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Properties of Thermally Treated CuZn27Al3 Shape Memory Alloy

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The work analyses the behaviour of thermally treated CuZn27Al3 shape memory alloys. The alloy is betatised and quenched from the temperatures in the range of $\vartheta_{\beta} = 600\,^{\circ}\mathrm{C}$ *to* $\vartheta_{\beta} = 800\,^{\circ}\mathrm{C}$. *The properties of materials are analyzed by means of differential scanning calorimetry, micrographic testing, testing of mechanical properties and pseudo-elastic effect. The results indicate significant dependence of classical and specific properties on thermal treatment temperature, particularly if* $\vartheta_{\beta} < 700\,^{\circ}\mathrm{C}$. *The change in transformation temperatures, hardness, mechanical resistance determined by static tensile loading as well as specific pseudo-elastic elongation is the consequence of the occurrence of sub-boundaries and formation of* α*-crystal mixes, thus changing the chemical composition of austenite. Betatisation at higher temperatures* ($700 \leq \vartheta_{\beta} \leq 800\,^{\circ}\mathrm{C}$) *contributes to martensitic transformation reducing the driving force necessary for the transformation in the form of conducted heat in thermally induced transformation i.e. required stress for mechanically induced martensitic reaction with simultaneous increase of pseudo-elastic shape memory, as well as the reduction of total mechanical resistance of the alloy.*

Keywords: CuZnAl alloy, shape memory, thermal treatment, transformation temperatures, mechanical properties

0 INTRODUCTION

Specific behaviour of shape memory alloys (SMA) is based on the crystallographic reversible martensitic austenitic transformation.

This transformation is generally known in steels since it represents the basic mechanism of the hardening and has been, therefore, already used for about 3500 years. However, in case of steel the transformation is irreversible [1].

Reversible martensitic transformation in shape memory alloys occurs at low temperatures at which the speed of diffusion reactions is practically zero and the mobility of atoms very low. Therefore, individual atom movement is not possible, but rather only their simultaneous movement [2]. The redistribution of atoms by means of homogeneous shear over distances smaller than crystal lattice parameter results in the change in the method of their arrangement. In shape memory alloys the starting structure of high temperature phase or austenite with symbol β is transformed into the structure of low temperature phase or martensite with symbol α_{M} [3]. The martensitic reaction occurs by cooling between temperatures M_s (martensite start) and M_f (martensite finish), and austenitic transformation by heating within the temperature range A_s (austenite start) and A_f (austenite finish) [4].

The change of crystal lattice results in the change of shape and dimension of SMA materials known as shape memory effects. There are three different shape memory effects: pseudo-elasticity, two-way effect and one-way effect or pseudo-plasticity. These effects can be induced by changing the temperature, with or without action of external mechanical stress. First, the pseudo-elastic material is deformed under stress purely elastically. After reaching the pseudo yield stress, R_{pp}, it comes to substantial material extension due to stress-induced transformation of austenite into martensite at temperature higher than A_f, and lower than M_d (M_d – the highest temperature at which mechanically induced martensitic transformation occurs). This deformation completely disappears with reverse transformation ($\alpha_{\mathrm{M}} \rightarrow \beta$) during unloading with occurrence of stress hysteresis $\Delta\sigma$ [5]. In case of a two-way effect the change of shape due to $\beta \leftrightarrow \alpha_{\mathrm{M}}$ transformation is induced exclusively by changing the temperature. After having carried out the “training” of the alloy, the change in shape occurs by cooling between M_s and M_f temperature, and the primary shape is established

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by heating from A_s to A_f temperature. One-way effect or pseudo-plasticity characterizes virtual plastic deformation under the action of stress R_{pp}. Since this is a deformation which results from $\beta \rightarrow \alpha_M$ transformation, at temperature greater than M_s, and lower than A_s by heating the alloy above A_f reverse transformation follows when the material returns to primary shape [6].

Today, mainly SMA materials are used based on NiTi due to their bio-compatibility, relatively high shape memory effect and good mechanical properties. However, the less expensive SMA materials are also being studied, such as copper-based alloys: CuZnAl and CuAlNi.

1 EXPERIMENT

The properties of SMA materials, as well as generally all other materials, are the consequence of structural condition of the material, i.e. its microstructure, which is determined by the chemical composition and technological treatment procedure.

Semi-products of the studied shape memory copper alloy were produced by induction re-melting and casting at a specialized foundry Wieland-Werke A.G. in Germany. Since the transformational temperatures that have significant influence on the exploitation characteristics of alloy are very sensitive to the change in the chemical composition, the alloying accuracy greater than 0.1% is required. The atoms of alloying elements have to be uniformly distributed in the main lattice free of any kind of segregation [7]. For experimental study the three-component copper alloy of the following composition was selected: Cu 69.51% mass, Zn 27.32% mass, Al 3.17% mass. The content of copper and zinc has been determined electrogravimetrically, and the control of the possibly remaining volumes after selective deposition of metal was performed in electrolyte spectrophotometrically. To determine the aluminium content, the atom-absorption spectrophotometry was used.

