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The Influence of Heat Treatment on Microstructure and Phase Transformation Temperatures of Cu-Al-Ni Shape Memory Alloy

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Abstract
This paper presents the results of thermal and microstructural analysis of Cu-Al-Ni shape memory alloy before and after heat treatment. After casting, a bar of Cu-12.8 Al-4.1 Ni (wt.%) alloy, obtained by the vertical continuous casting technique, was subjected to a certain heat treatment procedure. Solution annealing was performed at 850 °C for 60 min, followed by water quenching. Tempering was then performed at four different temperatures (150 °C, 200 °C, 250 °C and 300 °C). The micro-structural results were obtained by optical and scanning electron microscopy. Thermodynamic calculation of ternary Cu-Al-Ni system under equilibrium was performed using Thermo-Calc 5 software. Phase transformation temperatures were determined by differential scanning calorimetry (DSC). The DSC results show the highest values of transformation temperatures in as-cast state. After solution annealing and tempering, the transformation temperatures show lower values with exceptional stability of Ms temperature (martensite start temperature).

Keywords
Shape memory alloy, Cu-Al-Ni, heat treatment, phase transformation, microstructure

1 Introduction
Today there are a large number of known shape memory alloys (SMAs): nickel-based shape memory alloys, copper-based shape memory alloys, ferrous-based shape memory alloys, noble metal-based shape memory alloys, etc. The term shape memory alloys is applied to a group of metallic materials, which show the ability to return to their previously defined shape or size during a special heat treatment procedure. Shape change is a consequence of austenitic to martensitic transformation, which is characterised by the following temperatures: At – austenite start temperatures, Af – austenite finish temperatures, Mf – martensite start temperature and Mf – martensite finish temperature. 1–7

Compared to Ni-Ti SMAs that are generally considered to be superior to Cu-based alloys, Cu-Al-Ni alloys also offer some considerable advantages. Not only is the material cost 15–30 % of that for Ni-Ti, but the melting, composition control, and casting are less difficult, they exhibit higher Young’s modulus, better machinability, and better work/cost ratio. In addition, the stability of the two-way shape memory effect is better, which is very important when designing the actuators. 8

Phase diagrams are very important for designing and development of a material due to its functional properties, microstructure and phase stability under specific conditions. Thermodynamic modelling offers valuable information for equilibrium thermodynamics, modelling of diffusion processes and grain growth. It represents the advantage according to expensive and time-consuming experimental investigations. 9 Reliable thermodynamic databases, with optimised parameters, are crucial for thermodynamic calculations of Gibbs energy of all phases existing in an investigated system and accuracy of calculated phase equilibria. Thermodynamic descriptions of binary systems Cu-Al, Al-Mn, and Cu-Mn are given in a number of references, but there is a lack of relevant experimental and optimised thermodynamic data for ternary Cu-Al-Ni alloy. 9,10,11 Considering the wide application of Cu-Al-Ni alloys, it seems very interesting to analyse the thermodynamic properties of this ternary system.

This paper studies the influence of heat treatment procedure on microstructure and phase transformation temperatures of the alloy. The results obtained after heat treatment are compared with the results obtained on the sample in as-cast state.

2 Experimental
Thermodynamic calculation for equilibrate conditions was performed with Thermo-Calc 5 software, using database SSOL 6. Calculations of Gibbs energy were performed according to binary sub-systems Cu-Al, Cu-Ni and Al-Ni. 10–13 Cu-12.8 Al-4.1 Ni (wt.%) shape memory alloy was produced by vertical continuous casting procedure in a vacuum induction furnace connected to the device for vertical continuous casting. The alloy, in the shape of a bar of...
8 mm in diameter, solidified in a crystalliser and came out passing between two rolls rotating in opposite directions. The alloys’ casting temperature was 1240 °C and casting speed was 320 mm min⁻¹. After casting, the heat treatment procedure was performed as shown in Table 1.

