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UTJECAJ KALJENJA I POPUŠTANJA NA SVOJSTVA Cu-Al-Ni SLITINA S EFEKTOM MEMORIJE OBLIKA

THE INFLUENCE QUENCHING AND TEMPERING ON PROPERTIES OF Cu-Al-Ni SHAPE MEMORY ALLOY

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SAŽETAK

U radu je dana usporedba mikrostrukture i tvrdoće Cu-Al-Ni slitine s prisjetljivosti oblika prije i nakon toplinske obrade (kaljenje na 900°C/60 min/voda i popuštanje na 300°C/60 min/voda). Mikrostrukturna analiza provedena je optičkom mikroskopijom (OM) te pretražnom elektronskom mikroskopijom (SEM) opremljenom s energetsko disperzijskim spektrometrom (EDS). Na uzorku prije toplinske obrade (lijevano i kovano stanje) utvrđena je djelomično martenzitna mikrostruktura s prisutnošću γ_2 faze, dok je na uzorcima slitine nakon toplinske obrade uočena potpuno martenzitna mikrostruktura s uključcima kompleksnog kemijskog sastava, koji potencijalno mogu imati neželjeni utjecaj na svojstva slitine. Tvrdoća slitine prije toplinske obrade iznosila je 344,3 $HV_{0.5}$, nakon kaljenja 229,6 $HV_{0.5}$ i nakon popuštanja 300,2 $HV_{0.5}$.

Ključne riječi: *Cu-Al-Ni, slitine s prisjetljivosti oblika, mikrostruktura, tvrdoća*

ABSTRACT

The paper presents comparison of microstructure and hardness of Cu-Al-Ni shape memory alloy before and after heat treatment (quenching at 900°C/60 min/water and tempering at 300°C/60 min/water). Microstructural analysis was obtained by optical microscopy (OM) and scanning electron microscopy (SEM) equipped with energy dispersive spectrometry (EDS). Before heat treatment (casted and forged state) the sample has a partially martensitic microstructure with presence of γ_2 phase, while on samples after the heat treatment completely martensitic microstructure with inclusions of complex chemical composition was observed. These inclusions can have a potential unwanted influence on alloys properties. Hardness of the alloy before heat treatment was 344.3 $HV_{0.5}$, after quenching was 229.6 $HV_{0.5}$ and after tempering was 300.2 $HV_{0.5}$.

Keywords: *Cu-Al-Ni, shape memory alloy, microstructure, hardness*

1. INTRODUCTION

Cu-based shape memory alloys (SMA), such as Cu–Al–Ni are considered to be commercially attractive alloys for technological applications due to shape memory effect (SME) and pseudoelasticity (PE). Low cost, and the possibility of using these alloys at temperatures around 200 C represents an important advantage over other SMA that also exhibits a thermoelastic martensitic transformation, such as the Ni–Ti alloys [1]. The whole austenite to martensite transformation cycle can be described with four characteristic temperatures: martensite start temperature (M_s), martensite finish temperature (M_f), austenite start temperature (A_s) and austenite finish temperature (A_f). The main factors that have the influence on transformation temperatures are the chemical composition, heat treatment procedure, cooling speed, grain size and number of transformation cycles [1, 2].

The parent β phase can transform into a martensite below the M_s temperature. Temperature M_s is strongly composition dependent and may occur at temperatures where the β phase is no longer stable. Regarding this conditions, the alloy has to be solution treated followed by quenching procedure in order to avoid the decomposition of the β phase into lower energy phases (α and γ_2). In order to obtain stable transformation temperatures specimen should be aged for 30 minutes at 300 °C [3, 4].

