MICROSTRUCTURAL ANALYSIS OF CuAlNiMn SHAPE-MEMORY ALLOY BEFORE AND AFTER THE TENSILE TESTING

ANALIZA MIKROSTRUKTURE ZLITINE CuAlNiMn Z OBLIKOVNIM SPOMINOM PRED NATEZNIM PREIZKUSOM IN PO NJEM

Ivana Ivanić[1], Mirko Gojić[1], Stjepan Kožuh[1], Borut Kosec[2]

[1]University of Zagreb, Faculty of Metallurgy, Aleja narodnih heroja 3, 44103 Sisak, Croatia
[2]University of Ljubljana, Faculty of Natural Sciences and Engineering, Aškerčeva cesta 12, 1000 Ljubljana, Slovenia
iivanic@simet.hr

In this paper the results of a microstructural analysis before and after fracture along with the mechanical properties and hardness of the CuAlNiMn shape-memory alloy are presented. The melting of the alloy was carried out in a vacuum-induction furnace in a protective atmosphere of argon. The alloy was cast into an ingot of 15 kg. After casting the alloy was forged and rolled into rods with a diameter of approximately 10 mm. A microstructural characterization was performed with light microscopy (LM) and scanning electron microscopy (SEM) equipped with energy-dispersive spectrometry (EDS). Martensitic microstructure was observed in the rods after the deformation. The fractographic analysis of the samples after the tensile testing revealed some areas with intergranular fracture. However, the greater part of the fracture surface indicated the pattern of transgranular brittle fracture. The results of the tensile tests showed the tensile strength of 401.39 MPa and elongation of 1.64 %. The hardness of the CuAlNiMn alloy is 290.7 HV0.5.

Keywords: shape-memory alloy, CuAlNiMn, fracture analysis, microstructure, hardness

V prispevku so predstavljeni rezultati analize mikrostrukture pred prelomom in po njem skupaj z mehanskimi lastnostmi in trdoto zlitine CuAlNiMn z oblikovnim spominom. Taljenje zlitine je bilo izvedeno v vakuumski peči v zaščitni atmosferi argona. Zlitina je bila ulita v ingot mase 15 kg. Po litju je bila zlitina kovana in zvaljana na premer približno 10 mm. Karakterizacija mikrostrukture je bila izvedena s svetlobno mikroskopijo (SM) in vrstično elektronsko mikroskopijo (SEM), opremljeno z energijskim disperzijskim spektrometrom (EDS). Analizirana je bila martenzitna mikrostruktura zlitine CuAlNiMn pred izvedenim nateznim preizkusom. Izvedena sta bila natezni preizkus in meritve trdot. Fraktografska analiza je pokazala več področij z interkristalnim in pogosto transkristalnim krhkim prelomom. Rezultati nateznega preizkusa so pokazali, da je natezna trdnost 401,39 MPa in raztezek 1,64 %. Trdota zlitine CuAlNiMn je 290,7 HV0,5.

Ključne besede: zlitina z oblikovnim spominom, CuAlNiMn, analiza preloma, mikrostruktura, trdota

1 INTRODUCTION

Shape-memory alloys (SMAs) based on copper such as CuZnAl and CuAlNi are attractive for practical applications because of their special properties (shape-memory effect and pseudoelasticity) which are based on the crystallographic reversible thermoelastic martensitic transformation. They are also suitable due to lower costs (compared to NiTi) and the advantages with regard to electrical and thermal conductivities.[1–5]

However, the polycrystalline copper-based shape-memory alloys with coarse grains are very brittle and they are prone to intergranural fracture because of the high elastic anisotropy of the parent β phase, the existence of the brittle γ_2 (Cu_9Al_4) phase and the formation of the stress-induced martensites along the grain boundaries upon quenching.[6–10] The usual way to improve the disadvantages mentioned above is to alloy them with the elements that are grain refiners like Ti, B and Zr, which create the precipitates limiting the grain size and grain growth. Also, the production of the alloy with the rapid-solidification technique or powder metallurgy is very effective in obtaining a fine-grain microstructure.[2,11] The mechanical properties of the polycrystalline CuAlNi alloy can be improved effectively with grain refinement and texture control. Both of them play important roles in relaxing the stress concentration at grain boundaries, which prevents intergranular fracture and improves the plasticity of the alloy. The fatigue and memory properties of the CuAlNi alloy with fine grains are considerably limited because the fine grains inevitably tend to grow during hot-working or heat treatment, leading to a degradation of mechanical properties.[6,12]

