BEHAVIOUR OF THERMO-MECHANICALLY TREATED CuZnAl-SMA

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Hot rolling of CuZn27Al4 shape memory alloy results in the forming of defects in austenitic crystals. The defects such as dislocation and deformed boundaries of austenitic grains affect both "classical" material properties and the specific properties related to shape memory. Rolled and quenched alloy (ausforming treatment) shows hardening proportional to the value of introduced deformation. By increasing the level of true plastic deformation not only the yield stress and tensile strength are increased but also the pseudo yield stress thus making the mechanically induced martensitic transformation more difficult. Besides, the ausforming treatment reduces all the transformation temperatures of the austenitic-martensitic reaction, thus expanding the temperature field of pseudo-elasticity. In spite of the hardening, the thermo-mechanically treated CuZn27Al4 alloy retains the pseudo-elastic shape memory so that favourable combination of strength and transformation behaviour can be achieved by the ausforming treatment, which is required in the majority of applications of these alloys.

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

Ponašanje termomehanički obrađene CuZnAl-SEPO

Toplo valjanje CuZn27Al4 slitine s efektom prisjetljivosti oblika rezultira formiranjem defekata u austenitnim kristalima. Defekti kao što su dislokacije i deformirane granice austenitnih zrna utječu kako na "klasična" svojstva materijala tako i na specifična svojstva vezana uz prisjetljivost oblika. Valjana i gašena legura (ausforming obrada) pokazuje očvrsnuće proporcionalno iznosu uvedene deformacije. Porastom stupnja stvarne plastične deformacije povećava se ne samo granica razvlačenja i rastezna čvrstoća već i pseudo granica razvlačenja čime se otežava mehanički inducirana martenzitna transformacija. Osim toga, ausforming obrada snižava sve transformacijske temperature austenitno-martenzitne reakcije i time se proširuje temperaturno područje pseudo-elastčnosti. Usprkos očvrsnuću, termomehanički obrađena CuZn27Al4 legura zadržava pseudo-elastičnu prisjetljivost oblika tako da se ausformingom može ostvariti povoljna kombinacija čvrstoće i transformacijskog ponašanja, što se zahtijeva u većini primjena ovih slitina.

Ključne riječi: ausforming obrada, CuZnAl legura, mehanička svojstva, prisjetljivost oblika, transformacijske temperature

1
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 therefore been used already for about 3500 years. However, in case of steel the transformation is irreversible [1].

Reversible martensitic transformation that occurs 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 [5].

The properties of SMA materials, as well as all the other materials, are substantially determined by the existence of the defects in the crystal structure, among which an especially important role belongs to dislocations. During the martensitic transformation, the dislocations that exist in the structure of the high-temperature austenitic phase interact with the mobile β/α_M interface, which can facilitate or prevent its movement and thus affect the martenisitic ($\beta\rightarrow\alpha_M$) i.e. austenitic ($\alpha_M\rightarrow\beta$) transformation. Besides, the dislocations affect also the "classical" properties of materials such as: tensile strength, yield stress and hardness. One of the ways of introducing the dislocations into the crystal structure is certainly shaping by plastic deformation. Deformation can be carried out at the ambient temperature and reduced or raised temperature. Regarding the temperature of the thermo-mechanical treatment in SMA materials, three temperature ranges can be distinguished [6, 7, 8]:

I) $\vartheta_I \geq M_d$ (M_d – the highest temperature at which mechanically induced martensitic transformation occurs): stable austenite range;

II) $M_f < \vartheta_{II} < M_d$: transformable austenite ($\beta\rightarrow\alpha_M$);

III) $\vartheta_{III} < M_f$: fully transformed martensitic structure; Deforming below M_f temperature leads to the reorientation of the thermally induced martensitic crystals.

Additionally in range II one of the following reactions may occur:

IIa) $A_f << \vartheta_{IIa} < M_d$: austenite $\rightarrow$ plastic deformation induced martensite; Martensitic crystals are

mechanically induced from the previously plastic deformed austenite.

IIb) $M_s < \vartheta_{IIb} < \vartheta_{IIa}$: austenite $\rightarrow$ stress induced martensite; Martensitic transformation is not preceded by actual plastic deformation of austenitic crystals. $\beta \rightarrow \alpha_M$ transformation occurs at stress R_{pp} (pseudo yield stress) lower than the conventional yield stress [3].