Since the ternary alloys of Cu–Al–Ni with polycrystalline structures are typically too brittle, it can't be shaped into semi-product forms suitable for practical applications. The *β*-polycrystalline Cu–Al–Ni alloy is prone to intergranular fracture due to its high elastic anisotropy and usual large grain sizes (100 μm to 1 mm for conventionally processed alloys), and also because the existence of γ_2 (Cu_9Al_4) phase. To overcome this problem, grain size refinement techniques were used in order to improve the mechanical properties and to make the shaping and forming procedures easier [1, 5, 6]. The improving of mechanical properties can be provided by adding alloying elements and by heat treatment as well [7].

During heat treatment or hot-working the fine grains inevitably tend to grow up, leading to the degradation of mechanical properties [3, 6].

Heat treatment procedure has the influence on shape memory properties. The shape memory effect (SME) of the alloys is susceptible to aging whether in austenite phase (parent phase) or in martensite phase, and affects the applicability of the alloys. The shape memory properties of Cu-based SMAs are quite sensitive to alloying elements which are added to adjust the martensitic transformation temperatures and to optimize thermal stability as well as mechanical properties. In addition, the martensitic transformation and the associated mechanical shape reversibility in Cu-based SMAs are strongly influenced by quenching and aging treatments [8].

The aim of this paper is to present the influence of different heat treatment procedure on microstructure and hardness of the Cu-Al-Ni shape memory alloy. Hence, the measurements are obtained on alloy before and after heat treatment (quenching and tempering).

2. EXPERIMENT

The Cu-Al-Ni shape memory alloy was produced by melting in vacuum induction furnace in protective atmosphere of argon and casted into a classical iron mould dimensions 100x100x200 mm. The heating temperature was 1120 °C. After casting the alloy was forged with a step heating at 900 °C after every reduction into dimensions of approximately 41x41 mm. The sample A presents an alloy in casted and forged state. The samples after casting and forging are exposed to various heat treatment procedures. The samples B and C are heated in the β-phase equilibrium region (60 minutes at 900 °C) then water quenched. The tempering treatment was performed on alloy C at 300 °C for 60 minutes followed by water quenching. Microstructural analyze was performed by optical microscopy (OM) and scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS). Metallographic preparation of the samples was made by grinding (120-800 grade paper) and polishing (0.3 µm Al_2O_3). After polishing, the samples were etched in a solution composed of 2.5 g $FeCl_3$ and 48 ml methanol in 10 ml HCl for 15 seconds. Hardness of the alloy was carried out by Vickers method with applied force of 5 N.

3. RESULTS AND DISCUSSION

The Cu-Al-Ni shape memory alloy with average chemical composition of 81.7% Cu, 14.2% Al and 3.6% Ni (wt. %) was investigated. Among basic elements that are present in the alloy, the analysis has shown some amount of impurities (approximately 0.5% of Zn, Fe, Si, P, etc.), Table 1.

Table 1. Chemical composition of the Cu-Al-Ni shape memory alloy, wt.%

	Sn	Zn	Pb	Fe	**Ni**	**Al**	P	Si	Mn	**Cu**
CuAlNi	0.046	0.105	0.024	0.135	**3.6**	**14.2**	0.081	0.105	0.040	**81.7**

On Figs. 1a and 1b an optical micrographs of the sample A (casted and forged state) were presented. The partially martensitic microstructure can be noticed, along with low temperature dendritic γ_2 phase and probably residual α phase which appear due to slow cooling rates and low solidification velocities that originate during eutectoid decomposition at 565 °C [9]. However, when the solidification rate of the alloy was slow, namely the alloy had a poor cooling ability, numerous coarsely block and dendritic γ_2 phase (about 10-15 µm) would be precipitated easily in the grains or at the grain boundaries of the alloy. The consequence of this precipitation is the enlargement of the grain boundary embrittlement and the degradation of mechanical properties [10].