Manganese is added as an alloying element to improve the ductility of the CuAlNi alloy by replacing the partially aluminum content. It also increases the stability domain of the β phase and allows the betatising process to be performed at lower temperatures.[8,12] Also, manganese was provided to enhance the thermoelastic and pseudoelastic behavior.[11,13]

The aim of this paper was to carry out the strength testing, hardness measurements, microstructural characterization and a fractographic analysis of the CuAlNiMn alloy.

2 EXPERIMENTAL WORK

The CuAlNiMn shape-memory alloy was produced by melting in a vacuum-induction furnace in a protective atmosphere of argon and cast into a classical iron mould with the dimensions of 100 mm × 100 mm × 200 mm. The heating temperature was 1330 °C. After casting the alloy was forged and rolled with step heating at 900 °C after every reduction into the bars with a diameter of approximately 10 mm. From the bars the samples were prepared as standard round tensile-test probes with the dimensions of ϕ 6 mm × 100 mm. The tensile test was made with a Zwick/Roell Z050 universal tensile-testing machine at room temperature. Light microscopy (LM) and scanning electron microscopy (SEM) equipped with energy-dispersive spectroscopy (EDS) were applied for the microstructural characterization of the alloy. For the microstructural analysis, the samples were grinded (120–800 grade paper) and polished (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 s. A fractographic analysis using a JOEL JSM5610 scanning electron microscope was carried out to observe the surfaces of the samples after the tensile testing. The hardness of the alloy was carried out with the Vickers method with the applied force of 5 N.

3 RESULTS AND DISCUSSION

The average chemical composition of the alloy measured with EDS was Cu-8.05 % Al-3.51 % Ni-2.44 % Mn (*w*/%).

3.1 Microstructural characterization before fracture

The obtained microstructures are presented on **Figures 1** to **3**. It can be observed that the microstructure of the alloy after the deformation (forging and rolling) is martensitic. Because of the plastic deformation after the casting, it can be assumed that most of the martensite in
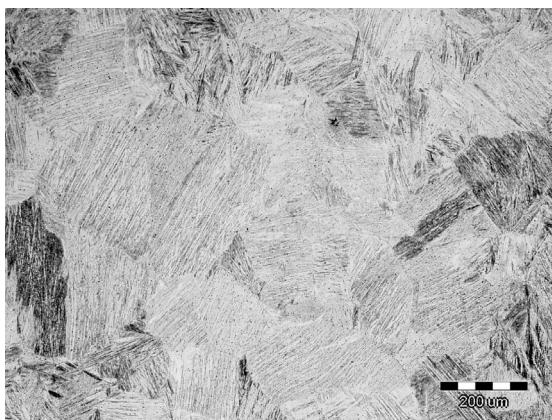

Figure 1: LM micrograph of the CuAlNiMn shape-memory alloy, magnificaton 100-times
Slika 1: Mikrostruktura zlitine CuAlNiMn z oblikovnim spominom, povečava 100-kratna
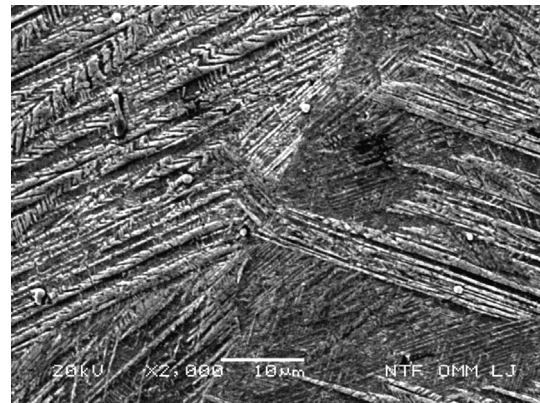

