

ISOTHERMAL DECOMPOSITION OF THE β' PHASE IN Cu-Zn-Al SHAPE-MEMORY ALLOYS

IZOTERMNA RAZGRADNJA β' -FAZE V ZLITINAH S SPOMINOM Cu-Zn-Al

Vanja Asanović, Kemal Delijić, Nada Jauković

University of Montenegro, Faculty of Metallurgy and Technology, Podgorica, Cetinjski put, bb, 81000 Podgorica, Montenegro
vanjaa@cg.ac.yu

Prejem rokopisa – received: 2005-12-20; sprejem za objavo – accepted for publication: 2006-04-16

The decomposition of the β' phase in Cu-25.7Zn-3.1Al and Cu-17.9Zn-5.4Al shape-memory alloys was studied. The B2 \rightarrow DO₃ order transition was not completely suppressed by quenching in icy water. The aging process at temperatures below 400 °C involved the formation of bainite or α phase. In specimens aged at higher temperatures the α phase was observed. The activation energies of α precipitation in the Cu-25.7Zn-3.1Al alloy and Cu-17.9Zn-5.4Al alloy were determined to be 109.85 kJ mol⁻¹ and 132.12 kJ mol⁻¹, respectively. The formation of γ precipitates was not observed.

Key words: shape-memory alloys, decomposition, precipitation

Raziskana je bila razgradnja β' -faze v zlitinah s spominom Cu-25,7Zn-3,1Al in Cu-17,9Zn-5,4Al. Premena urejenosti B2 \rightarrow DO₃ ni bila popolnoma preprečena s kaljenjem v ledeni vodi. Pri staranju pri nižji temperaturi od 400 °C je nastal bainit ali α -faza. V vzorcih, žarjenih pri višjih temperaturah, smo našli α -fazo. Aktivacijske energije za α -izločanje v Cu-25,7Zn-3,1Al in Cu-17,9Zn-5,4Al so bile 109,85 kJ/mol oz. 132,12 kJ/mol. Nastanka γ -izločkov nismo opazili.

Ključne besede: zlitine s spominom, razgradnja, izločanje

1 INTRODUCTION

"Shape memory" is the term used to describe an interesting property by which some materials "remember" their original shape and revert to it at characteristic transformation temperatures. This feature was observed in samples of Cu-Zn-Al alloys in the 1970s. Cu-Zn-Al shape-memory alloys are now being used for various applications.

The shape-memory effect is based on a diffusionless phase transformation called the thermoelastic martensitic transformation. In this transformation atoms move cooperatively. In Cu-Zn-Al alloys, the parent phase is the bcc β phase, and the transformation product is martensite. The high-temperature β phase has a disordered A2 structure, but cooling induces an ordering process, bcc \rightarrow B2, by which the B2 superlattice structure develops. Upon further cooling, the structure goes through a next-nearest-neighbor ordering, i.e., B2 \rightarrow DO₃, and the structure eventually becomes the DO₃. The lower-temperature phase (martensite) has a lower symmetry than the parent phase. The structures of martensites in Cu-Zn-Al shape-memory alloys are of a long-period stacking-order type: 6R, 18R and 2H.

In order to obtain a good reliable shape-memory effect in Cu-Zn-Al alloys a sufficiently rapid cooling (quenching) from a betatizing temperature is necessary to avoid a eutectoid decomposition, $\beta' \rightarrow \alpha + \gamma$.

The nature of both the parent β phase and the martensite in the Cu-Zn-Al alloys is metastable.

Consequently, the stability of their shape-memory properties is influenced strongly by aging¹⁻⁶.

This work is concerned with the decomposition of the β' phase (ordered parent phase) in two ternary Cu-Zn-Al shape-memory alloys. An optical microscope and X-ray diffractometer have been employed to examine the microstructural changes that occur in the alloys during aging.

2 EXPERIMENTAL

Two Cu-Zn-Al shape-memory alloys with the nominal compositions given in **Table 1** were prepared by melting high-purity copper, pre-alloy Cu-Zn (49.2 % Zn) and pre-alloy Cu-Al (47.8 % Al) in a graphite crucible using a resistance-heated furnace. The two billets were first homogenized at 800 °C for 2 h and quenched in water at room temperature, then extruded into 6-mm-diameter rods at 800 °C.

