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Heterogeneity of mechanical properties and fractures of Co-based metallic glass in a low-temperature thermal activation process

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ABSTRACT

Purpose: The paper presents the changes of mechanical properties and the fractures of $Co_{70.5}Fe_{2.5}Mn_2Mo_1Si_9B_{15}$ metallic glass ribbons after a low-temperature activation process.

Design/methodology/approach: The studied alloy was fabricated by continuous casting of the alloy stream on a turning wheel. The plastic properties were determined using the bend test. The investigations of unit cracking energy using the "tearing" test on the testing machine were carried out. The structure testing in transmission electron microscope and the static tensile test on the Instron testing machine were also carried out.

Findings: The studies for 5 samples and for 2 ribbon sides were carried out. The highest plasticity occurred after annealing at 200°C for 1 h. The differences of mechanical properties in a function of a cross section of the ribbon were also presented.

Practical implications: Despite the occurrence of heterogeneity of properties on the thickness of metallic glass ribbon the essential meaning have the averaging properties of a product which decided about possibility of practical application.

Originality/value: In the article there was found that studied samples obtain different plasticity and different value of the yield point in the different bending methods.

Keywords: Amorphous materials; Thermal activation; Plasticity; Yield Point

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MATERIALS

1. Introduction

The metallic glasses are achieved from alloys with a specific chemical composition of elements which allowed to obtain materials by casting methods of liquid alloy in the turning cooling surface which caused fast solidification of thin metal layer. Such materials are characterized by non-crystalline structure and exhibit an unconventional physical and chemical properties [1,2].

Depending on the chemical composition the majority of metallic glasses have significant plasticity making possible deformation under strongly concentrated compressive stresses, which in consequence lead to a low plasticity in a macroscopic scale [3]. These fractures have been described as "vein" system formed by convexities created by local contractions. The researches suggest that this type of cracks is caused by adiabatic heating generated by plastic flow, what leads to a local deformation as a result of which the sample cracks and leaves a "vein" system. The obtained cracks system is treated as a result of separation of the liquid layer between two solid surfaces. That also leads to reduction of viscosity inside this volume to the typical state for the fluid. In both models, an important role plays violent softening of the solid [3]. In another theory of the pseudo-distributing model the cracks are propagated from the nucleation site to the place where other magnifying cracks occur. In this way they create pseudo-distribution zone in surroundings of the main "vein" of the fracture area. The occurrence of the pseudo-distribution model is largely dependent on the manner in which the sample was macroscopically deformed. Lack of the "vein" system indicates that in order to fabricate the pseudo-distribution crack, the internal stresses must allow to formation of specified shear slip surfaces [3]. It was found that metallic glasses are inclined to brittleness and sensitive to cooling conditions. Many of metallic glasses, ductile in "as quenched" state, become brittle after annealing at low temperatures, due to the processes of the structure relaxation. Overall, the metallic glasses are treated as a ductile materials, what distinguish them from the group of brittle oxide glasses. The deformation in ductile materials locating in the shear bands leads to changes of the load on the section causing a characteristic course of fracture in this way [4]. For metallic glasses it was found that above a certain high values of stresses can be observed no significant deviations from the linear course of tensile curve; decohesion occurs at a value dependent on the state of a structure relaxation. Then a pseudo-elastic deformation occurs, which is reversible after elimination of the load. The pseudo-elastic property is assigned for a local no significant changes of atoms orientation in stress conditions functioning. Depending on the relaxation level the "veins" which can be observed on the fracture have diversified concentration and configuration [4]. With decreasing plasticity of metallic glasses the fractures take a "fine-vein", "scaly" and then almost "flat" nature after the brittle state obtainment [5-7]. In the transition metal-based alloys the brittleness occurs already during the short time of annealing at temperatures below the crystallization temperature [6-8].

