Influence of thermal activation on the changes of physical properties and structure of cobalt-based metallic glass

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ABSTRACT

Purpose: In this paper the analysis of influence of heat treatment on the structure and properties of AMM type (Co_{70.5}Fe_{2.5}Mn_2MoSi_{9}B_{15}) metallic glass was shown. Moreover the discussion of the changes of tensile strength, plasticity, cracking energy, remanence, coercive force, resistivity, crystallization effect and fracture morphology of alloy in “as quenched” state and hold at the temperature range of 100-400°C for 2 hours are presented.

Design/methodology/approach: Tensile test and investigation of elementary cracking energy of amorphous ribbon carried out using the testing machine were performed. Plastic properties of examined material was studied by using of transverse bend test. Investigation of magnetic properties with annular method with 50 Hz field frequency was carried out. The alloy electrical resistivity was determined with resistance bridge. Fractography investigation after tensile test was made using scanning microscope.

Findings: The investigations showed that for the analysed heat treatment temperature range of 100-400°C significant changes of physical properties, fracture morphology and alloy structure are observed.

Research limitations/implications: Usage of metallic glasses is possible only in a narrow range of temperatures which does not lead to significant changes of properties or after proper heat treatment carried out in the aim of specified physical properties obtaining.

Practical implications: Usage of metallic glasses depending on control and regulations of alloy properties changes with proper heat treatment. It is important the prediction of alloy properties changes during temperature changes and material using.

Originality/value: In the article influence of thermal activation processes on structure changes and significant changes of mechanical and magnetic properties of cobalt-based metallic glass were presented.

Keywords: Amorphous materials; Thermal activity; Mechanical; electrical and magnetic properties; Fracture morphology

Reference to this paper should be given in the following way:
1. Introduction

Metallic glasses are produced from alloys about the suitably well-chosen chemical composition, assuring attainment of thin ribbons by the casts methods of the liquid alloy stream on moving quickly cooling base, causing ultrafast solidification of the metal layer about the small thickness. The large group of these materials particularly cobalt, iron and nickel based, in this complex alloys layer about the small thickness. The large group of these materials include different transition elements and metalloids found wide application [1,2]. This group of materials have specific magnetic, mechanical, electrical and corrosive properties [3-9].

Metallic glasses are unstable by their nature and they are susceptible to structure and properties changes under the influence of thermal activation [10-14]. The thermodynamic metastable glass structure is characterized by almost unlimited durability in the ambient temperature. Irreversible transformation leading to the final effect to the glass crystallization occurs with the growth of temperature [15]. Masumoto distinguished and described stages of the processes course proceeding during heating of amorphous alloys on the transition metals (Fe, Co, Ni) based with metalloids (Si, B) (Fig. 1) [16,17]:

I. increase of the degree of short range order in microareas, with the amorphous structure conservation,
II. precipitation from the amorphous matrix of small crystalline areas of the element of basic metal or solution based on this element (MS I - metastable stage),
III. transformation of the amorphous matrix structure in metastable crystalline phase about the complex structure (MS II - metastable stage); formation of the stable crystalline structures which quantity depends on the chemical composition of the alloy (ST stage).

Fig. 1. Schema of the glass - crystal transformation for amorphous system of metal - non-metal type; SW - exit state, I - IV - next stages, MS - metastable state [16,17]

In low temperatures, first stage of the transformation depends on the structural relaxation, which accompanies the change of the physical properties of the material; this stage tends to partly reversible [18,22].

In the moment of glass formation the frozen atomic configuration approximate to the structure of the liquid metal obtain. We can distinguish the local areas, in which is accumulated so-called excess free volume (free volume) and areas around the large local atoms concentration. The consequence of this is occurrence the local stresses in the atomic lattice. Structural relaxation in such arrangement consists in the liquidation of these stresses. This is done by cooperative large atomic groups displacement in which disappears of free volume of the system which becomes more compact. The processes of the structural relaxation are very important from the point of view of creating of more stable atomic structure [23].

The changes of properties in the relaxation process are divided because of the effects resulting from two different processes, namely TSRO (topological short range order), which describes the irreversible decrease of free volume and CSRO (chemical short range order) describing the reversible changes in the nearest surroundings of the atom [17-20].