Figure 2: SEM micrograph of the CuAlNiMn shape-memory alloy
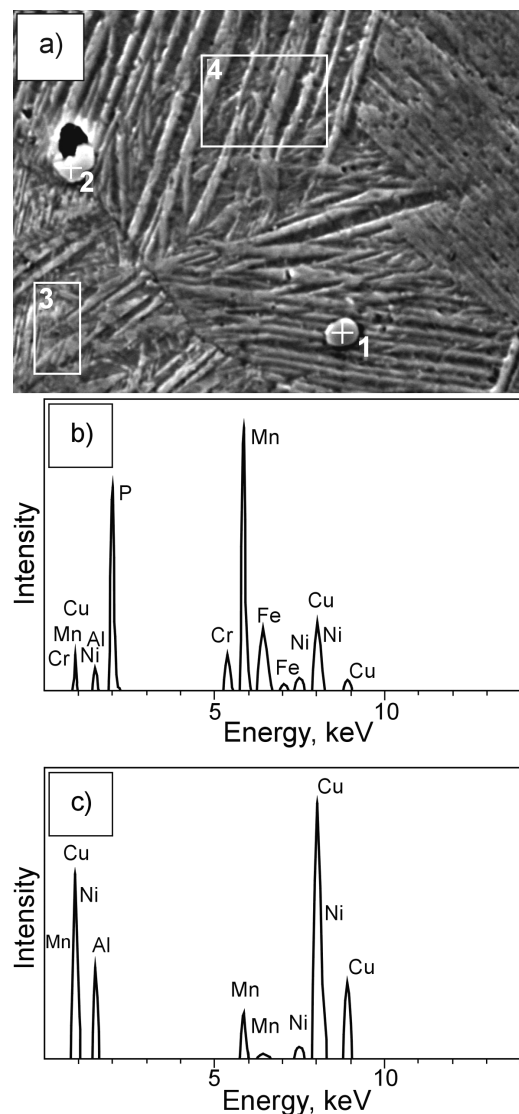**Slika 2:** SEM-posnetek mikrostrukture zlitine CuAlNiMn z oblikovnim spominom

Figure 3: a) SEM micrograph of the CuAlNiMn shape-memory alloy with the positions marked for EDS analysis, b) EDS spectrum for position 1 and c) EDS spectrum for position 3
Slika 3: a) SEM-posnetek mikrostrukture zlitine CuAlNiMn z oblikovnim spominom z označenimi mesti za EDS-analizo, b) EDS-spekter na mestu 1 in c) EDS-spekter na mestu 3
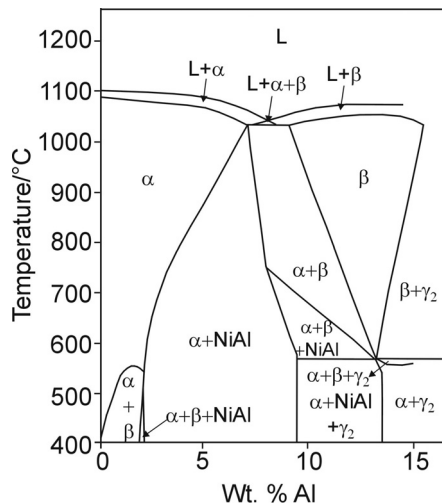
Figure 4: Ternary phase diagram of the CuAlNi alloy; a vertical cross-section at the mass fraction of Ni w = 3 % [9]
Slika 4: Ternarni fazni diagram zlitine CuAlNi; vertikalni prerez pri masnem deležu Ni w = 3 % [9]