The phase diagram and TTT diagram for CuZnX shape memory alloys, Fig. 1, represent the basis for determining of thermal treatment parameters.

Thermal treatment can be performed either at high temperatures in the range of homogeneous β-phase or at temperatures lower than M_f when thermally induced formation of martensite occurs.

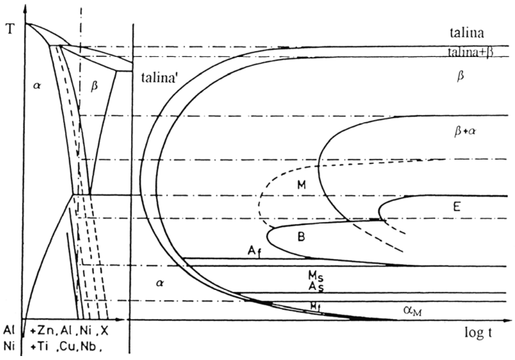


Fig. 1. *Phase diagram and TTT diagram for CuZnX alloys [3]*

Thermal treatment in the mean range of temperatures would result in mixed transformations such as "massive" (M), eutectoid (E) and bainitic reaction (B) and precipitation which results in heterogeneous microstructure incapable of reversible $\beta \leftrightarrow \alpha_M$ transformation [3].

The procedure of homogenization of SMA material within the range of non-ordered reversibly transformable austenite structure is generally known as betatisation [8]. The alloy is betatised at temperatures (ϑ_β): 600, 620, 650, 660, 670, 680, 700, 750, and 800 °C over a period of 20 minutes. After betatisation, the material is cooled at super-critical rate in water (quenched) in order to avoid undesirable transformations in solid state that change the structure of β-phase.

Reversible austenite ⇒ martensite transformation is influenced by the following factors, [6] and [9]:

1) absence of diffusion processes in the transformational temperature range: $\Delta T = A_f - M_f$;
2) negligible change in volume during $\beta \leftrightarrow \alpha_M$ transformation;
3) high shear deformation of the lattice during $\beta \leftrightarrow \alpha_M$ transformation;
4) crystallographic order of the austenite;
5) internal plastic deformation of α_M - crystals without change in crystal lattice;
6) high yield stress of austenite;
7) absence of magnetic transformation during phase transformation.