Table 1: The mass fraction *w*/% of the chemical composition of alloys

Tabela 1: Kemična sestava zlitin

Alloy	Zn	Al	Cu
A	25.7	3.1	rest
B	17.9	5.4	rest

In order to study the isothermal decomposition of the β' phase in the alloys, test specimens were cut from the rods, solution treated at 850 °C for 10 min and quenched

into icy water. Quenched specimens were introduced into a 60 % KNO_3 and 40 % NaNO_2 salt bath at fixed temperatures: (200, 240, 280, 320, 360, 400, 440, 480, 520, 560, 600 and 640) °C. Then, they were taken one by one, for various times up 2048 min, and quenched into icy water. Afterwards, the analysis of the phases formed was performed using optical microscopy and X-ray diffraction.

3 RESULTS AND DISCUSSION

Optical microscopy observations of the quenched specimens revealed the parent-phase grain boundaries and the martensite structure, as shown in **Figure 1**. From the X-ray diffraction patterns of the quenched specimens, the lattice parameters a , b , c , β and φ were obtained (**Table 2**). The directly quenched martensite was M18R type.

Table 2: Lattice parameters of M18R martensite

Tabela 2: Mrežni parametri, artenzita M18R

Lattice parameters of M18R martensite					
Alloy	a/nm	b/nm	c/nm	$\beta/^\circ$	$\varphi/^\circ$
A	0.4472	0.5318	3.8370	89.39	61.47
B	0.4440	0.5285	3.7080	89.20	61.52

The cooling rate during direct quenching is very high; hence, the supercooling for the $\text{A2} \rightarrow \text{B2} \rightarrow \text{DO}_3$ transitions in the Cu-Zn-Al alloys is large. The ordering of the bcc β phase to the B2 superlattice is so rapid that it is almost impossible to quench-in the disordered bcc

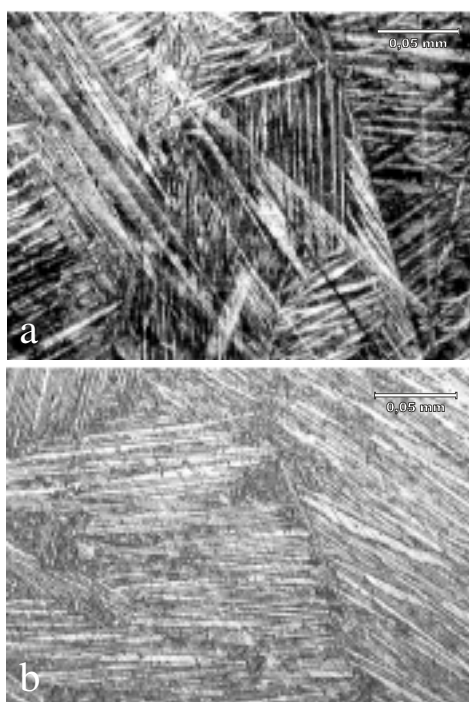


Figure 1: Microstructure of the quenched specimens

Slika 1: Mikrostruktura gašenih vzorcev

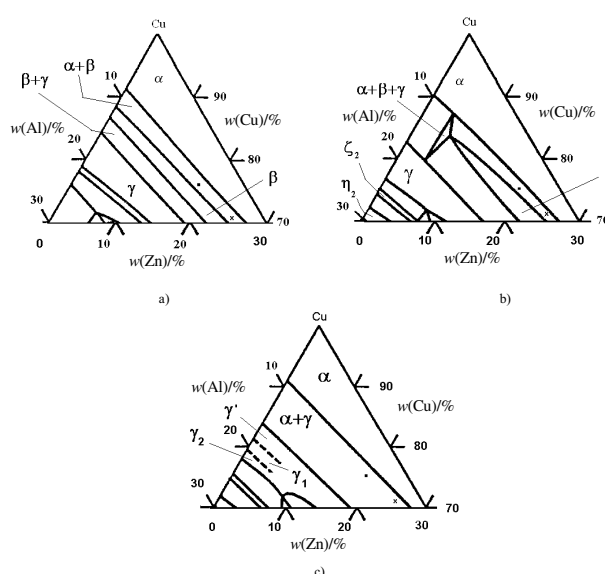


Figure 2: Isothermal sections of the Cu-Zn-Al phase diagram at 700 °C (a), 550 °C and 350 °C (c)⁷

Slika 2: Izotermni precez faze Cu-Al-Zn pri (a) 700 °C, (b) 550 °C in (c) 350 °C⁹

structure⁷. This transformation is second order and occurs at high temperatures (about 550 °C). It is thought⁸ that the ordering process $\text{bcc} \rightarrow \text{B2}$ in the Cu-Zn-Al alloys is completely finished during quenching. The Cu-Zn-Al alloys exhibit a secondary $\text{B2} \rightarrow \text{DO}_3$ ordering reaction prior to the martensitic transformation. The critical temperature for $\text{B2} \rightleftharpoons \text{DO}_3$ varies greatly from one alloy to another. The presence of M18R martensite in quenched specimens indicates that the $\text{B2} \rightarrow \text{DO}_3$ order transition cannot be completely suppressed by rapid cooling.