the structure is the stress-induced martensite. The grains appear clearly and the martensite plates have different orientations in individual grains. We also noticed a large grain size which commonly appears in Cu-based alloys.[12]
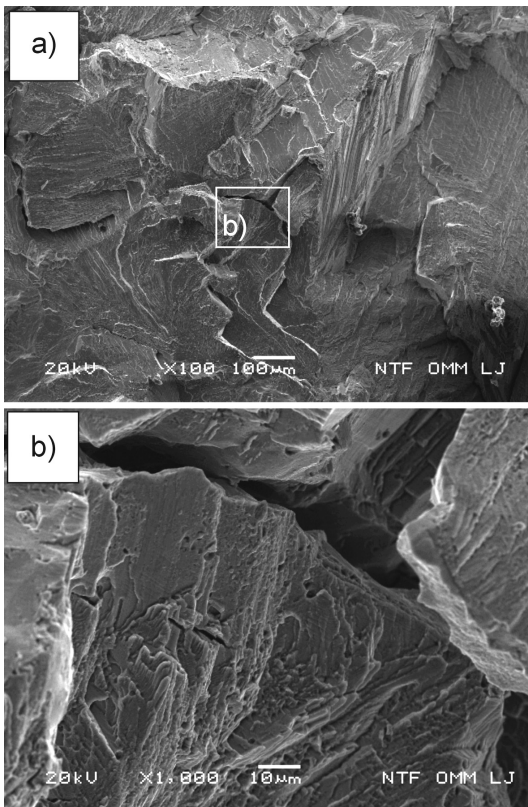

Figure 5: SEM microfractographs of the CuAlNiMn shape-memory alloy after tensile testing: a) magnification 100-times and b) the magnified section
Slika 5: SEM-posnetek preloma zlitine CuAlNiMn z oblikovnim spominom po izvedenem nateznem preizkusu: a) povečava 100-kratna in b) povečano območje

In our previous paper[14] it was observed that the CuAlNiMn SMA in the as-cast state has a martensitic microstructure with some areas of the γ_2 phase.

The CuAlNi ternary phase diagram, **Figure 4**, shows the main phases that appear in the CuAlNi shape-memory alloy. The β phase, which is essential for the shape-memory effect, can exist independently and stably above 565 °C. The eutectoid reaction ($\beta \rightarrow \alpha + \gamma_2$) occurs in the alloy at 565 °C. Meanwhile, the adequate cooling rate can suppress the eutectoid reaction, and the β phase can be totally transformed into martensites when the temperature decreases to M_s (the martensite start temperature).[2,6]

On the SEM micrographs (**Figures 2** and **3**), martensitic microstructure is confirmed. Several inclusions can be noticed and their chemical compositions (positions 1 and 2 on **Figure 3a**) are presented in **Table 1**. It can be seen that the inclusions contain the highest amount of Mn, along with Cu, Al and Ni (which are the main constituents of the alloy), and there are also other elements – "impurities" (Fe, Cr, P) (**Figure 3b**).

Table 1: Results of the EDS analysis before tensile testing for the positions marked on **Figure 3a**, (w/%)
Tabela 1: Rezultati EDS-analize, izvedene pred nateznim preizkusom na mestih označenih na **sliki 3a**, (w/%)

Position	Cu	Al	Ni	Fe	Mn	Cr	P
1	25.20	1.73	3.58	8.59	40.65	4.75	15.50
2	17.28	1.86	3.82	9.63	46.18	5.23	15.99
3	86.07	8.04	3.53	–	2.36	–	–
4	85.95	8.06	3.48	–	2.51	–	–

The usual chemical composition of the CuAlNi SMA is Cu-(11–14) % Al-(3–4.5) % Ni (w/%). According to the literature[12] an addition of manganese replacing the aluminum content is effective as it can improve the ductility. The EDS analysis of positions 3 and 4 (**Figure 3a**) and the EDS spectrum on **Figure 3c** confirm such a replacement.

U. Sari[13] investigated the influence of the mass fraction w = 2.5 % of manganese on the CuAlNi SMA, and he concluded that, due to a manganese addition, the grain size, which is over 1 mm for CuAlNi, is reduced by 75 %, to the average value of 350 μm.

