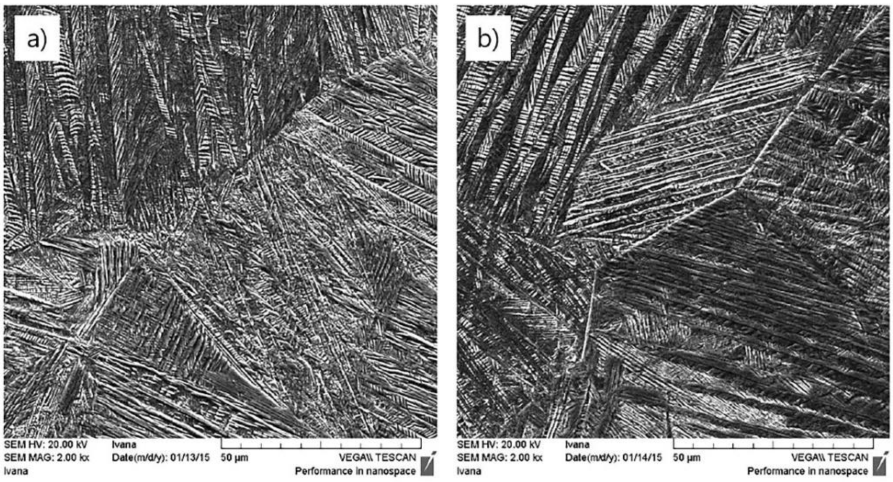


***Figure** 4. SEM images of CuAlNi shape memory alloy: a) as-cast sample (L) and b) quenched sample at 885 °C/60 min H_2O (K2)*

As seen in Figure 4, the SEM micrographs of the samples show the typical martensite microstructure. The continuous casting at a cooling rate of 320 mm/min was satisfied with the formation of martensite microstructure. Martensite laths have different orientations into particular grains. It can be explained by the nucleation of groups of martensite plates in numerous places within the grain and the creation of local strain within the grain. This microstructure is the result of the beta-phase of CuAlNi alloys transforming into a martensite phase by cooling below the M_s-temperature. Martensite appears primarily as needle-like martensite. This microstructure consists of self-accommodating needle-like shape martensite in as-cast state and after heat treatment, which is characteristic for the β'_1 martensite in the CuAlNi alloy [13].

Grain boundaries are clearly visualized before and after heat treatment. The results showed that the size of grains increases after solution annealing and quenching in water. It was found that the average grain size of samples in as-cast condition was about 150 µm (Figure 4a)), while after quenching, the average grain size was several times higher, up to about 1 mm (Figure 4b)).

Average values of microhardness testing showed that, after quenching in water, microhardness is higher (480 HV10) than that in the as-cast state (344 HV10).

5.2 Mass loss during cavitation testing

The results of mass loss, obtained by periodical weighting the samples during the entire cavitation period of 420 min, are given in Figure 5.

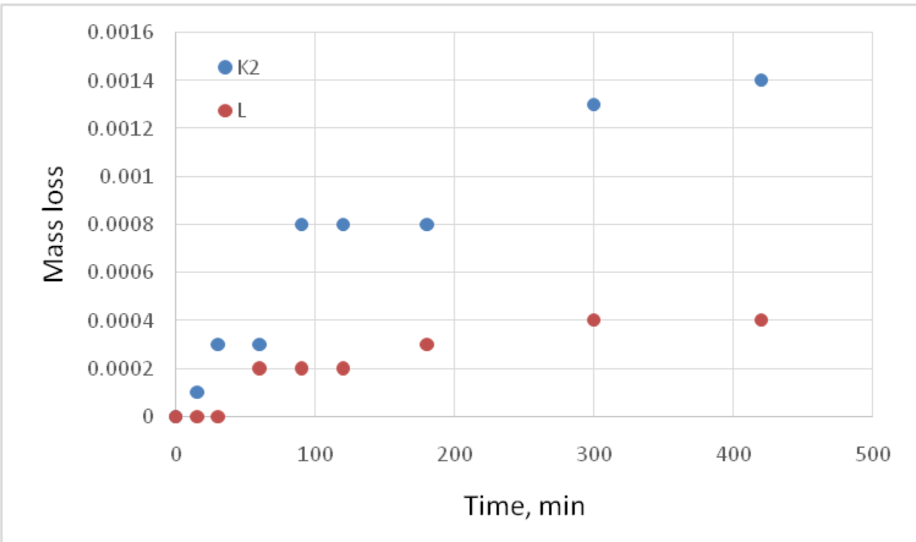


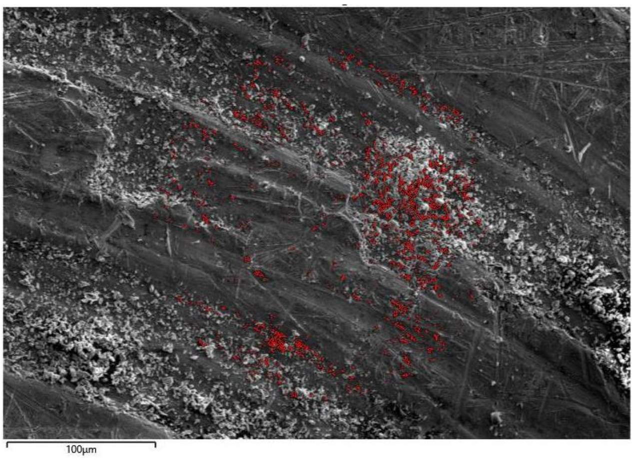
***Figure** 5. Mass loss of CuAlNi shape memory alloy during cavitation testing: L- as-cast samples and K2- quenched samples at 885 °C/60 min H_2O*