On the basis of the isothermal sections of the equilibrium phase diagram of the Cu-Zn-Al ternary alloy system⁹ shown in **Figure 2**, the following phase transformations and reactions are possible for the alloys under investigation:

$$\beta \rightarrow \alpha + \beta \quad \text{at } T = 700 \text{ }^\circ\text{C}$$

$$\beta \rightarrow \beta' \quad \text{at } T \leq T_c \text{ (} T_c \text{ is the critical temperature for ordering)}$$

$$\beta' \rightarrow \alpha + \beta' \quad \text{at } T = 550 \text{ }^\circ\text{C}$$

$$\beta' \rightarrow \alpha + \gamma \quad 350 \text{ }^\circ\text{C} < T < 550 \text{ }^\circ\text{C}$$

At temperatures from 350 °C to 550 °C, the alloys are expected to remain within the three-phase field of α , β and γ . Therefore, the eutectoid reaction occurs in the examined alloys at a temperature that is lower than 550 °C but higher than 350 °C. The reaction can be expressed as:

$$\beta' \rightarrow \alpha + \gamma$$

The α phase is face-centered cubic, while the γ phase has a cubic structure.

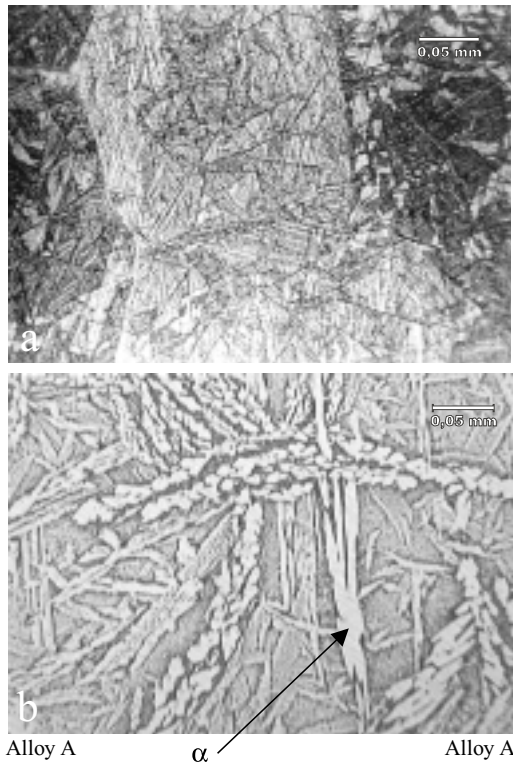


Figure 3: Optical micrographs of the microstructure in specimens aged for: a) 512 min at 200 °C, b) 2048 min at 200 °C

Slika 3: Optični posnetek mikrostrukture vzorca, ki je bil staran: a) 512 min pri 200 °C, b) 2048 min pri 200 °C

The microstructures of all the specimens after various aging treatments were investigated by optical microscopy. It was found that a plate-like product is developed in specimens after aging treatments at temperatures below 400 °C (**Figure 3a**). The phase was identified

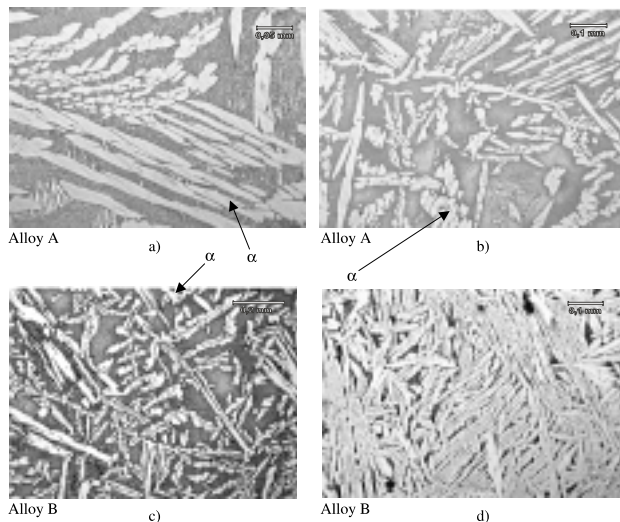


Figure 4: Optical micrographs of the microstructures in specimens aged for: a) 256 min at 440 °C, b) 128 min at 520 °C, c) 64 min at 520 °C, d) 128 min at 640 °C