IIc) $M_f < \vartheta_{IIc} < M_s$: transformation and reorientation in the already partially transformed structure; The deformation of two-phase austenitic martensitic structure produces mechanically induced oriented martensitic crystals with simultaneous reorientation of thermally induced martensite.

Regarding the temperature of the thermo-mechanical treatment this paper focuses primarily on the area of stable austenite where the following conditions may be distinguished:

Ia) disordered monophase austenitic structure β-solid solution with lattice A2;

Ib) ordered monophase austenite – intermetal compound with lattice B2, DO_3;

Ic) multiphase structure that apart from austenite contains α-phase or precipitates of intermetal phase γ.

The purpose of the paper is to study the behaviour of the thermo-mechanically treated alloy, its transformability and total mechanical resistance in order to determine the possibilities and restrictions in the applied treatment so as to improve the exploitation characteristics of SMA materials. Although the majority of applications require martensitic transformability in combination with high strength, there are very few systemic studies regarding the structure of interrelations.

2
Alloy composition and thermo-mechanical treatment

Semi-products of the studied Cu-shape memory 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 the 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 [9]. For experimental study the three-component copper alloy of the following composition was selected: Cu 69,63 % mass, Zn 26,52 % mass, Al 3,85 % mass. The content of copper and zinc has been determined electro-gravimetrically, 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.

After casting, the specimens undergo thermo-mechanical treatment known as ausforming treatment, by analogy to the procedure of obtaining high-strength steels, Fig. 1.
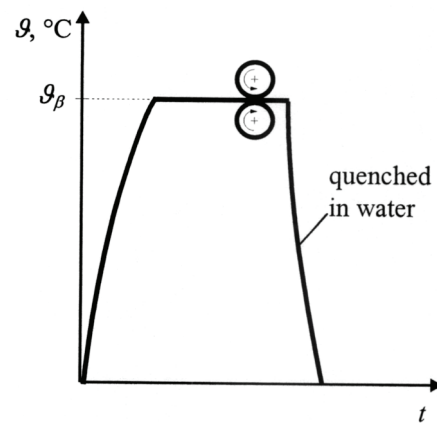

Figure 1 Schematic presentation of the ausforming treatment

Ausforming treatment includes the following phases:
1) heating to ausforming treatment temperature, $\vartheta_\beta = 800\ °C$;
2) rolling at this temperature with various deformation amounts in one pass;
3) quenching of deformed pieces immediately after rolling.

The homogenization treatment of SMA material within the range of disordered reversibly transformable austenite structure is generally known as betatisation [7]. The values of plastic deformation introduced by hot rolling expressed in the form of true deformation φ_g were varied in a wide range from 0,25 mm/mm to 1,54 mm/mm. After betatisation and hot rolling the material is cooled at super-critical rate in water (quenched) in order to avoid undesirable transformations in the solid state (massive, eutectoid, bainitic reaction, precipitation) that change the homogeneous structure of β-phase. Furthermore, quenching disables the processes such as recovery or recrystallization thus preventing the elimination of deformation-introduced defects [10].

3
Experimental procedures

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 analysis using light microscopy was used to study the effects of thermo-mechanical treatment on the micro-structural condition of the alloy. After cutting, grinding, pre-polishing, final polishing, the specimens were electro-etched in the D2 electrolyte 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. The electro-etching was performed at the voltage of 6 V and amperage of 80 mA. The specimens were electro-etched in the time interval of 30 s.

The DSC method represents the most direct method of analysing the reversible martensitic transformation and is especially suitable for precise determination of the temperatures of the initial and final phase transformations as well as for determining the extremes (peaks) of endothermic and exothermic processes. The method is

based on the measuring of heat absorbed or conveyed by a small sample of material during heating and cooling within the transformational temperature range. The temperatures of martensitic transformation (M_s, M_m, M_f) that is, austenitic transformation (A_s, A_m, A_f) have been determined for the first thermal cycle. M_m and A_m represent temperatures of thermal flow peaks during cooling and heating. These peaks are marked by the maximum speed of the martensitic and austenitic reaction, respectively. The values of characteristic temperatures M_s, M_f, A_s, A_f have been determined by the method of tangents on the base line and the peak curve in the DSC thermogram. The 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 cooling/heating speed of 5 °C/min.