Based on the presented results in Figure 5, the sample after quenching K2 underwent more intensive mass loss in comparison with the as-cast sample L. However, it is evident that both samples showed excellent resistance to cavitation. After 420 min of exposure to cavitation testing, the mass loss was 0.0014 g for the specimen in a quenched state, while the mass loss was 0.0004 g for the sample after casting.

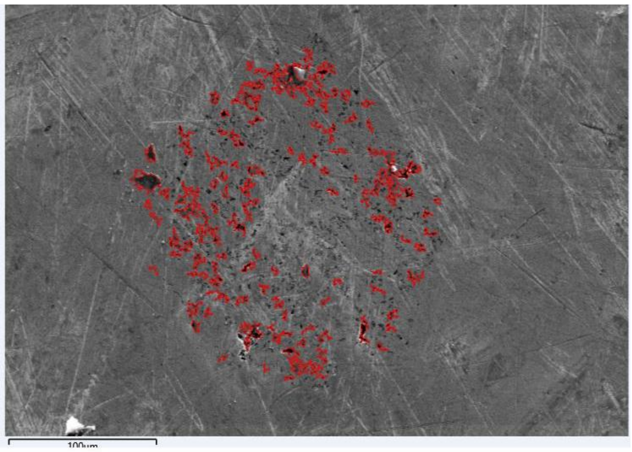
It can be concluded that the finer grain size after continuous casting of CuAlNi alloy resulted in better resistance to cavitation erosion than the sample in heat treated state. Moreover, it was observed that the CuAlNi alloy in as-cast condition is softer (344 HV10) than after quenching (480 HV10), which suggested that resistance to cavitation erosion is better after quenching than that in the as-casted state. This is in contrast to the behaviour of other materials, which show that higher hardness of the materials gives better resistance to cavitation erosion [3].

5.3 Microscopy analysis during cavitation testing

Figure 6 shows the SEM micrographs of CuAlNi shape memory alloys microstructure in both as-cast and quenched states, after 420 min of exposure to cavitation testing, whereby the formed pits are marked for better visibility.



a)



b)

***Figure** 6. SEM images of CuAlNi shape memory alloy in the as-cast state (a) and after solution annealing at 885 °C/60 min H_2O (b)*

According to the SEM images presented in Figure 2, there are differences in samples' behavior. Detected surface defects are more pronounced on the quenched sample (K2) thus indicating better cavitation resistance of the as-cast sample (L). Moreover, the formation of the typical cavitation ring is obvious on the sample after heat treatment, unlike on the sample in the as-cast state.

These results are consistent with the results of mass loss (Figure 5). It has to be emphasized that the obtained results for both samples suggested very good cavitation resistance.

The influence of heat treatment on cavitation behavior of the samples can be related to different grain size, as it was about 150 μm in the as-cast sample (Figure 4a)), while after quenching, the average grain size was several times higher, up to about 1 mm (Figure 4b)). It is well known that grain size has a great influence on mechanical properties, as well as hardness, which can also be related to cavitation resistance. The hardness values that were higher for the as-cast state confirmed this explanation for the mutually different behavior of the samples.

6 Conclusion

Shape memory alloys are alloys with a unique characteristic that provide them returning to their original shape under certain conditions. The shape memory effect is a key factor for the wide application of these materials (electrical industry, mechanical engineering, medicine).

Technologies for the production of shape memories alloys are induction melting, vacuum induction melting, rapid solidification (melt spinning), vertical continuous casting, electron beam melting, plasma arc melting, as well as powder metallurgy and mechanical alloying processes.

Examination of the microstructure of CuAlNi shape memory alloy reveals martensite microstructure after casting and heat treatment (solution annealing at 885 °C for 60 min followed by quenching in water). The grain size of samples is higher after solution annealing and quenching in water than in the as-cast state. Martensite appears primarily as needle-like martensite. This microstructure consists of self-accommodating needle-like shape β´1 martensite in as-cast state and after heat treatment. Measurements of microhardness showed that, after quenching in water, hardness was higher (480 HV10) than that in the as-cast state (344 HV10).

Samples in as-cast and quenched states were investigated in order to estimate the cavitation erosion behavior. After an exposure time of 420 min to cavitation erosion testing, very low values of mass loss were measured for both as-cast and quenched samples. Based on the obtained results, both samples showed excellent cavitation erosion resistance. Mass loss and microstructure analysis pointed out differences between the samples' behavior and better cavitation resistance for the as-cast state (L).

7 Acknowledgement

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