Slika 4: Optični posnetek mikrostrukture vzorcev, staranih: a) 256 min pri 440 °C, b) 128 min pri 520 °C, c) 64 min pri 520 °C, d) 128 min pri 640 °C

with X-ray diffraction as α_1 bainite [9R] with the following lattice parameters: $a = 0.469$ nm, $b = 0.264$ nm and $c = 1.950$ nm. But the α_1 bainite transformed ultimately into the fcc α phase (**Figure 3b**). The rod-like product is observed after annealing at higher temperatures (**Figure 4**), which was identified as fcc α phase with the lattice parameter $a = 0.369$ nm. The γ phase was not detected in the aged specimens.

To determine the amount of α phase that can occur in the Cu-25.7Zn-3.1Al and Cu-17.9Zn-5.4Al alloys as a result of isothermal aging treatments, a microstructural analysis was made. The progress of an isothermal phase transformation is represented by plotting the fraction of transformation as a function of time and temperature. The time-temperature-transformation curves were obtained for the alloys, as shown in **Figure 5**. The increase in the amount of α phase with aging time at each temperature was observed. The required durations to form an α precipitate in the Cu-17.9Zn-5.4Al alloy is greater than for the Cu-25.7Zn-3.1Al alloy. It has been reported^{10,11} that the solute contents (Zn and Al) in the α phase are less than those in the parent phase. Since both the melting point and atomic size of aluminum exceed those of zinc the diffusion of aluminum atoms will be the dominant factor in the precipitation rate. Therefore, the specimens of Cu-17.9Zn-5.4Al alloy require longer aging times for the aluminum atoms to diffuse away and form α phase than those of the Cu-25.7Zn-3.1Al alloy.

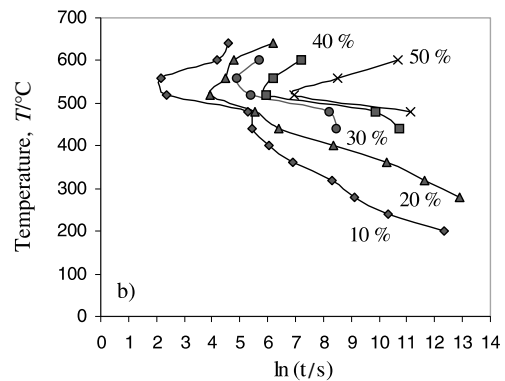
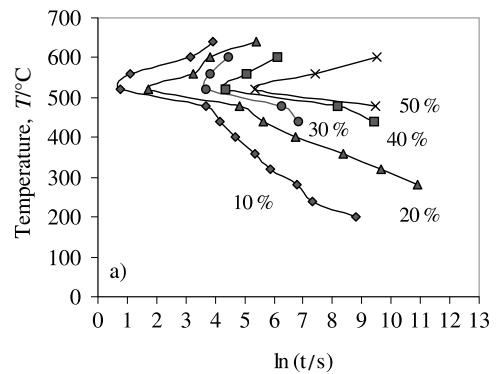


Figure 5: The TTT-transformation diagram of α -precipitation in a) Cu-25.7Zn-3.1Al alloy (A alloy), b) Cu-17.9Zn-5.4Al alloy (B alloy)

Slika 5: TTT-diagram α -izločanja v: a) zlitini Cu-25,7Zn-3,1Al (zlitina A), b) zlitini Cu-17,9Zn-5,4Al zlitini (zlitina B)

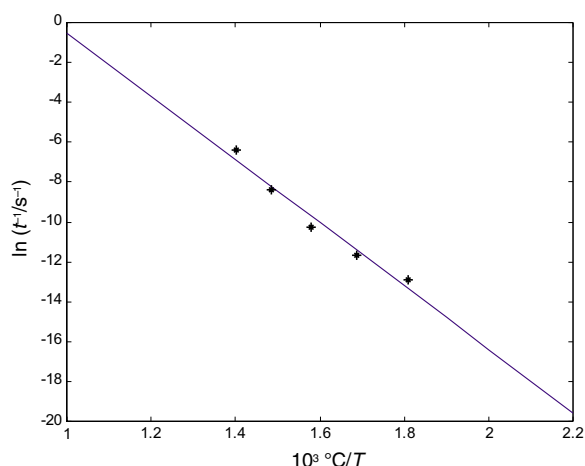


Figure 6: Arrhenius plot of the length of aging period vs. temperature to develop a microstructure with the volume fraction 20 % of α -precipitation (alloy Cu-17.9Zn-5.4Al)