The metallic glasses are metastable materials, and therefore their properties change both during ageing at room temperature and annealing at temperature considerably below the crystallization temperature, what is associated with the phenomenon of the amorphous structure relaxation [9-11]. During the low-temperature annealing many changes of physical properties occur including density, specific heat, viscosity, stress relaxation, electrical resistance, internal friction, and above all fall of the plasticity [12,13]. It was also found that the physical properties of metallic glass and glass relaxation processes course can be different depending on the casting conditions and thickness of the cast ribbon what is undoubtedly connected with the cooling rates and advancement of the relaxation processes at the fabrication stage of metallic glass [11].

2. Research methodology

The studied alloy with amorphous structure was fabricated by continuous casting of the alloy stream on the surface of the turning wheel. The investigations were carried out on the metallic glass ribbons with the chemical composition: $Co_{70.5}Fe_{2.5}Mn_2Mo_1Si_9B_{15}$, thickness of 0.038 mm and width of 10.2 mm. The ribbons sections were annealed for 1 hour at a temperature range from 100°C to 400°C with 50°C increments.

The studies of plasticity were carried out for 5 samples in "as quenched" state and after annealing. The length of the samples was 120 mm. The studies were carried out for 2 sides of the ribbon: for the ribbon side that has not contact with the wheel (glossy side) and for the surface adhering to the cooling wheel during ribbon casting directed outside of the bending loop (matt side).

The plastic properties of the studied material were determined using the bend test, applied for metallic glasses. In this method the sample was bent in measuring jaws up to durable rise of maximum deformation or to a crack creation. The plasticity deformation equalled to yield stress was calculated from the expression:

$$\varepsilon = \frac{g}{D-g} \quad (1)$$

where:
g – ribbon thickness,
D – distance between jaws at which plastic durable deformation follows or fracture.

The value of yield point was determined by using the spring-back method based on the methodology described in [7]. The sample was bent into "U"- like shape squeezed between the jaws of the slide caliper for a given distance (D) of 0.4-0.7 mm in order to obtain the plastic deformation of the ribbon. After the jaws were opened the plastic deformation of the ribbon by measurement of a spring-back angle (α) value was evaluated (Fig. 1).

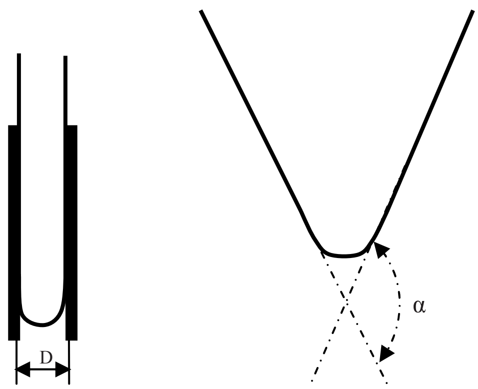

Fig. 1. Illustration of the yield point measurement of metallic glasses by the spring-back method

After determination of the angle α at the predetermined distance (D), the yield point (σ_y) was determined from the relationship [14]:

$$(1-\alpha/180°)\ t/D = [1{,}5\ (\sigma_y / E) - 0{,}5\ (\sigma_y / E)^3\ ]\ (D / t)^2 \quad (2)$$

where:
E – Young's modulus (for the studied alloy was accepted E = 110 GPa),
t – ribbon thickness,
σ_y – yield point,
D – distance between the jaws, at which a permanent deformation occurs.

The yield point using DRIVER computer program was calculated.

After annealing at 350°C and 400°C, the samples were too brittle, they cracked with minimal deformation and therefore it was not possible to determine the yield point.

The studies of unit cracking energy (C_e) of amorphous ribbons were carried out using the "tearing" test on the testing machine. The strength registration during tearing makes possible determination of unit cracking energy on the basis of formula:

$$C_e = \frac{E}{l \cdot g} \qquad E = F \cdot 2 \cdot l$$
$$C_e = \frac{2 \cdot F}{g} \quad (3)$$

where:
E – energy used to crack propagation,
F – tearing force,
g – ribbon thickness,
l – length of the crack.

The static tensile test was carried out on the Instron testing machine 1295 type (10 samples for each state). The speed of the tension was 5 mm/minute. In order to eliminate the influence of the micro-unevenness of the ribbon edges on the results of studies, the length of the measuring sample (50 mm) were cut from each side edges of the ribbon to give a sample with width of 6 mm.