Both types of structural changes accompanying the relaxation connected with displacement of individual atoms or the group of atoms at short distances. As a result of this, atoms position of the alloying components change or the spatial resolution improve what leads to formation of the atomic configuration about more and more smaller free enthalpy [23].

Long-lasting annealing at the temperature on the first stage causes transformation about the aging character. Its product is the metastable structure of the supersaturated solid solution based on the metallic element with a very fine dispersive crystalline precipitates (10-50 nm) [24].

At higher temperatures the irreversible crystallization process is dominant process which is realised by the nucleation and diffusive growth of crystals. The second stage of the transformation in a higher temperature is the formation of very small crystallites of the metallic element regularly distributed in the amorphous matrix. In the third stage the transformation of the amorphous matrix in crystalline phase about the complex structure occurs. In the last stage, in highest temperature, takes place a return to stable crystalline structure, proper for the material. These crystalline phases of the transformation take place in the characteristic temperature dependent on the material chemical composition. These temperatures are decreased in the case of extension of annealing time [25,26].

In many cases the use of metallic glasses is possible only in a narrow range of temperatures which does not lead to significant changes of properties. The usage of metallic glasses is also possible after a proper heat treatment to impart specific physical properties (e.g. heat treatment in a magnetic field, attainment of the nanocrystalline structure, etc.) [27-31].

2. Research methodology

The complex alloy with amorphous structure was produced by continuous casting of the alloy stream on the surface of the vibrant roll. The investigations were conducted on the metallic glass ribbons about the chemical composition: $\text{Co}_{70.5}\text{Fe}_{2}_{.5}\text{Mn}_{2}\text{Mo}_{3}\text{Si}_{15}B_{15}$, 0.03 to 0.04 mm thickness and 10.2 mm width. The ribbons sections were annealed for 2 hours at the 100 to 400°C temperature range with 50°C increments.

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

The plastic properties of the studied material were determined using the transverse bend test, in accordance with the methodology applied commonly to evaluation of amorphous materials.

The investigations of unit cracking energy of amorphous ribbons were carried out using the “tearing” test on the testing machine. The strength registration during tearing make possible determination of unit cracking energy on the basis of formula:

\[
E_f = \frac{F}{g}
\]

\[
E = F \cdot 2 \cdot l
\]

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

The resistivity of the material tested on samples with 1100 mm length with accuracy of measurement 0.001 Ω using the resistance bridge with sample powered by DC. On the basis of measurements of electrical resistance, \(\rho\) was calculated from dependence:

\[
\rho = \frac{R \cdot S}{l}
\]

where:
- \(R\) - resistance of the sample,
- \(l\) - sample length among the jumper terminal,
- \(S\) - section of the sample.

The magnetic investigations were conducted for the coiled cores from the studied ribbons which were subjected to heat treatment. The internal diameter of cores was 15 mm and external 19 mm. The cores were annealed at temperature 100 to 400°C with 50°C increments, keeping the annealing time 2 hour. Additionally the heat treatment at 350°C in the longitudinal magnetic field about intensity 937 A/m carried out. The cooling of material after annealing was carried out in still air.

The magnetic properties of AMM type metallic glasses were studied on the computer controlled system with automatic bridge RLCG. As a result of investigations the hysteresis loop and the initial magnetization curve were obtained. The residual magnetism, coercive force, maximum induction and magnetic field strength, initial and maximum magnetic permeability were determined. The investigations of magnetic properties were conducted for the magnetic field 50 Hz frequency.

The fractures obtained in the tensile test have been investigated in a scanning electron microscope DSM 940 type of the „Opton“ firm.

The thin foils were prepared to investigate of structure using TEM Tesla BS 540.

3. Results and discussion

The Co_{80}Fe_{20}Mn_{3}Mo_{1}Si_{8}B_{15} alloy in the “as quenched” state has an amorphous structure (Fig. 2). It characterizes high tensile strength 1770 MPa, high plasticity (\(\varepsilon = 1\)) and the rate of cracking energy 5.43 J/cm². The electrical resistivity of the alloy is 1.291 μΩ·m. The alloy in this state is characterized by narrow hysteresis loop, characteristic for soft magnetic materials. It has the highest value of remanence \(B_r\) which is 0.722 T and the lowest, among the studied states of the material, value of the coercive force \(H_c\) equal 0.032 A/cm. This alloy also characterizes a high magnetic permeability \(\mu_{r, max} = 170169\).