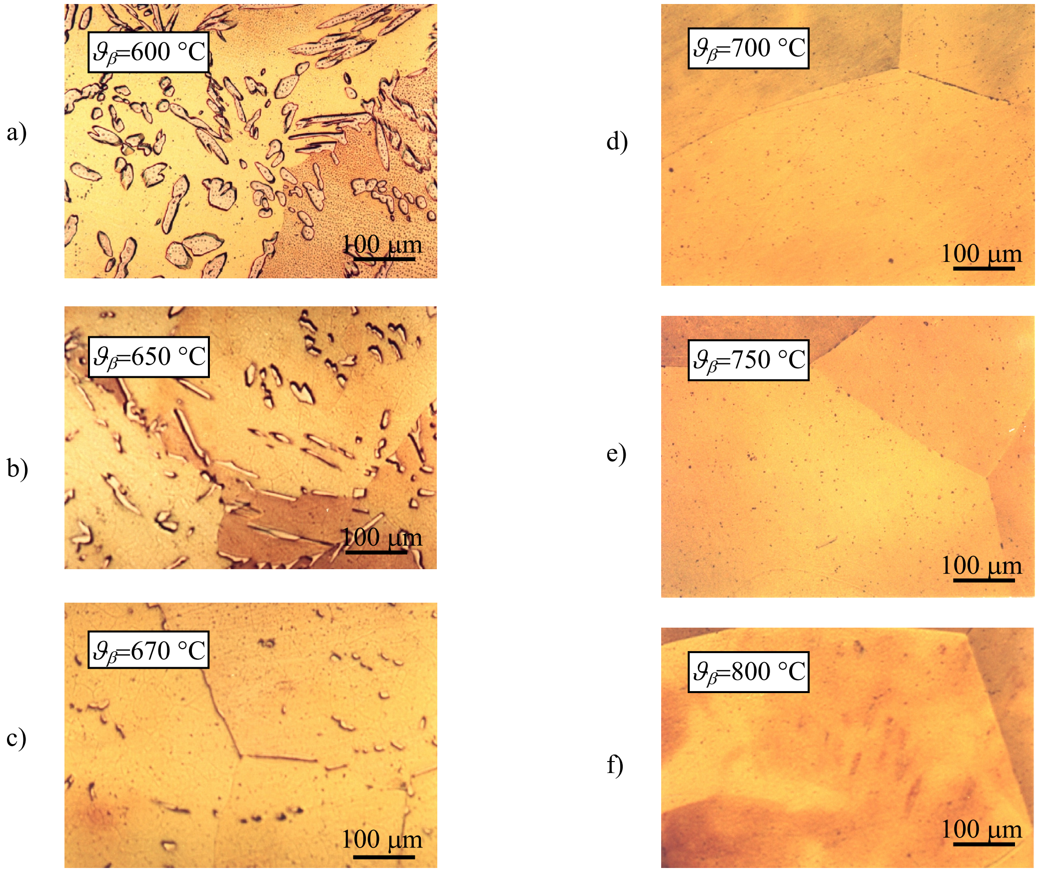


Fig. 2. *Microstructure of thermally treated alloy*

Martensitic austenitic transformation has been analysed by means of various experimental methods such as: differential scanning calorimetry (DSC), metallographic analysis and tensile testing until fracture and testing of pseudo-elasticity.

Micrographic tests by means of optical microscopy were used to analyse the influence of thermal treatment on the microstructure of the alloy. After the samples were classically prepared for metallographic analysis (marking, cutting, mounting, grinding, pre-polishing, final polishing), the specimens were electro-etched in electrolyte marked D2 of the following composition: 250 ml H_3PO_4, 500 ml H_2O, 250 ml ethyl alcohol, 2 ml dye, 50 ml propanol, 5 g urea. In electro-etching (U = 6 V, I = 80 mA) in the duration of 30 s, the specimen represents the anode, and the austenitic bowl the cathode. Fig. 2 shows the microstructure of a thermally treated alloy.

Figures 2a, b and c present the multi-phase structure which consists of the mixture of α- and β-crystals. β-crystals are intermetallic compound with body-centred cubic lattice (BCC). At room temperature β-phase has an ordered structure, but at elevated temperatures it becomes disordered. Ordered β-phase is hard, but still quite tough. α-crystal mixes have, the same as copper, face-centred cubic lattice (FCC) [10]. In this lattice part of copper atoms is replaced with dissolved zinc and aluminium atoms. The precipitation of α-phase particles occurs along the boundaries of β-grains as well as within the grain. Precipitation is especially strong for betatisation temperature ϑ_β = 600 °C (Fig. 2a). The dislocation regrouping causes formation of sub-boundaries and the appearance of sub-grains within the β-crystal. With the increase of betatisation temperature share and grain size of α-crystals is decreasing. So for $\vartheta_\beta \geq 680$ °C the alloy is pure austenitic, Figures 2 d, e and f. The occurrence of big β-grains of straight boundaries indicates that after homogenization the duration for the growth of the grain was relatively long. The sub-boundaries are no longer visible because of the resulting recrystallization processes.

Quantitative micrographic analysis of the alloy of the two-phase α+β -structure ($600 \leq \vartheta_\beta \leq 670$ °C) was used to determine the mass shares (*w*) of α- and β-phases, Fig. 3, and the size of α-crystal, Fig. 4.

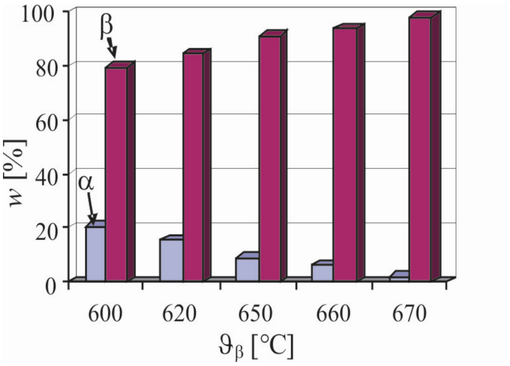


Fig. 3. *Shares of α- and β-phases*

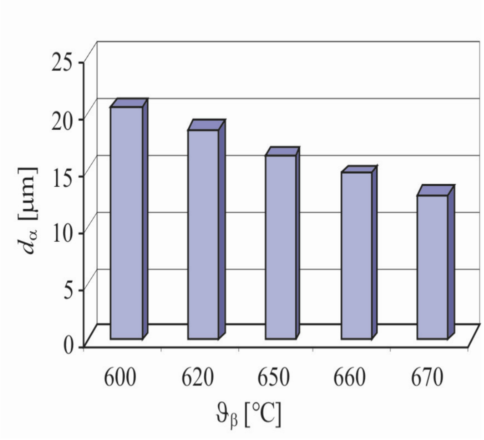


Fig. 4. *Size of α-grains*

Electronic micro-analysis was used to determine the change in the share of zinc in α- and β-phase after thermal treatment at $\vartheta_\beta = 600$ °C and $\vartheta_\beta = 670$ °C. The parameters of spot microanalysis were the voltage $U = 25$ kV, and intensity of electricity $I = 3 \cdot 10^{-8}$ A. The intensity of characteristic X-ray radiation was determined on the basis of measuring the number of impulses within a time interval of 10 s. The results of electronic microanalysis are presented in Table 1.