3.2 Fracture analysis of the CuAlNiMn shape-memory alloy

The results of the SEM microfractography analysis after the tensile testing of the CuAlNiMn shape-memory alloy are presented on **Figures 5** to **8**.

It can be seen that a crack often occurs at a three-fold node of grain boundaries, **Figure 5**. It is known that the brittleness of copper-based alloys arises from the high degree of order in the parent phase with B2, DO$_3$ and L2$_1$ structures; the brittleness was also attributed to their high elastic anisotropy ($A \cong 13$) which is a reason for the brittle-grain-boundary cracking.[15–17] The second cause is
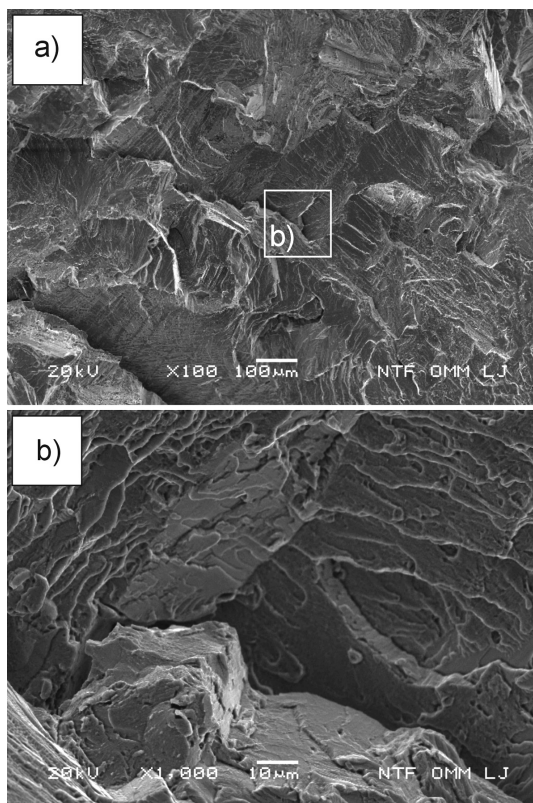
Figure 6: SEM microfractographs of the CuAlNiMn shape-memory alloy: a) magnification 100-times and b) the magnified section
Slika 6: SEM-posnetka preloma zlitine CuAlNiMn z oblikovnim spominom: a) povečava 100-kratna in b) povečano območje

the grain size of β-phase alloys which is usually in order of 1 mm.[12,13] The causes mentioned above probably constitute the essential differences between NiTi alloys and Cu-based alloys, influencing the fracture behavior. A large stress concentration occurs at the grain boundaries due to a large elastic anisotropy under loading. The result is that very brittle intergranular cracking occurs even during elastic deformation.[16]