![Fig. 2. The structure of the alloy in “as quenched” state. Amorphous structure with the characteristic contrast, thin foil, 52 000 x](image)

The investigations of fracture achieved in a tensile test showed that it is ductile like „river” type, characteristic for metallic glasses about high plasticity and high ductility. However, sometimes locally decohesion area has the “flake” character. On the fracture surface there is the characteristic “vein” pattern which is the effect of local deformation and viscous flow of the material in the decohesion process (Fig. 3).

![Fig. 3. Structure of the fracture of sample in “as quenched” state. The “vein” fracture and locally area about „scale” morphology, SEM, 3000 x](image)
The alloy annealing at 100°C for 2 hours leads to a slight increase of tensile strength (1893 MPa). The alloy maintains high plasticity and high resistance on cracking. The electrical resistivity of the ribbons after annealing at this temperature did not undergo a significant change. The magnetic properties of the alloy are similar to the “as quenched” state of the material.

The fractography investigations showed that annealing at this temperature causes the fractures formation in the tensile test about partly „scale” morphology with the very small mesh of „veins” about the large density. In this state the alloy does not show significant changes of studied properties. It indicates that relaxation processes are very faintly advanced or almost do not exist. The changes of the fractures morphology may indicate that the state of the amorphous structure undergoes certain changes.

The complementary relaxation investigations conducted at 100°C with long times of annealing (up to 64 h) disclosed, that the relaxation processes in these conditions of thermal activation are more advanced. This indicates the beginning of the structural relaxation process. The investigations of the structure in the transmission electron microscope showed the occurrence of the amorphous structure.

The alloy annealing at 150 and 200°C causes the small changes of tensile strength and cracking energy in the comparison with the state after annealing at the temperature 100°C. The tensile strength is close to 1900 MPa. The investigations of stretched samples showed the occurrence of characteristic areas for „scale” fracture and areas about large thickening of small „veins” on the „scales” surface, and also locally smooth areas (Fig. 4). This fracture morphology indicates the occurrence of the relaxation phenomena leading at the later stage to the loss of high plasticity of the studied material. After annealing of the samples in this temperature range quite significant changes of magnetic properties were affirmed.

![Fig. 4. Structure of sample fracture in the state after annealing at 200°C. „Scale” fracture with smooth fracture areas, SEM, 3000 x](image)

After annealing at 150°C investigated the magnetic properties showed the considerable reduction of remanence to 0.484 T and increase of coercive force to the value 0.064 A/cm. The form of the hysteresis loop was changed significantly. The observed changes of resistivity, coercive force and remanence are the effects of the structural relaxation process at 150°C. These phenomena in particular are attributed to slight changes in the arrangement of atoms which lead to the chemical and topological changes in the short range areas. The result of this is also considerable increase of unitary power of remagnetization which is connected with the deterioration of physical conditions to the changes of magnetic domains directions under the influence of external magnetic field.

After annealing of the samples at 200°C the resistivity of the material increases to 1.347 µΩ·m. The material also shows a further decrease of remanence to 0.471 T and increase of coercive force to 0.088 A/cm. The changes of the properties of studied material annealed in 200°C they are associated with development of relaxation process of amorphous structure. Increasing of the resistivity in the comparison with “as quenched” state mainly may be caused by the loss of free volume at unchanged arrangement of atoms in the areas of short range. The phenomena of Hc growth, Br decrease and change of resistivity are mainly the effects of the changes in the arrangement of atoms in the areas of the short range in the amorphous structure. At this annealing temperature the relaxation processes about both the topological and chemical character probably occur.