Table 1. *Number of impulses on α- and β-phase (X-rays)*

ϑ_β [°C]	Phase	Measurement				
		1	2	3	4	5
600	α	1166	1164	1158	1156	1140
	β	1435	1422	1441	1425	1448
670	α	1356	1329	1315	1324	1323
	β	1329	1333	1315	1310	1301

Relative shares of zinc in α- and β-phase follow from the ratio of mean values of the measured impulses:

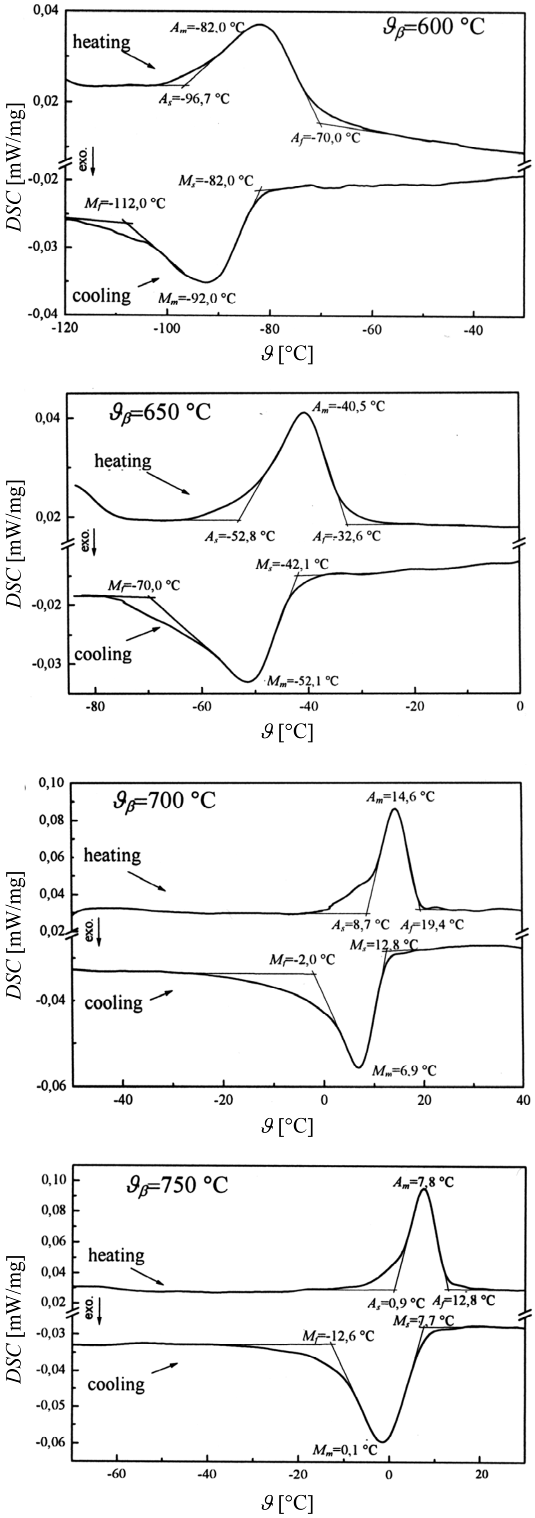
$w_{Zn\beta}:w_{Zn\alpha} = 1434:1157 = 1{,}2 : 1$ ($\vartheta_\beta = 600$ °C);

$w_{Zn\beta}:w_{Zn\alpha} = 1318:1329 \approx 1 : 1$ ($\vartheta_\beta = 670$ °C).

From the aspect of shape memory the reduction of zinc content in austenite with the increase in thermal treatment temperature is interesting. Microanalysis of the chemical composition was carried out on the electronic micro-analyzer as part of the scanning microscope JSM-50A.