The fractures obtained in the tensile test have been studied in a scanning electron microscope DSM 940 type of the "Opton" firm. The studies of structure were performed on thin foils by the transmission electron microscopy method (Tesla BS 540).

3. Results and discussion

The structure of $Co_{70.5}Fe_{2.5}Mn_2Mo_1Si_9B_{15}$ metallic glass is totally amorphous in "as quenched" state. The alloy in this condition has a high plastic properties (ε = 1) apart from a study method. The structure testing in a transmission electron microscope shown amorphous structure (Fig. 2). The strength samples show ductile "vein" fracture and locally "scaly" (Fig. 3).

The highest plasticity ensuring the possibility of a bend to a contact with the ribbon surface without cracks formation (ε =1) occurs after annealing at 200°C for 1 h apart from a method of the study. For the samples held at a temperature of 250°C and higher different plasticity of ribbons apart from a method of the identified study (Table 1, Fig. 4).

In a tensile test for condition after annealing at 250°C/1 h there was found that the fracture about diversified morphology on the ribbon thickness occurs. The "thick-scaly" fracture with "fine-vein" on the surface of the scales occurs from one side and "fine-scaly" fracture occurs from the other side (Fig. 5). That confirms the occurrence of areas about changing plasticity on the ribbon thickness.

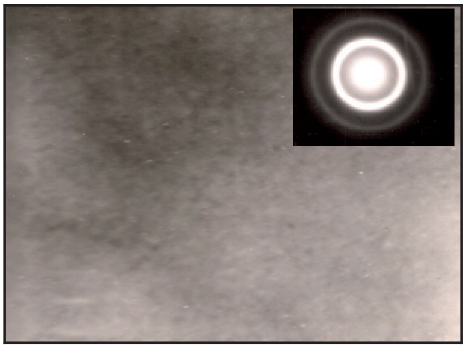

Fig. 2. The structure of the alloy in "as quenched" state. Amorphous structure with the characteristic contrast, thin foil, 52 000 x

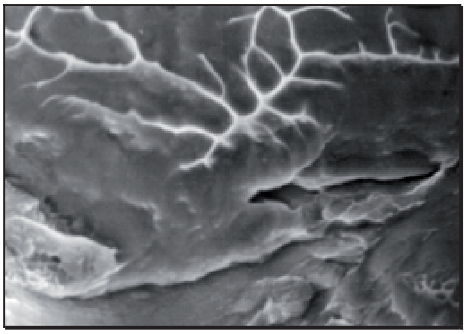

Fig. 3. The structure of the sample fracture in "as quenched" state. "Vein" fracture and a local area with "scaly" morphology

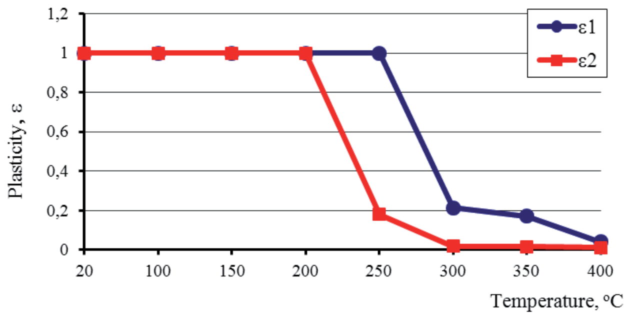

Fig. 4. Influence of annealing temperature of $Co_{70.5}Fe_{2.5}Mn_{2.5}Mo_1Si_9B_{15}$ metallic glass on the changes of plasticity (ε): 1) for the surface of the ribbon that has not contact with the wheel ($\varepsilon 1$), 2) for the surface of the ribbon adhering to the cooling wheel ($\varepsilon 2$)

Table 1.
Results of plasticity studies of $Co_{70.5}Fe_{2.5}Mn_{2.5}Mo_1Si_9B_{15}$ alloy in a condition after annealing for 1 h in a range up to 400°C