Furthermore, tensile testing at ambient temperature determines the mechanical properties of thermo-mechanically treated alloy including also the 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);
- tensile strength (R_m).

Pseudo yield stress is the stress value at which stress-induced austenite→martensite transformation with pseudo-elastic deformation of materials starts. The true yield stress, like other conventional materials, characterises the appearance of plastic deformation, in our case the plastic deformation of martensite. The tensile strength is the stress value at maximal load during tensile test. The process of testing the pseudo-elastic effect is similar to the 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.

4
Experimental results

Fig. 2 shows the effect of plastic deformation by hot rolling on microstructure of CuZn27Al4 alloy.

Small and medium amount of true plastic deformation results in curling of the austenite grain boundaries (Fig. 2a, 2b). The beginning of formation of α-phase takes place at the grain boundaries. α-crystal mixes have, the same as copper, face-centred cubic lattice (FCC). β-crystals are intermetallic compounds with body-centred cubic lattice (BCC). At room temperature the β-phase structure is ordered, but at elevated temperatures it becomes disordered. With more plastic deformation the shape of crystal changes correspondingly. Greater amount of deformation brings also more nucleation of α-phase at grain boundaries (Fig. 2c, 2d).

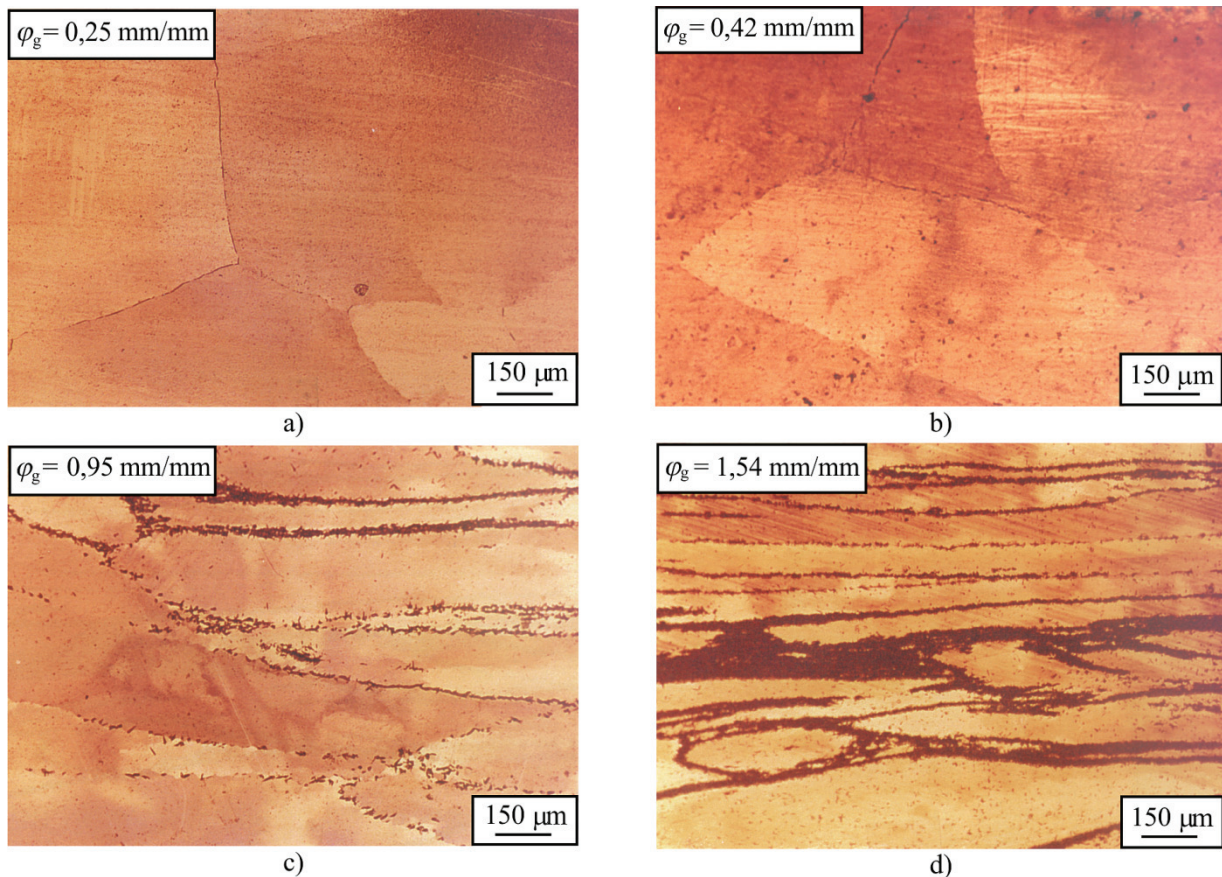Fig. 3 shows the characteristic curves of the thermal flow recorded by DSC analysis.