On Figs. 1c and 1d were shown optical micrographs of samples after quenching at 900 °C/60 min/water (sample B) and tempering at 300 °C/60 min/water (sample C), respectively. On both samples martensitic microstructure was observed with presence of some inclusions. SEM micrographs (Figs. 2 - 4) confirm the results obtained by optical microscope. On casted and forged sample (Fig. 2a) is visible partially martensitic microstructure with some low temperature equilibrium phases. A precipitation of γ_2 phase along grain boundary (Fig. 2a) and in the grains (Fig. 3) is visible. Completely martensitic microstructure was noticed on samples in which the heat treatment has been carried out. The heat treatment procedure in β-phase area is very important for induction of reversible martensite transformation. The two types of thermally induced martensites appear in Cu-Al-Ni SMA from the parent β phase depending on alloys composition and heat treatment. In low aluminum content alloy preferred type of martensite is β_1’ (18R) and in a high aluminum content alloy is γ_1’ (2H) [11]. During heat treatment the microstructure (the type of martensite) of Cu-Al-Ni shape memory alloy changes, either varying the quenching rate or aging at different temperatures. It is known, that the driving force necessary for nucleation of different types of martensites is different (larger driving force is necessary for nucleation of γ_1’ martensite) [11]. The martensites that exists in this alloy appear in different morphology and can be characterized as β_1’ and γ_1’ martensites, considering to the shape of martesite laths. The characteristic morphology of zig-zag β_1’ martensite and coarse variants of γ_1’ martensite can be noticed on Fig. 2b, which is in agreement with the literature [11, 12].

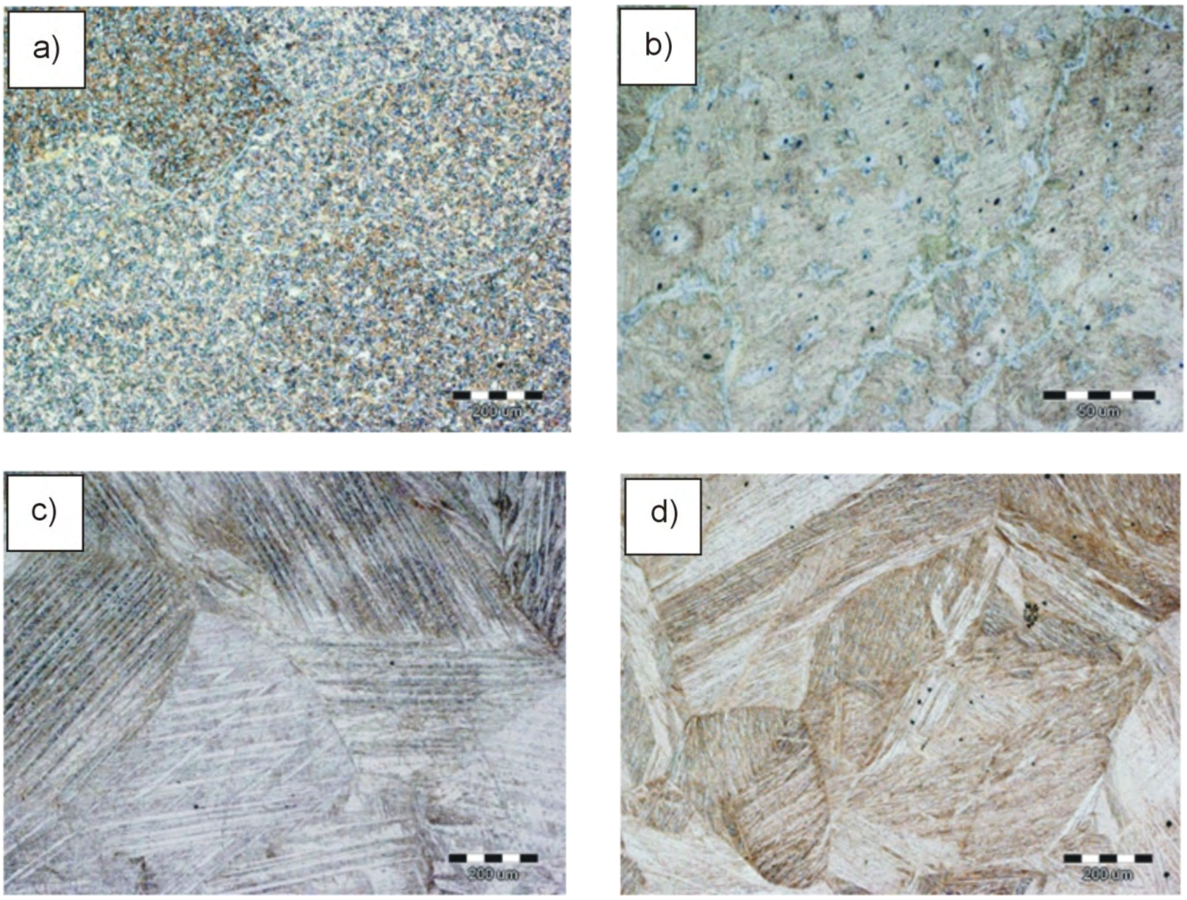
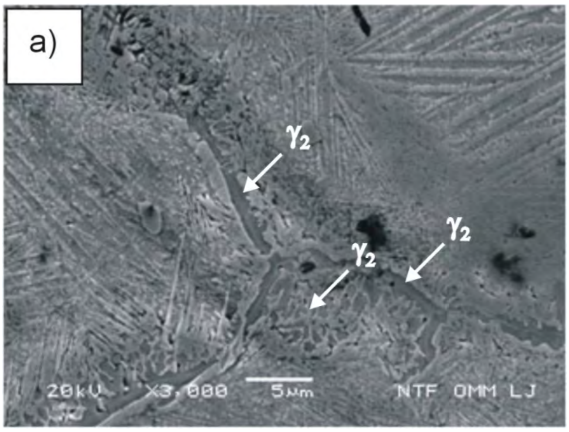