With DSC, the most direct method for the analysis of reversible martensitic transformation and especially suitable for determining the temperature of the start and end phase transformations (M_s, A_s, M_f, A_f) and the extremes (peaks) of endothermic and exothermic process (A_m, M_m), the values of characteristic transformational temperatures were determined. The method relies on the measurement of heat which is absorbed or conveyed by the material specimen during heating and cooling within the temperature range of transformational reactions [11]. The values of temperatures M_s, M_f, A_s, A_f have been defined by the method of tangents on the base line and peak curve in DSC thermogram. Differential scanning calorimetry was performed on the calorimeter of the Netsch Company, type DSC 200, in the temperature range from 100 °C to –120 °C at the rate of cooling/heating of 5 °C/min. Fig. 5 shows the characteristic curves of thermal flow.

The peaks of thermal flow of martensitic and austenitic transformation during cooling and heating are clearly noticeable. With the increase in temperature of betatisation heating both transformation processes move to the range of higher temperatures, and peaks of transformation reactions become narrower.



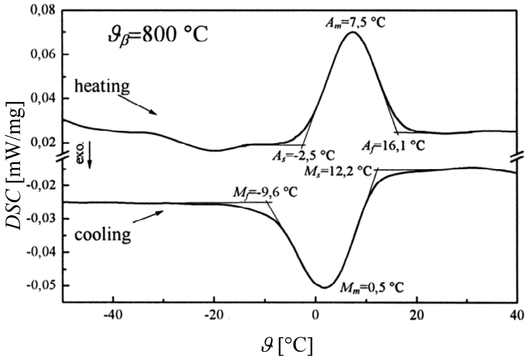


Fig. 5. *DSC transformation cycles of thermally treated alloy*

Based on the position of transformation peaks the values of characteristic temperatures are determined: M_s, M_f, M_m, A_s, A_f, A_m, Table 2.

Table 2. *Values of transformation temperatures*

ϑ_β °C	M_s °C	M_f °C	M_m °C	A_s °C	A_f °C	A_m °C
600	-82.0	-112.0	-92.0	-96.7	-70.0	-82.0
650	-42.1	-70.0	-52.1	-52.8	-32.6	-40.5
700	12.8	-2.0	6.9	8.7	19.4	14.6
750	7.7	-12.6	0.1	0.9	12.8	7.8
800	12.2	-9.6	0.5	-2.5	16.1	7.5

All transformation temperatures are lower than ambient temperature and the alloy shows pseudo-elastic behaviour or pseudo-plasticity (one-way effect) if martensite, which is stable when the stress is removed, is induced at ambient temperature and by subsequent heating it is transformed into austenite [12].

Fig. 6 presents the position of transformation temperatures M_m and A_m for different thermally treated conditions.

With betatisation above 700 °C the position of thermal transformation cycle practically does not change whereas treatment at lower temperatures significantly influences the reduction of A_m and M_m temperatures followed by other transformation temperatures as well.

By measuring hardness using the Vickers method with load 0.0098 daN (*HV* 0.01) the hardness of the phase constituents of the thermally treated alloy was determined, Fig. 7. Hardness was tested at the ambient temperature over A_f value.

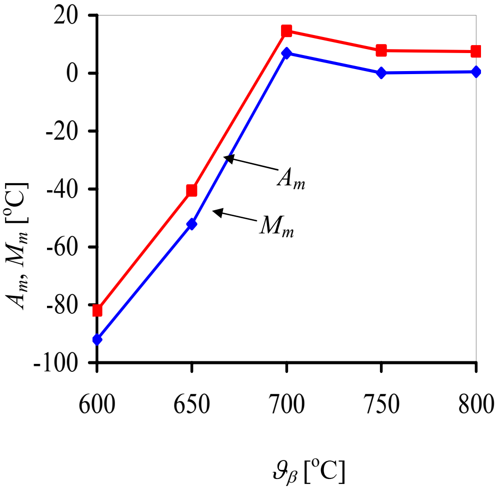


Fig. 6. *Transformation temperatures of a thermally treated alloy*

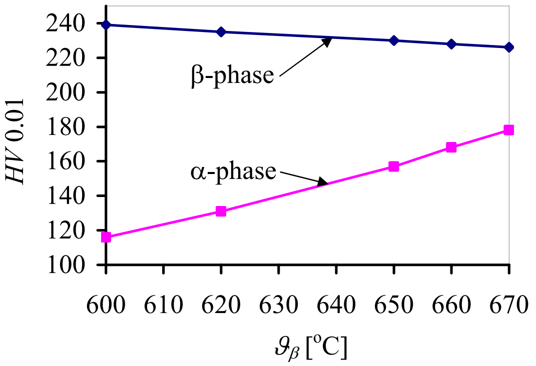


Fig. 7. *Hardness of structural phases of thermally treated alloy*

With the increase in betatisation temperature the austenite hardness changes very little. It falls slightly as the temperature approaches 670 °C. At the same time the hardness of α-phase increases. β-phase is harder than α-phase at all treatment temperatures, particularly the lower ones.