For microstructural observation, the samples were metallographically prepared by grinding, polishing, and etching. The detailed metallographic preparation of the samples is explained elsewhere. The samples were investigated with optical microscope (OM) and scanning electron microscope (SEM). To determine phase transformation temperatures, differential scanning calorimetry (DSC) was performed. The samples were heated and cooled in one cycle from room temperature to 400 °C by heating/cooling speed of 10 K min⁻¹.

Table 1 – Samples with heat treatment conditions

| Samples | Heat treatment parameters |
|---------|---------------------------|
| L       | As-cast state of Cu-Al-Ni SMA |
|         | Lijevano stanje Cu-Al-Ni slitine s prisjetljivošću oblika |
| K-1     | Solution annealed at 850 °C/60'/WQ |
|         | Kaljenje na 850 °C/60'/voda |
| K-1-1   | Solution annealed at 850 °C/60'/WQ and tempered at 150 °C/60'/WQ |
|         | Kaljenje na 850 °C/60'/voda i popuštanje na 150 °C/60'/voda |
| K-1-2   | Solution annealed at 850 °C/60'/WQ and tempered at 200 °C/60'/WQ |
|         | Kaljenje na 850 °C/60'/voda i popuštanje na 200 °C/60'/voda |
| K-1-3   | Solution annealed at 850 °C/60'/WQ and tempered at 250 °C/60'/WQ |
|         | Kaljenje na 850 °C/60'/voda i popuštanje na 250 °C/60'/voda |
| K-1-4   | Solution annealed at 850 °C/60'/WQ and tempered at 300 °C/60'/WQ |
|         | Kaljenje na 850 °C/60'/voda i popuštanje na 300 °C/60'/voda |

Results and discussion

3.1 Results of thermodynamic calculation of Cu-Al-Ni ternary phase diagram

Thermodynamic calculation was performed by CALPHAD method, based on minimisation of the free Gibbs energy of system. The Figs. 1 and 2 show the vertical section of calculated phase diagram for Cu-4.1Ni-Al.

Figs. 1 and 2 show precipitation of austenite, parent β-phase in B2 crystal structure at 1237 °C, under equilibrate conditions. Solidus temperature was observed at 1031 °C, and under this temperature, the β-phase exists as two crystal structures, B2 and A2. The γ-phase starts to precipitate at 611 °C. At 567 °C, the β-phase in A2 crystal structure decomposes to α-phase, and at room tempera-
ture, the coexistence of α-, β-(B2) and γ-phase is obvious. Decomposition of parent β-phase can be suppressed by fast cooling or quenching in water, which causes formation of martensitic structure.

During heat treatment, microstructural changes occur, affecting the phase transformation temperatures. Such behaviour of Cu-Al-Ni alloys, obtained by melt-spinning process, was observed by Morawiec et al. The change in phase transformation temperatures can also be attributed to the effect of internal strains caused by different grain size in the microstructure, as confirmed by Pelegrina and Romero on Cu-Al-Zn SMA.

3.2 Optical, scanning electron microscopy, and DSC results

Cu-Al-Ni shape memory alloys from the initial austenitic β phase, if casting conditions (e.g. sufficient cooling speed) were satisfied, form a martensitic microstructure, which is responsible for the shape memory effect. However, during the casting, due to unfavourable cooling conditions, equilibrium low temperature phases can be created according to the equilibrium phase diagram of Cu-Al-Ni alloy.

In order to avoid the possible forming of residual low temperature phases during casting, a heat treatment process in the austenitic β phase area was performed. According to the literature, copper-based SMAs are alloys in which heat treatment process cannot be avoided.

In the microstructure of the investigated Cu-Al-Ni alloy, the existence of a completely martensitic microstructure (Figs. 3 and 4) was found. It can be noticed that the microstructure consists of self-accommodating needle-like shaped martensite. In addition, the orientation of the crystal was different.

The Cu-Al-Ni alloy microstructure can change depending on the heat treatment procedure. Optical micrographs of solution annealing and tempering are presented in Figs. 3b–3d. The grain boundaries are clearly visible, and the microstructure after heat treatment was completely martensitic. Martensite needles had different orientation within each grain, which could be explained by the nucleation of groups of martensitic plates in numerous places within the grain, and creation of local strain within the grain, which allowed the formation of several groups of differently oriented plates.