Figure 1. OM Cu-Al-Ni shape memory alloy (a) casted and forged state-sample A, magn. 100x and (b) magn. 500x, (c) quenched state at 900°C/60 min/water-sample B, magn. 100x and (d) tempered state at 300°C/60 min/water-sample C, magn. 100x



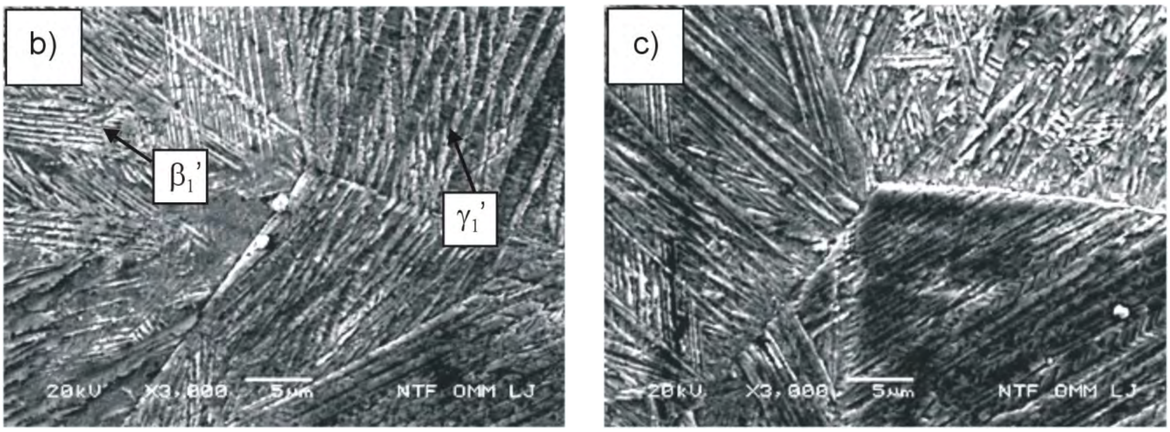


Figure 2. SEM micrographs of Cu-Al-Ni shape memory alloy (a) casted and forged state-sample A, (b) quenched state at 900°C/60 min/water-sample B and (c) tempered state at 300°C/60 min/water-sample C