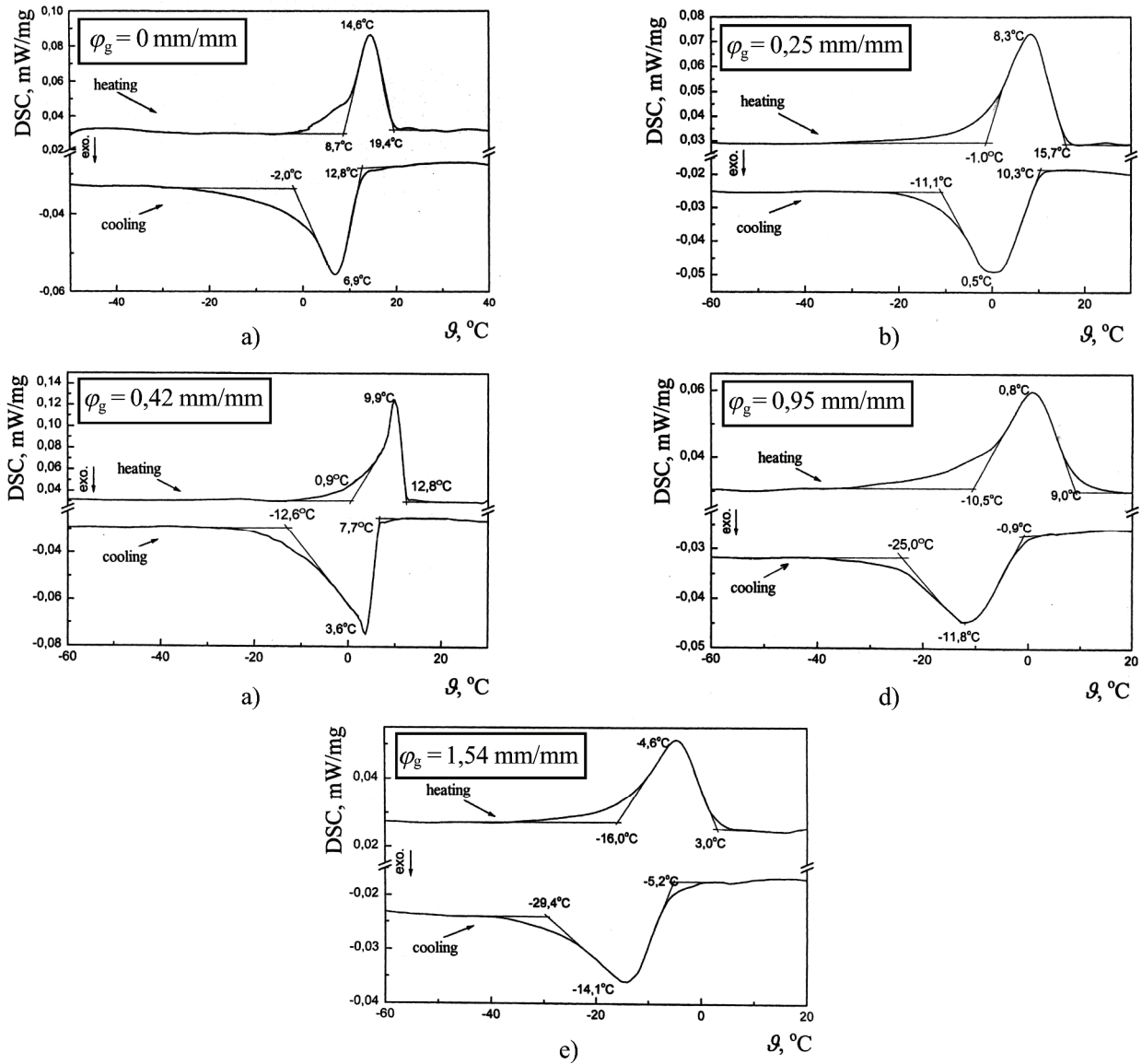**Figure 2** Microstructure of thermo-mechanically treated alloy