Furthermore, tensile testing at ambient temperature determines the mechanical properties of a thermally treated alloy including shape memory properties (pseudo-elasticity). The properties that characterize mechanical resistance of SMA material in conditions of tensile load are pseudo yield stress (R_{pp}), true yield stress (R_p) and tensile strength (R_m). Pseudo yield stress R_{pp} is stress value at which stress induced austenite → martensite transformation with pseudo-elastic deformation of materials starts. The true yield stress R_p, like other conventional materials, characterise appearance of plastic deformation, in our case the plastic deformation of martensite. The tensile strength (R_m) is stress value at maximal load during tensile test.

The process of testing the pseudo-elastic effect is similar to tensile testing, but the loading is stopped before fracture occurs, at the end of the deformation range characteristic for the shape memory. The stress has to be greater than the pseudo yield stress, and lower than the true yield stress. The amount of this stress is estimated from the respective σ - ε diagrams.

For testing of pseudo-elasticity and test-specimen fracture the micro-machine Mi 34, by Alfred J. & Co., was used.

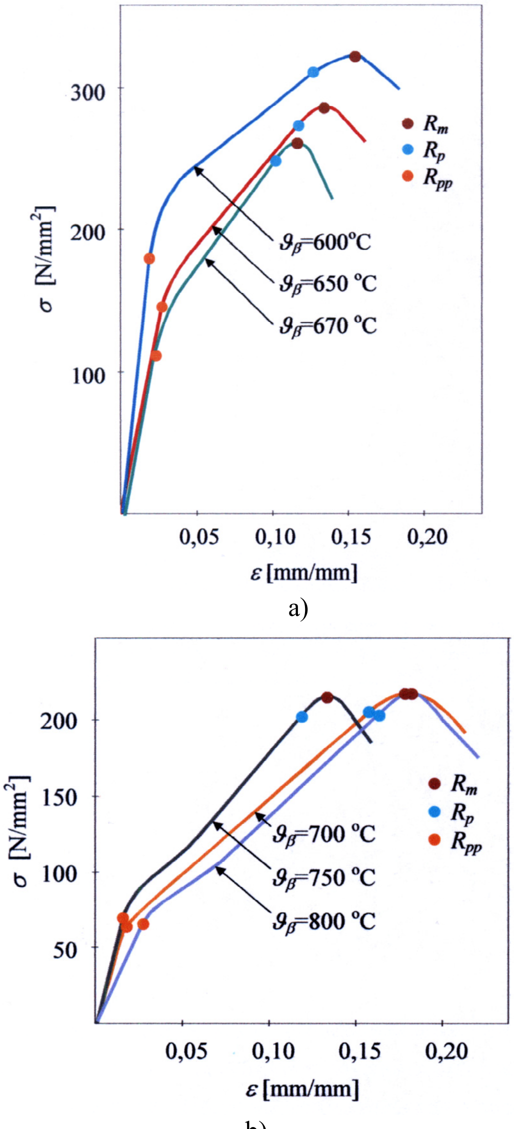
All diagrams (Figs. 8 and 9) were recorded for the first cycle of mechanical loading.

The occurrence of pseudo-elastic effect in mono-phase austenite alloy could have been expected, but the same effect, only of a smaller amount, also occurs in two-phase structures. σ - ε diagrams of pseudo-elastic effect in Fig. 9 clearly show that the alloy treated in the temperature range $600 \leq \vartheta_\beta \leq 670$ °C shows smaller pseudo-elastic deformation than mono-phase austenite alloy.

2 DISCUSSION OF THE RESULTS

Transformation behaviour of CuZn27Al3 alloy rests on high-temperature austenite structure, which is characterized by the reversible transformability into low-temperature martensitic structure. Therefore, after the homogenization treatment in the range of austenitic structure, the alloy has to be super-critically quenched in order to preserve the β-phase until the ambient temperature.