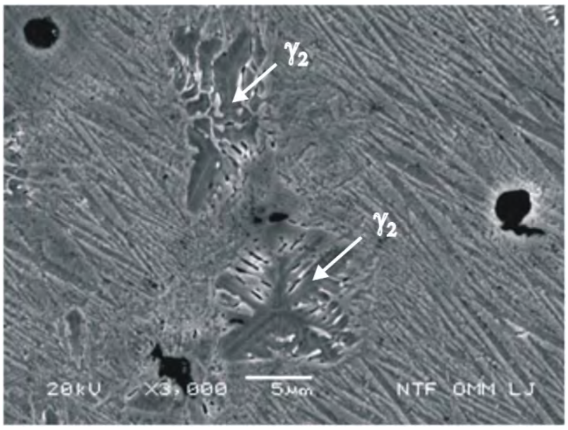


Figure 3. SEM micrograph of Cu-Al-Ni shape memory alloy – casted and forged state (sample A)

On Fig. 4 is shown SEM micrograph of sample after quenching at 900°C/60 min/water with marked positions that have been analyzed by EDS method. Positions 1, 2 and 3 are inclusions that were noticed during examination, and their chemical composition is presented in Table 2. As can be seen, the inclusions are complex compounds which probably appear as a consequence of melting and deoxidization procedure. Inclusions are definitely not acceptable due to its influence on the properties of the alloy. Background of this inclusions can lie in unreliable raw materials, unclean molds etc. Position 4 marks the matrix of the alloy, which average chemical composition amounts 88.09% Cu, 8.55% Al and 3.32% Ni (wt.%).

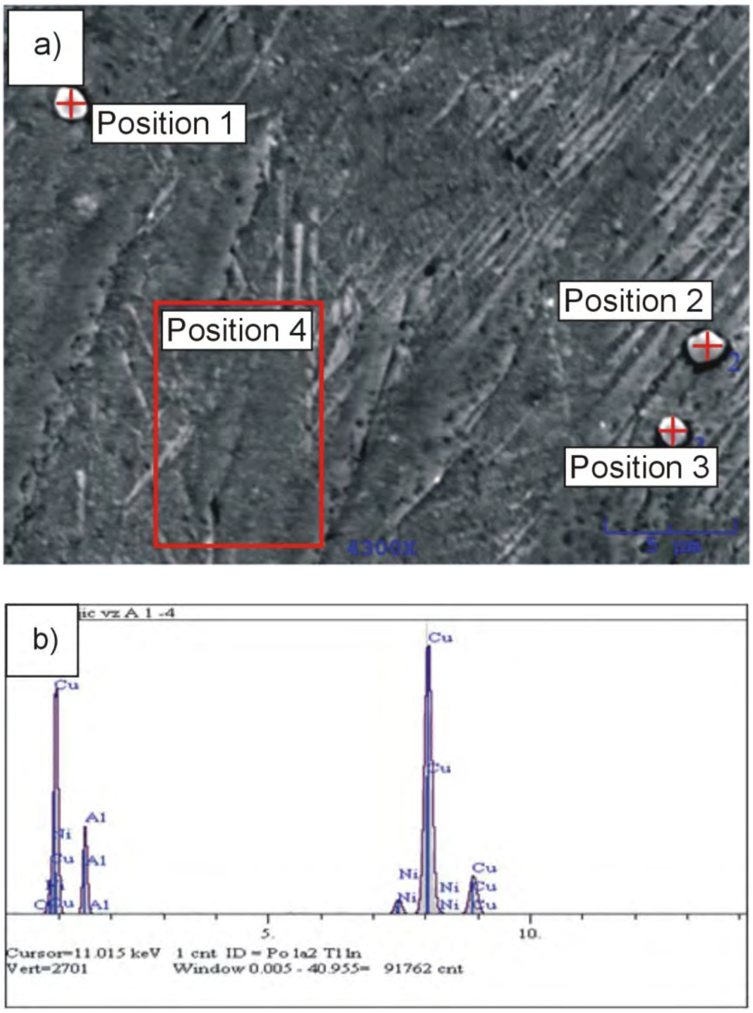


Figure 4.(a) SEM micrograph and (b) EDS spectrum for position 4 of Cu-Al-Ni SMA after quenching at 900°C/60 min/water-sample B