Changes in microstructure influence changes in the alloy’s properties, which occur due to thermal processing. Solution annealing of the Cu-Al-Ni shape memory alloy must be performed in order to achieve a fully martensitic microstructure. Along with the martensitic phase which is formed from the initial austenitic (β) phase, the change in grain size varies depending on the process conditions of heat treatment (heat treatment temperature, holding time at the selected temperature, or cooling agents).

The martensitic microstructure was confirmed on all samples by scanning electron microscopy (Fig. 4). The resulting microstructure appeared by transformation of β phase to martensite below Mₙ temperature. Martensite originated primarily as a needle-like martensite. On some of the samples, after solution annealing and tempering (Figs. 4b–4d), the V-shape of the martensite can be noticed. The morphology of the resulting martensitic microstructure is a typical self-accommodating zig-zag morphology, which is
I. IVANIĆ et al.: The Influence of Heat Treatment on Microstructure and Phase Transformation..., Kem. Ind. 68 (3-4) (2019) 111−118

The changes in microstructure can be seen in samples after tempering. OM and SEM micrographs (Figs. 3c, 3d, 4c, and 4d) reveal a different type of martensite plate characteristic for γ′' martensite. According to the literature, the fine needles and V-shaped laths are typical morphologies of β′ and γ′ martensites, respectively. Alloys with aluminium content of 11–13 wt.% in the microstructure, transform into 18R (β′) martensite from the β parent phase. Higher aluminium content (>13 wt.% %) follows the formation of 2H (γ′) martensite. If the chemical composition is on the boundary between both martensites, then both can coexist in the microstructure. Which of them will appear in the microstructure depends on the chemical composition, temperature conditions, and stress conditions.

The appearance of martensite in the microstructure can be described by the transformation mechanism of austenitic β phase through the transformation β → β′. Only after heat treatment, another type of martensite in the microstructure appeared. It can be assumed that γ′ martensite appears in the microstructure. The appearance of γ′ martensite can be described by the following transformation mechanism from β → γ′. Also, not only is one type of martensite present in the microstructure, but both types of martensite, which can be described by the transformation β → β′ + γ′.

It was observed that changes in temperature of phase transformations occur due to changes in temperature of heat treatment process (Table 2 and Figs. 5–7). Figs. 5 and 6 present DSC curves for alloy in as-cast state and solution annealed, respectively. The phase transformation temperatures (M_s, M_f, A_s, and A_f) were determined by tangent method and marked in Figs. 5 and 6.

Fig. 7 shows the effect of heat treatment temperature on the phase transformation temperatures before and after heat treatment. It can be noticed that the temperature of the phase transformation is the highest for as-cast sample. The reason for this may be a large amount of internal strain and imperfection in the microstructure, as a result of casting and solidification.

Since the heat treatment procedure (solution annealing and tempering) was carried out in order to achieve order in the alloy’s structure and stabilisation of the phase transformation temperatures, the characteristic behaviour...
I. IVANIĆ et al.: The Influence of Heat Treatment on Microstructure and Phase Transformation..., Kem. Ind. 68 (3-4) (2019) 111−118

of Ms temperature was observed after solution annealing and tempering (Fig. 7, Table 2). The graph shows the Ms temperature matching in all cases after heat treatment. The values of Ms temperature only slightly differ, ranging from 213.1 °C to 216.8 °C.

4 Conclusion

The influence of heat treatment on microstructure and phase transformation temperatures was investigated. The results of thermal and microstructural analysis of Cu-Al-Ni shape memory alloy before and after heat treatment suggest the following conclusions:

− Microstructural analysis in this study confirmed the complete transformation of β phase into martensite phase in the as-cast and heat treated samples at all investigated temperatures. A detailed analysis of the results, suggests that, in the as-cast state, the only micro-constituent is a β′ martensite, which arises from the mechanism of austenitic β phase through the transformation β → β′. After heat treatment, another type of martensite in the microstructure appears (γ′ martensite), which can be described by the following transformation mechanism from β → γ′. The presence of both types of martensite in the microstructure can be described by the transformation β → β′ + γ′.