It may be assumed that the cracks nucleate at the grain-boundary nodes where the stress concentrations develop.[15] This assumption is confirmable with the cracks visible on **Figures 5** to **7**. Grain boundaries provide the easiest crack-propagation path. The cracks nucleate at the grain boundaries where the stress-level concentration is high and the intergranular fracture is obtained. It is mostly a transgranular type of fracture with the characteristic river pattern that can be observed (**Figures 5** and **6**) but sporadic intergranular fracture can also be noticed. At a higher magnification it is visible that the plane of fracture displays the river patterns typical of a cleavage – like a rupture (**Figures 5b** and **6b**).[18] On **Figures 7a** and **7b** there are parallel lines near the grain-boundary plane that probably represent the stress-induced martensite. There are some small and shallow dimples on the fracture surface of the investigated alloy, indicating that the alloy underwent a certain plastic deformation during the fracture (**Figure 7c**).
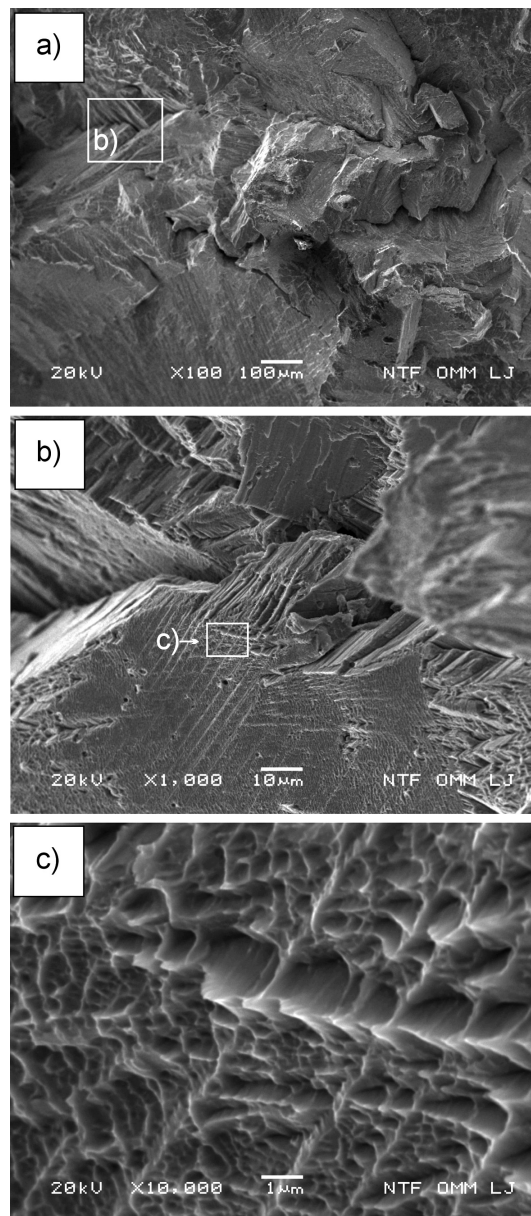

Figure 7: SEM microfractographs of the CuAlNiMn shape-memory alloy: a) magnification 100-times, b) the magnified section and c) the area with transgranular brittle fracture – the magnified section
Slika 7: SEM-posnetek preloma zlitine CuAlNiMn z oblikovnim spominom: a) povečava 100-kratna in b) povečano območje ter c) področje z transkristalnim krhkim prelomom – povečano območje

The fracture surface was examined with an EDS analysis (**Figure 8**), and the chemical composition of the fracture surface is presented in **Table 2**. It can be noticed that the amount of Cu was from 88.15–93.55 %, Al was from 1.78–5.81 %, Ni was from 3.19– 3.46 % and Mn was from 1.25–2.60 % (*w*/%). Lower concentrations of alloying elements probably influence the fracture mechanism and properties of the alloy by decreasing the strength in the region of grain boundaries. Reduced concentrations of the alloying elements at the grain boundaries are probably due to slow cooling rates and
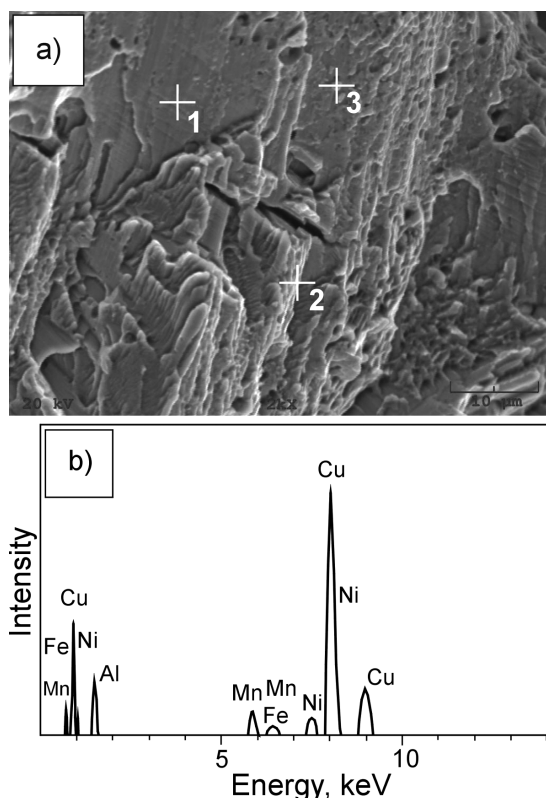
Figure 8: a) SEM microfractograph of the CuAlNiMn shape-memory alloy with the positions marked for EDS analysis and b) EDS spectrum of position 1
Slika 8: a) SEM-posnetek preloma zlitine CuAlNiMn z oblikovnim spominom z označenimi mesti za EDS-analizo in b) EDS-spekter na mestu 1