Temperature of annealing, °C	Plasticity, ε for the samples studied at the side that has not contact with the wheel	Plasticity, ε for the samples studied at the side that has contact with the wheel
"as quenched" state	1	1
100	1	1
150	1	1
200	1	1
250	1	0.18
300	0.214	0.019
350	0.172	0.015
400	0.041	0.011

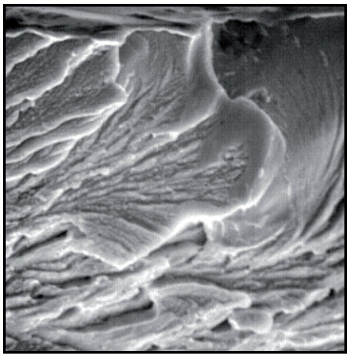

Fig. 5. The structure of the sample fracture after annealing at 250°C/h. On the ribbon thickness "thick-scaly" fracture with not large quantity of small "vein" (about higher plasticity) undergoes in "fine-scaly" is visible, SEM, 3 000 x

Such changes are caused by metallic glass properties obtained in the structural relaxation process. It proceeds for studied metallic glass in a diversified manner depending on the cooling conditions which occurred in a casting process of the ribbon.

It should be expected that the ribbon surface adhering to the wheel during a casting process is relaxed lesser in "as quenched" state than the freely solidifying side. The different properties of the ribbon in the higher temperatures range of 300-350°C were identified. For studies carried out on the ribbon side that has not contact with the wheel during the test much higher plasticity in comparison with the ribbon side adhering to the wheel was found. For example at 300°C, ε value totals 0.214 and

0.019 depending on a study method. The fracture for the sample held at a higher temperature of 350°C still shows a diversified morphology on the ribbon thickness (Fig. 6). The ribbon side that has not contact with the wheel shows the higher plasticity. The samples held at a temperature of 400°C are already very brittle apart from a study method. The fracture does not show significant differences on the ribbon thickness (Fig. 7).

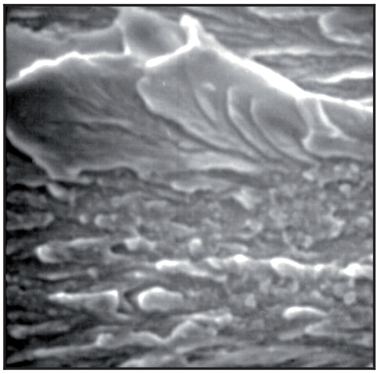

Fig. 6. The structure of the sample fracture after annealing at 350°C/1h. On the ribbon thickness areas of transition of "thick-scaly" fracture in area about small expansion of lumpy surface are visible, SEM, 3 000 x

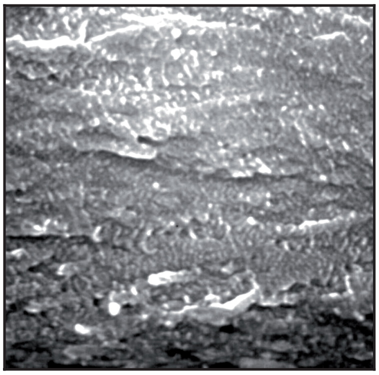

Fig. 7. The structure of the fracture of the brittle alloy sample held at a temperature of 400°C/1h. On the sample thickness the fracture is homogeneous with not large unevenness of surface, SEM, 5 000 x

The obtained results indicate that the process of ribbon fabrication and decreasing cooling rates obtained in a gradient of the ribbon thickness connected with a heat flow to the cooling surface also in the total vitrification condition have an effect on relaxation processes during annealing which affect mechanical properties.

In the further part of studies the tests of yield point by the spring-back method determination for the ribbons deformed after annealing at 300°C were carried out for confirmation of those changes. The testing in the higher temperatures was not possible because the material was too brittle. The results of yield point calculation were presented in Table 2 and in Figure 8.