Table 2. EDS analysis of Cu-Al-Ni SMA after quenching at 900°C/60 min/water-sample B

Position of analysis	Chemical composition, wt.%									
	Cu	Al	Ni	Fe	Mn	P	Cr	O	V	Ti
1	23.91	1.98	5.34	27.71	1.02	17.82	21.47	-	0.43	0.32
2	49.82	4.60	4.75	15.47	0.75	12.57	11.81	0.23	-	-
3	42.20	3.36	4.93	20.67	0.97	12.91	14.81	0.15	-	-
4	88.09	8.55	3.32	-	-	-		0.04	-	-

The variation of Vickers hardness with heat treatment procedure is shown in Fig. 5. Casted and forged sample has the highest value of hardness (344.3 $HV_{0.5}$) due to deformation that has been provided after casting. The quenched sample (900°C/60 minutes/water) has the smallest value of hardness (229.6 $HV_{0.5}$) which is the consequence of the disappearance of the internal stress during heating at β-phase equilibrium region. After tempering the hardness of sample has been increased (300.2 $HV_{0.5}$) probably due to the presence of precipitates of secondary phases that appear in Cu-Al-Ni shape memory alloys, and negatively influence on alloys properties [2, 13]. Aydogdu et al. were investigated the improvement of hardness on CuAlNi shape memory alloys by ageing at 330°C for 30 minutes and concluded that step annealing improves the hardness of the alloys [14]. The change in hardness of the samples indicates that the mechanical properties of the Cu-Al-Ni shape memory alloy can be changed by the thermal treatment.

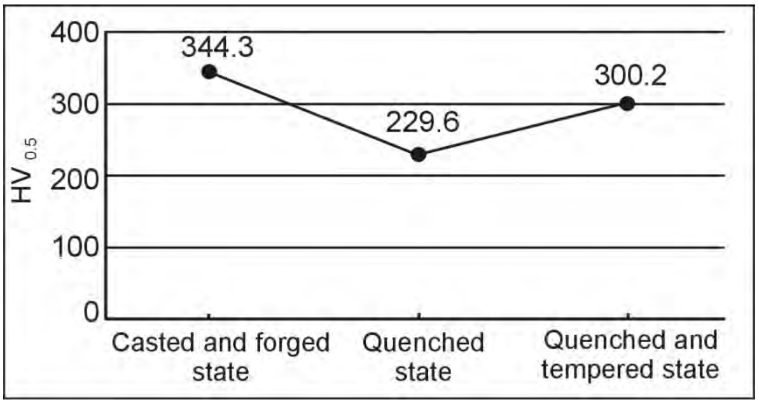


Figure 5. Dependence of hardness of the different state of the samples

4. CONCLUSION

CuAlNi shape memory alloy was produced by conventional casting method. The alloy was forged to appropriate dimensions and the different heat treatment procedures have been carried out. From the microstructural analysis and hardness testing can be concluded:

- Microstructure of the CuAlNi alloy in as-cast and forged state shows partially martensitic microstructure with parts of low temperature phases (α and γ_2).
- Microstructure of CuAlNi alloy after quenching and tempering has martensitic microstructure with some inclusions of complex chemical composition.
- Two types of martensites exist in this alloy. The characteristic morphology of zig-zag β_1' and coarse variants of γ_1' martensites are noticed.
- The inclusions that probably appear as a consequence of unreliable raw materials, unclean molds, melting and deoxidization procedure might have the influence on alloys properties.
- The hardness of the alloy shows that the mechanical properties of the CuAlNi shape memory alloy can be changed by the thermal treatment.

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