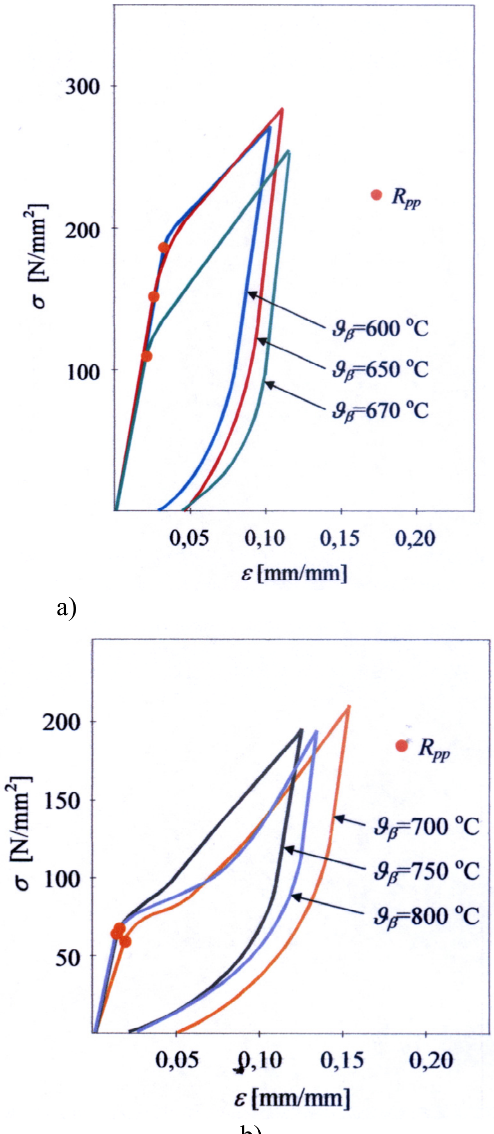
By quenching from the temperature lower than 680 °C a multi-phase structure is formed, which, apart from austenite, also contains α-crystal mixes. The precipitation of α-particles along boundaries of β-grains and within grains causes the change of chemical composition of austenite. With the increase in temperature the share



a)

b)

Fig. 8. *σ - ε diagrams of tensile testing*
a) alloy of two-phase α+β-structure
b) alloy of mono-phase β-structure



a)

b)

Fig. 9. *σ - ε diagrams of pseudo-elastic effect*
a) alloy of two-phase α+β-structure
b) alloy of mono-phase β-structure

and size of α-phase gradually decreases with a simultaneous decrease in the content of zinc in austenitic matrix. For temperatures of $\vartheta_\beta \geq 680$ °C the alloy has the mono-phase β-structure.

DSC testing provides evidence of cooling-induced martensitic transformation and heating-stimulated reverse austenitic transformation. The martensitic reaction starts at temperature M_s with the occurrence of sufficient driving force for diffusion-free formation of α_M-crystals. Since martensitic reaction is an exothermic process, the alloy has to be continuously cooled in order to conduct heat released by the reaction and thus, ensure uninterrupted flow of transformation. Complete martensitic transformation occurs by cooling to a sufficiently low temperature, lower or equal to M_f. On the other hand, the transformation into austenite which starts at temperature A_s is an endothermic reaction, characterized by heat consumption. For an uninterrupted reaction it is necessary to continuously conduct heat in order to overcome forces that oppose transformation. Transformation into austenite is complete only after heating to a sufficiently high temperature equals or is higher than A_f.

Thermally induced crystallographic reversible $\beta \leftrightarrow \alpha_M$ transformation occurs independently of precipitation and occurrence of structural defects such as sub-grain boundaries. With the increase of ϑ_β temperature the thermal transformational cycle shifts into the range of higher temperatures. M_m and A_m temperatures vary within the range of –92.0°C (ϑ_β= 600 °C) to 6.9 °C (ϑ_β= 700 °C) and from –82.0°C (ϑ_β= 600 °C) to 14.6 °C (ϑ_β= 700 °C). Practically the same tendency of transformational temperatures change was determined in other papers dealing with alloys of similar chemical composition [8] and [9]. The increase in transformational temperatures is the consequence of an increased mobility of dislocations and easier motion of β/α_M -transformational interface in the range of few tiny grains of α-phase. An additional reason is certainly also the resulting change in the chemical composition of austenite.

Furthermore, the properties of a material, such as hardness and properties defined by tensile testing also indicate the presence of martensitic transformation although not thermally but mechanically induced.

The results of hardness, measured with small load (*HV* 0.01) at temperatures above A_f, indicate dependence of the measured hardness on the treatment temperature. As temperature rises towards 670 °C the austenite hardness decreases, and α-phase increases, whereas with quenching from higher temperatures the hardness of austenite remains unchanged.

In tensile loading the alloy expresses pseudo-elastic shape memory. The occurrence of pseudo-elastic deformation (A_{pe}) at room temperature was recorded in all samples thermally treated in the range of $600 \leq \vartheta_\beta \leq 800$ °C, Fig. 10.

However, the amount of pseudo-elasticity is determined by the microstructure condition of the alloy. In the alloy of a two-phase structure α-phase decreases the value of pseudo-elastic deformation to only 4% whereas mono-phase β-alloy shows a significantly higher pseudo-elasticity, which amounts to as much as 8.2% after treatment at ϑ_β= 800 °C which was actually expected according literature data [5] and similar results received by other researchers. Apart from pseudo-elasticity the alloy also shows pseudo-plasticity when, after unloading, a certain deformation component lags behind because of occurrence of highly deformed α_M-crystals that are transformed into austenite only by subsequent heating.