Table 2.
The yield point σ_y determined by the spring-back method

Temperature of annealing, °C	The yield point σ_y, MPa; for the samples studied at the side that has not contact with the wheel	The yield point σ_y, MPa; for the samples studied at the side that has contact with the wheel
"as quenched"	912	998
100	1006	1298
150	1090	1386
200	1121	1380
250	1215	1305
300	902	1195

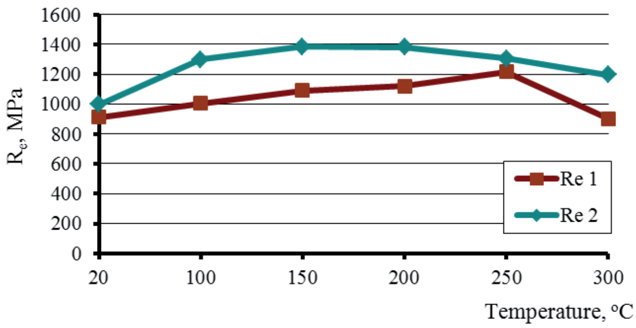

Fig. 8. Influence of annealing temperature on the changes of the yield point σ_y determined in the spring-back test: 1) R_e 1; for the freely solidifying surface of the ribbon directed outside of a bending loop; 2) R_e 2; for the surface of the ribbon adhering to the cooling wheel directed outside of a bending loop

The yield point of studied alloy for samples tested at the side that has not contact with the wheel in condition just after casting totals 912 MPa. For the samples adhering to the wheel directed outside of a bending loop the yield point is about 10 % higher and totals 998 MPa. The fact is that in "as quenched" state the changes of strength properties occur on the ribbon thickness.

The general tendency showing that the higher yield point have the samples which were bent in a manner that tensile stresses occur at the faster-cooled side – adhering to the surface of a cooling wheel in the casting process. This tendency is kept at a constant level in a whole range of study of an influence of annealing temperature on the changes of σ_y. The annealing at temperature of 100°C causes increase of yield point, σ_y were 1006 and 1298 MPa for two tests, adequately. Further annealing in temperature range up to 200°C causes not large increase of σ_y value. After annealing at 200°C the changes for samples which were bent at the side that has not contact with the wheel were observed, the yield point grows up to 1215 MPa. While for samples studied at the side adhering to the wheel directed outside of a bending loop decrease of the yield point (σ_y) to 1305 MPa was observed. The annealing of the samples at 300°C causes decrease of σ_y up to 902 and 1195 MPa (Fig. 8, Table 2). The presented results of investigations show that the higher yield point and possibilities of obtainment the higher elastic strains connected with it occur at the side of the ribbon which adheres to the surface carrying off the heat in the casting process. While compressive stresses occur at the opposite side. This kind of strain makes possible obtainment of different permanent plastic strain without crack of the sample what is impossible in the tensile test from the practical point of view.

The tensile strength tests in the earlier results presented only averaging material properties and showed the general tendencies of changes which occurred in the metallic glass as a result of relaxation and crystallization processes. The determination of the unit cracking energy in a "tearing" test does not give a possibility of distinction of an influence of heterogeneity of properties at the section of the ribbon on the results of measurements. This is because of the ribbon is simultaneously torn from the freely solidifying side and from the side of surface adhering to the wheel in the casting process.

The obtained results of analysis of the influence of annealing temperature on the changes of tensile strength and unit cracking energy were presented in Table 3 and in Figure 9.

The different methodology used for determination of σ_y and strength does not give the comparable results in the range of stresses level. Generally, the strength of investigated samples is higher. The visible differences are connected with different condition and stress pattern in the bent and stretched sample. In the plastic material the results of tensile strength measurement are higher from calculated σ_y values. For metallic glasses the yield point level should quickly lead to activation of mechanisms of plastic strain and decohesion of the sample during the tension. This phenomenon does not occur at the sample bending where obtainment of intermediate conditions of different macroscopic plastic strain is possible.