low solidification velocities that are the consequences of the alloy-casting procedure.

Table 2: Results of the EDS analysis after tensile testing for the positions marked on **Figure 7a**, (*w*/%)
Tabela 2: Rezultati EDS-analize po izvedenem nateznem preizkusu na mestih označenih na **sliki 7a**, (*w*/%)

Position	Cu	Al	Ni	Fe	Mn
1	88.96	4.89	3.46	0.22	2.47
2	93.55	1.78	3.19	0.23	1.25
3	88.15	5.81	3.44	0.00	2.60

3.3 Mechanical properties of the CuAlNiMn shape-memory alloy

The results obtained after the tensile testing are given in **Table 3**. The tensile strength/elongation curves are presented in **Figure 9**. The tensile strength was 401.39
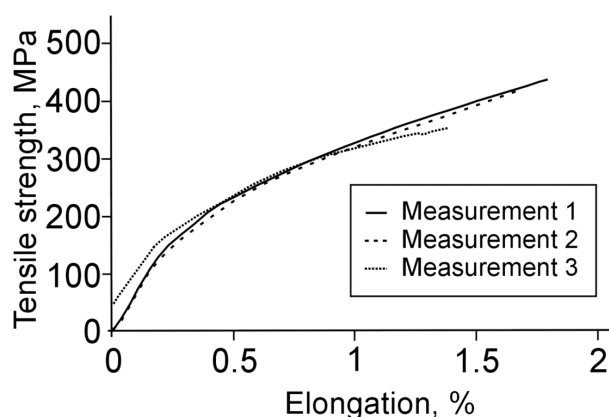

Figure 9: Tensile stress – elongation curves of the CuAlNiMn SMA
Slika 9: Krivulje natezna napetost – raztezek zlitine CuAlNiMn SMA

MPa, calculated as the average value of three measurements. The Young's modulus and yield strength were 67.72 GPa and 242.81 MPa, respectively. According to the literature,[19] this value of the tensile strength is satisfactory for a Cu-based alloy. The elongation (*A*) after fracture was very low (1.64 %) and without a measurable contraction. In the literature[19] the maximum elongation after tensile testing for a continuously cast Cu-13 % Al-4 % Ni (*w*/%) SMA was 1.45 % and this is below the limit of the typical recoverable strain of 4–6 %. U. Sari[13] found that the compression strength for Cu-11.6 % Al-3.9 % Ni-2.5 % Mn (*w*/%) amounts to 952 MPa and the ductility is 15 %.

The hardness of the CuAlNiMn shape-memory alloy was 290.7 HV0.5. As manganese favorably influences the alloy plasticity, it is fair to assume that the hardness of the CuAlNiMn alloy should be lower than that of the alloy without manganese.[13,14]

4 CONCLUSIONS

The microstructure analysis of CuAlNiMn before the tensile testing shows the presence of a martensitic microstructure. According to the plastic deformation carried out after the casting, it is fair to assume that the martensite existing in the microstructure is stress induced. The fracture surface indicates intergranular fracture and mainly transgranular brittle fracture with the characteristic river pattern. There are also some parts with shallow dimples indicating that the alloy was plastically deformed. The cracks nucleate at the grain boundaries where the stress-level concentration is high. Mechanical properties of CuAlNiMn show satisfactory results for the

Table 3: Tensile-test results for the CuAlNiMn shape-memory alloy
Tabela 3: Rezultati nateznega preizkusa zlitine CuAlNiMn z oblikovnim spominom

Mechanical properties	Young's modulus / GPa		Yield strength / MPa		Tensile strength / MPa		Elongation / %	
Measurement results with mean value	60.76	**67.72**	244.04	**242.81**	350.78	**401.39**	1.41	**1.64**
	66.94		245.99		416.10		1.74	
	75.45		238.39		437.30		1.79	

tensile strength (401.39 MPa) and a very low value for the elongation (1.64 %). The hardness of the alloy is 290.7 HV0.5.