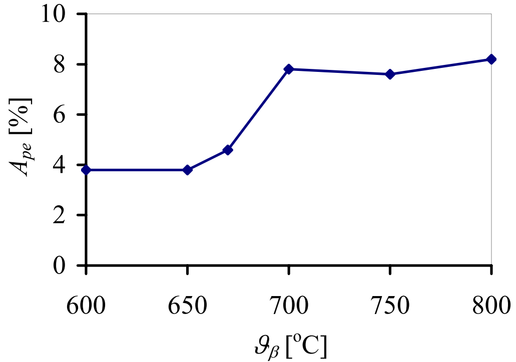


Fig. 10. *Pseudo-elastic deformation of thermally treated alloy*

The results of tensile testing, regarding the thermal treatment effect on the value of the characteristic stresses: pseudo yield stress (R_{pp}), true yield stress (R_p) and tensile strength (R_m) are presented in Fig. 11.

There is an obvious reduction of pseudo yield stress, true yield stress and tensile strength as the temperature approaches 700 °C. In the alloy betatised at $\vartheta \geq 700$ °C the martensitic transformation is mechanically induced at lower stresses due to an easier movement of β/α_M transformational interface in the absence of α-phase precipitate, which as a rule hinder the movement of the transformational front which completely fits results in [6], where non coherent precipitates were found as the reason for irreversibility because of their negative effect on $\beta \leftrightarrow \alpha_M$ transformation. The mechanically induced $\beta \rightarrow \alpha_M$ transformation is certainly also affected by the change in the chemical composition of the β-phase. If the driving force necessary for the transformation is considered, then the flow of pseudo yield stress relevant for mechanical martensitic transformation fully corresponds to the flow of transformational temperatures in case of thermal transformation.

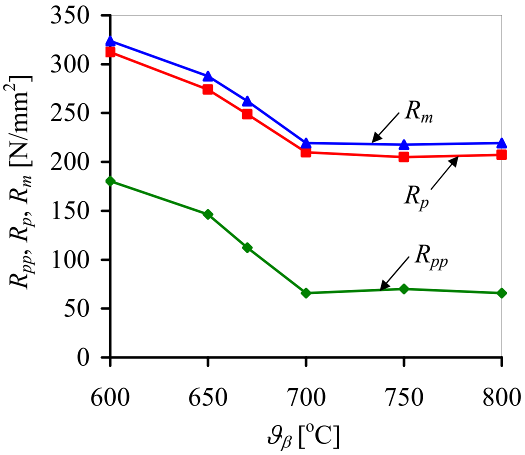


Fig. 11. *R_{pp}, R_p, R_m depending on betatisation temperature*

The same change of pseudo yield stress is followed also by other stresses: true yield stress and tensile strength. Higher mechanical resistance of the alloy treated at lower temperatures is the consequence of an interactive action of several factors. The strength of a two-phase structure that apart from α-phase also contains mechanically-induced martensite, is determined, among other things, by the hardness of structural constituents, their share, distribution and size. Since the hardness of martensite depends on the hardness of austenite, and at lower betatisation temperatures, austenite is somewhat harder, the alloy also shows higher mechanical resistance additionally contributed by reinforced precipitation processes i.e. numerous boundaries of anti-phase areas as well as the formation of sub-boundaries within austenitic crystals.

3 CONCLUSION

1. Betatisation treatment of shape memory CuZn27Al3 alloy has to be performed between the melting temperature and the temperature of ϑ_β = 680°C, so that subsequent quenching would result in mono-phase austenitic structure.
2. Independent of the betatisation temperature within the range of $600 \leq \vartheta_\beta \leq 800$ °C the alloy has the ability of austenitic martensitic reversible transformability. However, transformational temperatures that define the thermal transformational behaviour depend on the amount of the betatisation temperature, particularly if $\vartheta_\beta < 700$ °C. Betatisation treatment at lower temperatures significantly influences the reduction of all transformation temperatures.
3. Martensitic transformation can also be induced mechanically by the action of external stress (stress - induced martensite) or plastic deformation (deformation - induced martensite) at temperature higher than M_s and lower than M_d.
4. Apart from elastic and plastic deformations, the alloy thermally treated in the temperature range $600 \leq \vartheta_\beta \leq 800$ °C also expresses pseudo-deformation in the form of pseudo-elastic and pseudo-plastic deformation components.
5. By reducing the temperature of betatisation the heating the mechanical resistance of the alloy increases, but at the same time its pseudo-elastic deformation decreases from 8.2% (ϑ_β = 800 °C) to only 4% (ϑ_β = 600 °C).

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