− Thermodynamic calculation shows firstly precipitation of parent β-phase under equilibrate conditions. At solidus temperature (1031 °C), β-phase exists as two crystal structures. Also, the precipitation of γ-phase starts at 611 °C. Decomposition of β-phase to α-phase is at 567 °C. The α-, β-(B2) and γ-phases were obvious at room temperature.

− The DSC analysis show the highest values of phase transformation temperatures for the as-cast sample. After heat treatment, the characteristic behaviour of Ms temperature was observed. The stabilisation of Ms temperature was accomplished by heat treatment, and varied only slightly in the range from 213.1 °C to 216.8 °C.
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Popis kratica o simbola

A<sub>s</sub> – austenite start temperature, °C
A<sub>f</sub> – austenite finish temperature, °C
A<sub>2</sub> – form of crystal structure
bcc – body-centred cubic crystal structure
B<sub>2</sub> – form of crystal structure
DSC – differential scanning calorimetry
fcc – face-centred cubic crystal structure
M<sub>s</sub> – martensite start temperature, °C
M<sub>f</sub> – martensite finish temperature, °C
M<sub>r</sub> – martensite finish temperature, °C

M<sub>r'</sub> – martensite phase
M<sub>f'</sub> – martensite phase
M<sub>r</sub> – martensite form
M<sub>f</sub> – martensite form

2H – form of crystal structure
18R – form of crystal structure
α – phase, primary solid solution of Al and Ni in copper, fcc crystal structure
β – austenite phase
β<sub>1</sub> – martensite phase
γ – equilibrium phase
γ<sub>1</sub> – martensite phase

L – L
K-1 (650 °C/60’WQ) – K-1
K-1-1 (150 °C/60’WQ) – K-1-1
K-1-2 (200 °C/60’WQ) – K-1-2
K-1-3 (250 °C/60’WQ) – K-1-3
K-1-4 (300 °C/60’WQ) – K-1-4

Fig. 7 – Influence of heat treatment procedure on phase transformation temperatures of the CuAlNi shape memory alloy
Slika 7 – Utjecaj toplinske obrade na temperature fazne transformacije CuAlNi slitine s pristojivošću oblika
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SAŽETAK
Utjecaj toplinske obrade na mikrostrukturu i temperature faznih transformacija Cu-Al-Ni slitine s prisjetljivosti oblika

Ivana Ivanić, a Stjepan Kožuh, a Tamara Holjevac Grgurić, a Borut Kosec b i Mirko Gojić a

U radu su prikazani rezultati toplinske i mikrostruktura analize Cu-Al-Ni slitine s prisjetljivosti oblika prije i nakon toplinske obrade. Nakon lijevanja, šipka slitine Cu-12.8 Al-4.1 Ni (mas. %) dobivena tehnikom vertikalnog kontinuiranog lijevanja, podvrgnuta je određenom postupku toplinske obrade. Provedeno je homogenizacijsko žarenje pri 850 °C, zadržavanje na toj temperaturi 60 min i hlađenje u vodi. Nakon toga je provedeno popuštanje na četiri različite temperature (150 °C, 200 °C, 250 °C i 300 °C). Mikrostruktura analiza provedena je optičkim i pretražnim elektronskim mikroskopom. Termodinamički proračun ravnotežnog ternarnog Cu-Al-Ni sustava proveden je pomoću Thermo-Calc 5 softvera. Temperature fazne transformacije određene su diferencijalnom pretražnom kalorimetrijom (DSC). Rezultati DSC-a pokazuju najveće vrijednosti temperature fazne transformacije u lijevanom stanju. Nakon homogenizacijskog žarenja i popuštanja temperature fazne transformacije pokazuju niže vrijednosti s iznimnom stabilnošću M temperaturu (temperatura početka nastajanja martenzita).

Ključne riječi
Legura s prisjetljivosti oblika, Cu-Al-Ni, toplinska obrada, fazna transformacija, mikrostruktura

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