Figure 3 DSC transformation cycles of thermo-mechanically treated alloy

The peaks of thermal flow of martensitic and austenitic transformation during cooling and heating are clearly noticeable. With the increase in true plastic deformation both transformation processes move to the range of smaller temperatures. Based on the position of transformation peaks the values of characteristic temperatures are determined: M_s, M_m, M_f, A_s, A_m, A_f, Tab. 1.

Table 1 Values of transformation temperatures of thermo-mechanically treated alloy

φ_g / mm/mm	M_s / °C	M_m / °C	M_f / °C	A_s / °C	A_m / °C	A_f / °C
0	12,8	6,9	−2,0	8,7	14,6	19,4
0,25	10,3	0,5	−11,1	−1,0	8,3	15,7
0,42	7,7	3,6	−12,6	0,9	9,9	12,8
0,95	−0,9	−11,8	−25,0	−10,5	0,8	9,0
1,54	−5,2	−14,1	−29,4	−16,0	−4,6	3,0

All transformation temperatures are lower than the room temperature and the alloy shows pseudo-elastic behaviour or pseudo-plasticity (one-way effect) if martensite is induced at room temperature, which is stable when the stress is removed, and by subsequent heating is transformed into austenite [11].

Fig. 4 presents the position of transformation temperatures M_s, M_f, A_s and A_f for different thermo-mechanically treated conditions.
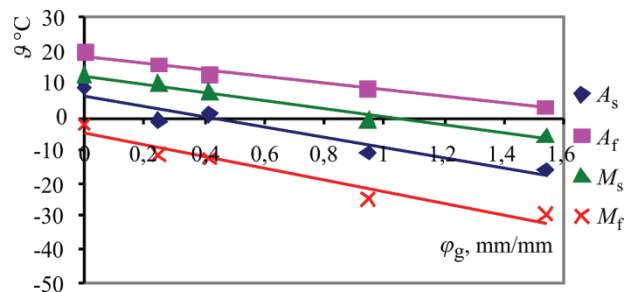

Figure 4 Transformation temperatures as a function of true plastic deformation

The diagram in Fig. 4 shows that the alloy is fully transformable for all the regimes of thermo-mechanical treatment, but at greater deformations the transformation reactions occur at lower and lower temperatures.

The analysis of mechanical properties indicates the change of mechanical resistance of the thermo-

mechanically treated alloy. Fig. 5 presents σ - ε diagrams of tensile testing until fracture, and Figure 6 pseudo-elastic behaviour of the alloy for different amounts of true plastic deformation. All diagrams have been recorded for the first cycle of mechanical loading.
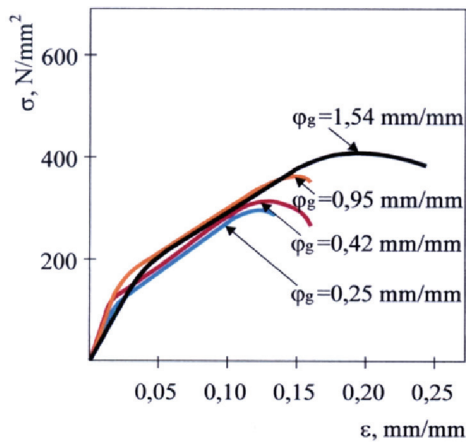

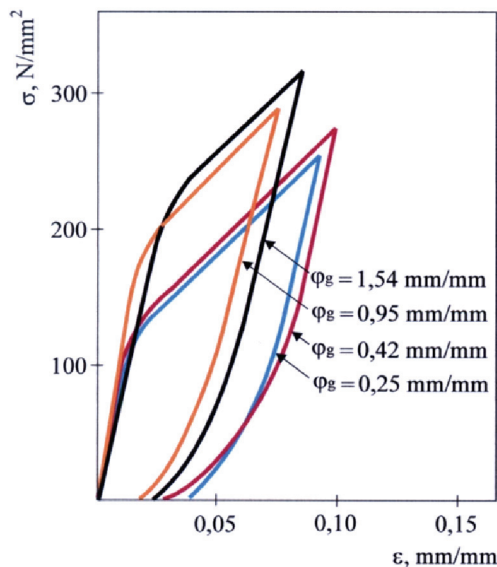**Figure 5** σ - ε diagrams of tensile testing