Table 3.
The strength of the samples and the cracking energy of $Co_{70.5}Fe_{2.5}Mn_{2.5}Mo_1Si_9B_{15}$ alloy

Temperature of annealing, °C	Tensile strength, R_m, MPa	Cracking energy Unit cracking energy, kJ/m^2
"as quenched"	1772	54.3
100	1999	59.8
150	2023	52.9
200	1872	54.6
250	1937	45.2
300	1620	too brittle
350	1764	-
400	788	-

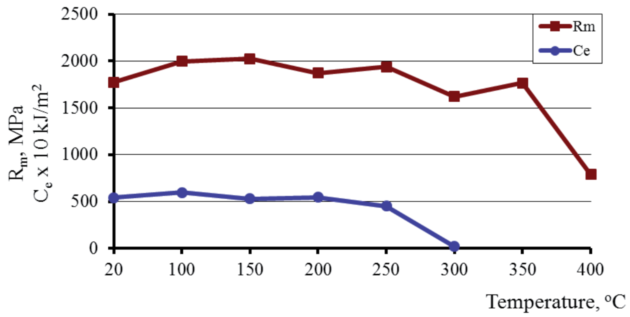

Fig. 9. The influence of annealing temperature of $Co_{70.5}Fe_{2.5}Mn_{2.5}Mo_1Si_9B_{15}$ metallic glass on the changes of strength and cracking energy of the ribbon

The tension curves do not contain the distinct part where the sample is subject to plastic strain. That should be connect with the fact that the already small plastic strain in this stress condition leads to the sample stripping in consequence.

The earlier investigations [7,8] showed that in $Co_{70.5}Fe_{2.5}Mn_2Mo_1Si_9B_{15}$ alloy in the analyzed range of temperature proceed a complex structural relaxation phenomena which lead to changes and initiation of crystallization. The influence of a decay of free volume, topological and chemical changes in the relaxation process proceeds to changes of plasticity, strength, resistivity of the alloy and the changes of magnetic properties [7,8]. In the presented elaboration the differences of mechanical properties on the section of the sample connected with the influence of vitrification phenomena of the casting process at different cooling rates occurring in the gradient of ribbon thickness were showed. These changes of mechanical properties are visible in the structure relaxation process, also.

4. Conclusions

In the study the changes of mechanical properties and fractures morphology of $Co_{70.5}Fe_{2.5}Mn_{2.5}Mo_1Si_9B_{15}$ metallic glass ribbon were analyzed. There were shown that studied samples obtain different plasticity and different value of the yield point in the different bending methods. The technological process of a casting on a turning wheel of the metallic glass ribbon causes that the heat from a liquid metal is quickly by the contact with a cooling surface only from one side carried away. Cooling of the external side of the ribbon was done by a conduction. It may be argued that in spite of a total ribbon vitrification as a result of decreasing cooling rates on the ribbon thickness there is a different degree of a structure self-relaxation.

The thermal activation of the ribbons especially in the range of structural relaxtion temperatures (up to 300°C) caused still higher diversification of plasticity ε and determined yield point (σ_y) by the spring-back method. For example, after annealing at 250°C, plasticity $\varepsilon = 1$ for the ribbon side that has not contact with the wheel, and $\varepsilon = 0.18$ when the ribbon was bent at the side adhering to the wheel. The determined yield point (σ_y) are 1215 MPa and 1305 MPa, adequately.

Determination of plasticity (ε) and yield point (σ_y) were made in the elastic-plastic range. So, obtained results of studies concern of material for which the limiting elastic, plastic load capacity state was exceed or plastic articulation was obtained.

The complex stress and strain condition in an elastic-plastic state resulted that in a bend test after structural relaxation the ribbon side that has not contact with the wheel about lower yield point had a higher plasticity (ε). That dependence shows that the ribbon side about lower yield point in the bend test earlier obtains the plastic strains as a result of tensile stresses. It ensures higher plasticity of the bent ribbons at this condition. The ribbon side which was cooled faster during the casting process, and adhered to the surface of a cooling wheel shows the higher yield point.

The analysis of the sample fractures shows that especially in a range of decreased plasticity the differences in a "scaly" fractures morphology are observed. The fracture with developed "scales" occurs from the ribbon side with higher plasticity, on the other side much more "scales" were formed. The studies of tensile strength and determination of unit cracking energy present the averaging material properties. The differences of a surface morphology related with the sample thickness were also observed.

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