Slika 6: Arrheniusova odvisnost med trajanjem staranja in temperaturo za nastanek mikrostrukture s prostorninskim deležem α -izločanja 20 % (zlitina Cu-17,9Zn-5,4Al)

The effects of aging treatments on shape-memory capacity have not been examined in this study. However, in our recent research work¹² we found that the precipitation of the volume fraction 20 % α phase causes a degradation of the shape-memory capacity. An Arrhenius plot of the length of annealing period vs. temperature to develop a microstructure with 20 % α phase in the examined alloys is shown in **Figure 6**. The activation energies of α precipitation in the Cu-25.7Zn-3.1Al alloy and the Cu-17.9Zn-5.4Al alloy are thus determined to be 109.85 kJ mol⁻¹ and 132.12 kJ mol⁻¹, respectively. These values are lower than the activation energies for the diffusion in the ordered β phase of the Cu-Zn alloys that were reported as 135–200 kJ mol⁻¹ by several investigators^{13–16}. This implies that the processes occurring during aging are diffusional, but enhanced by a superconcentration of quenched-in vacancies².

4 CONCLUSIONS

The directly quenched martensite in the examined alloys was the M18R type. This indicates that the B2 \rightarrow DO₃ order transition cannot be completely suppressed by rapid cooling.

During aging at temperatures below 400 °C, the β' phase decomposed into bainite, which was ultimately transformed into α phase. At temperatures above 400 °C, only α phase was formed. The formation of γ precipitates was not observed.

An increase in the amount of α phase with aging time at each aging temperature was observed.

The aging times required for the aluminum atoms to diffuse away and form the α phase are greater for the Cu-17.9Zn-5.4Al alloy than for the Cu-25.7Zn-3.1Al alloy.

The activation energies of α precipitation in the Cu-25.7Zn-3.1Al alloy and the Cu-17.9Zn-5.4Al alloy were determined to be 109.85 kJ mol⁻¹ and 132.12 kJ mol⁻¹, respectively.

5 REFERENCES

- ¹ D. Schofield, A. P. Miodownik, *Metals Technology*, (1980), April, 167
- ² N. F. Kennon, D. P. Dunne, L. Middleton, *Metallurgical Transactions A*, **13A** (1982), 551–555
- ³ M. M. Reyhani, P. G. McCormick, *Scripta Metallurgica*, 21 (1987), 550
- ⁴ J. Pons, E. Cesari, *Thermochemica Acta*, 145 (1989), 242
- ⁵ E. S. Lee, Y. G. Kim, *Metallurgical Transactions A*, 21A (1990), 1687
- ⁶ Y. Nakata, O. Yamamoto and K. Shimizu, *Materials Transactions, JIM*, 34 (1993) 5, 437
- ⁷ D. A. Porter, K. E. Easterling, *Phase Transformations in Metals and Alloys*, Chapman and Hall, London, 1990
- ⁸ K. Oocuka, K. Simizu, J. Suzuki, J. Cekiguti, C. Tadaki, T. Homa, S. Mijayaki, *Splavi s efektom pamjati formi, Mettalurgija, Moscow*, 1990
- ⁹ T. Lyman (ed.), *Metals Handbook (Vol. 8.): Metallography, Structures and Phase Diagrams*, American Society of Metals, Metals Park, Ohio, 1975
- ¹⁰ Y. Nakata, T. Tadaki, K. Shimizu, *Trans. Jpn. Inst. Met.*, 30 (1989), 107–116
- ¹¹ M. H. Wu, C. M. Wayman, *Proc. ICOMAT-1986, Jpn. Inst. Met.*, Nara, Japan 1986, 619–624
- ¹² V. Asanovic, K. Delijic, Z. Leka, *Materials Science Forum*, 191 (2004), 453–454
- ¹³ Y. E. Ugaste, V. N. Pimenov, *Fiz. Met. Metalloved.*, 31 (1968), 363–367
- ¹⁴ P. Camagni, *Proc. 2nd Geneva Conf. Atomic Energy, Geneva*, 20 (1958), 1365–68
- ¹⁵ A. B. Kuper, D. Lazarus, J. R. Manning, C. T. Tomiyuka, *Phys. Rev.*, 104 (1956), 1536–1541
- ¹⁶ C. I. Smithells, *Metals Reference Book*, 5th ed., Butterworths, London 1976, 860