Figure 6 σ - ε diagrams of pseudo-elastic effect

The results of tensile testing, regarding the thermo-mechanical 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. 7.
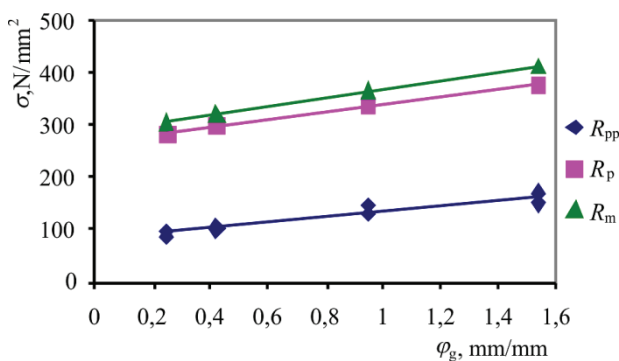

Figure 7 R_{pp}, R_p and R_m as a function of true plastic deformation

5
Discussion and conclusion

Transformation behaviour of CuZn27Al4 alloy rests on high-temperature austenite structure which is characterized by the reversible transformability into low-temperature martensitic structure. Therefore, after the homogenisation treatment in the range of austenite, the alloy needs to be supracritically quenched in order to keep the β-phase all the way to the room temperature. Austenitic microstructure can be modified by hot rolling procedure at the betatisation temperature. The rolling results in the extension of the β-crystal and occurrence of deformed grain boundaries with intensified precipitation processes marked by the formation of α-phase at the boundaries of β-grains, as well as within the grains. Besides, in the β-phase the density of dislocations significantly increases.

DSC testing provides evidence of cooling-induced martensitic transformation and heating-stimulated reverse austenitic transformation. Thermally induced crystallographic reversible β↔α$_M$ transformation occurs in all the ausforming-treated conditions independent on the level of deformation and the density of the introduced defects. 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, and for 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 equal or higher than A_f. Austenitic reaction during heating occurs within the narrower temperature range compared to the martensitic reaction during cooling. With the increase of the deformation amount both transformation reactions move to the range of lower temperatures. M_m and A_m temperatures vary within the range of 6,9 °C (φ_g = 0 mm/mm) to –14,1 °C (φ_g = 1,54 mm/mm) and from 14,6 °C (φ_g = 0 mm/mm) to –4,6 °C (φ_g = 1,54 mm/mm). The relation between true plastic deformation φ_g and M_s and other transformation temperatures is approximately linear. The reduction of transformation temperatures results from increased density of defects in β-crystals and more difficult motion of β/α$_M$-transformational interface.

Furthermore, the properties of material defined by tensile testing also indicate the presence of martensitic transformation although not thermally but mechanically induced. By increasing the deformation amount, the martensitic transformation starts at higher stresses. The change of the pseudo yield stress which marks the moving force for the mechanically-induced martensitic transformation corresponds fully to the flow of the transformation temperatures in case of thermally-induced β→α$_M$ transformation. The same change of pseudo yield

stress is followed also by other stresses: true yield stress and tensile strength and it is obvious that higher values of deformation result in the increase of the mechanical resistance of alloy. Despite the strengthening the alloy has remained pseudo-elastic. The occurrence of pseudo-elasticity at room temperature was recorded in all thermo-mechanically treated samples. Apart from pseudo-elasticity the alloy shows also pseudo-plasticity when, after unloading, a certain deformation component lags behind because of the occurrence of highly deformed α_M-crystals that are transformed into austenite only by subsequent heating.

The results of the performed research indicate that by adequate thermo-mechanical treatment it is possible to realize a favourable combination of strength and transformation behaviour, which is required in the majority of applications of the pseudo-elastic effect with simultaneous increase in the alloy resistance to fatigue.

6
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