Acknowledgement

5 REFERENCES

[1] M. Gojić, L. Vrsalović, S. Kožuh, A. Kneissl, I. Anžel, S. Gudić, B. Kosec, M. Kliškić, Journal of Alloys and Compounds, 509 (**2011**), 9782–9790

[2] G. Lojen, I. Anžel, A .C. Kneissl, A. Križman, E. Unterweger, B. Kosec, M. Bizjak, Journal of Materials Processing Technology, 162–163 (**2005**), 220–229

[3] M. Čolić, R. Rudolf, D. Stamenković, I. Anžel, D. Vučević, M. Jenko, V. Lazić, G. Lojen, Acta Biomaterialia, 6 (**2010**), 308–317

[4] Y. Sutou, T. Omori, K. Yamauchi, N. Ono, R. Kainuma, K. Ishida, Acta Materialia, 53 (**2005**), 4121–4133

[5] Y. Sutou, R. Kainuma, K. Ishida, Materials Science and Engineering A, 273–275 (**1999**), 375–379

[6] Z. Wang, X. F. Liu, J. X. Xie, Progress in Natural Science, Materials International, 21 (**2011**), 368–374

[7] A. C. Kneissl, E. Unterweger, M. Bruncko, G. Lojen, K. Mehrabi, H. Scherngell, Metalurgija, 14 (**2008**) 2, 89–100

[8] C. Segui, E. Cesari, Journal de Physique IV, Colloque C2, supplement au Journal de Physique III, 5 (**1995**), 187–191

[9] K. Otsuka, C. M. Wayman, Shape memory alloys, Cambridge University Press, Cambridge 1998, 97–116

[10] Z. G. Wei, H. Y. Peng, W. H. Zou, D. Z. Yang, Metallurgical and Materials Transactions A, 28 (**1997**), 955–967

[11] Z. Li, Z. Y. Pan, N. Tang, Y. B. Jiang, N. Liu, M. Fang, F. Zheng, Materials Science and Engineering A, 417 (**2006**), 225–229

[12] J. Van Humbeck, L. Delaney, A comparative review of the (Potential) Shape Memory Alloys, ESOMAT 1989 – Ist European Symposium on Martensitic Transformations in Science and Technology, Germany, 1989, 15–26

[13] U. Sari, International Journal of Minerals, Metallurgy and Materials, 17 (**2010**) 2, 192–198

[14] I. Ivanić, M. Gojić, I. Anžel, S. Kožuh, M. Rimac, O. Beganović, K. Begović, B. Kosec, Microstructure and properties of casted CuAlNi and CuAlNiMn shape memory alloys, Proceedings of the 13th International Foundrymen Conference, Opatija, 2013, 153–162

[15] G. N. Sure, L. C. Brown, Metallurgical Transactions, 15A (**1984**), 1613–1621

[16] H. Sakamoto, Y. Kijima, K. Shimizu, Transactions of the Japan Institute of Metals, 23 (**1982**) 10, 585–594

[17] Y. Sutou, T. Omori, R. Kainuma, N. Ono, K. Ishida, Metallurgical and Materials Transactions A, 33 (**2002**), 2817–2824

[18] L. A. Matlakhova, E. C. Pereira, A. N. Matlakhov, S. N. Monteiro, R. Toledo, Materials Characterization, 59 (**2008**), 1630–1637

[19] G. Lojen, M. Gojić, I. Anžel, Journal of Alloys and Compounds, 580 (**2013**), 497–505