The increase of annealing temperature to 250°C causes the further significant changes of observed properties, particularly decrease of plasticity and cracking energy. The material after annealing for 2 hours shows the highest strength Rm on the level 1935 MPa and simultaneously reduced plasticity (ε = 0.24). The temperature of annealing 250°C causes the insignificant increase of the resistivity to the value 1.359 µΩ·m. The cores of the material show a further deterioration of the magnetic properties what causes reduction of remanence to 0.424 T and increase of coercive force to the value 0.11 A/cm. The fractography investigations confirmed the occurrence of the „scale” fracture with small unevennesses on the fracture surface (Fig. 5). In this state the alloy has an amorphous structure on the stage of advanced structural relaxation immediately preceding crystallization.

The changes of tensile strength, plasticities, fracture morphology, cracking energy, changes of electrical resistance and magnetic properties of the alloy may be connected with the occurrence of the phenomenon of advanced structural relaxation. It consists in the topological and chemical changes in the areas of short range in amorphous phase. They are phenomena preceding crystallization of the metallic glass.

![Fig. 5. Structure of fracture after annealing at 250°C. „Scale” fracture with the large concentration of scales, SEM, 3000 x](image)

The tapes annealed at 300°C show a significant reduction of value of tensile strenght to 1187 MPa and plasticity (ε = 0.015) in
the comparison with properties obtained after annealing at lower
temperature. After annealing at this temperature there is a
significant increase of the resistivity $\rho$ to the value 1.617 $\mu\Omega\cdot m$. The
magnetic properties in this state undergo the changes because the
amorphous structure of the alloy is in advanced state of the
relaxation process. The loss of plasticity and decrease of strength
probably result from increase of internal stresses previous the
crystallization process. The fracture of the samples shows small
unevennesses of surface with “fine-scale” character and almost
smooth areas (Fig. 6). The cracking energy of the alloy is so small
that its measurement is practically impossible in the consequence of
breaking the samples during assemble in the grips of machine. After
annealing of the alloy samples at higher temperature the cracking
energy wasn’t measured because of the considerable embrittlement
of the material.

After the alloy annealing at 350 and 400°C for 2 hours there is
a significant decrease of strength with very high brittleness of the
alloy. This decrease is related to the initiation of the amorphous
matrix crystallization.

The fracture surface achieved in the tensile test has the
smooth brittle fracture character after annealing at 350°C (Fig. 7).

After annealing at 400°C slight unevennesses probably in
places of occurrence of crystallites in the amorphous matrix are
perceptible on the surface (Fig. 8).

The achievement of the annealing temperature 350°C causes
initiation of the crystallization process by creating in amorphous
matrix not many, very small spherical crystallites of $\alpha$-Co and
cobalt borides (Figs. 9, 10). The beginning of the alloy
crystallization appears in the form of sudden decrease of
resistivity to 1.341 $\mu\Omega\cdot m$. There is observed a further reduction of
remanence to 0.441 T and reduction of coercive force to the value
0.105 A/cm also.

![Fig. 6. Structure of fracture after annealing at 300°C. Mixed fracture with the part of smooth and „fine-scale” area, SEM, 3000 x](image)

![Fig. 8. Structure of sample fracture after annealing at 400°C. Fracture fragile, smooth, locally with roughness of surface, SEM, 3000 x](image)

![Fig. 7. Structure of sample fracture after annealing at 350°C. Fracture totally flat and smooth, SEM, 3500 x](image)

![Fig. 9. Structure of alloy after annealing at 350°C. In the amorphous matrix spherical crystallites Co$_3$B and very small spherical areas of the crystal nucleuses about diversified contrast, thin foil, 52 000 x](image)

![Fig. 10. Electron diffraction to Fig. 9](image)
The process of glass crystallization (Figs. 11, 12) is connected with increase of mean free path of conduction electrons, what leads to decrease of electrical resistivity, which after the alloy annealing at the temperature 400°C is 1.25 µΩ·m.

The magnetic properties of the alloy considering the blocking of magnetic domains by the areas of interfacial boundaries are further deteriorated. The remanence value decreased to 0.333 T, and coercive force increased to 0.11 A/cm. There is observed reduction of magnetic permeability $\mu_{\text{max}}$ to value 27780. It can be assumed that the change of this value is caused by that the quantity of the active pairs of atoms can be blocked in a consequence of more stable atomic structure obtainment.

For comparison of the magnetic properties the heat treatment in a longitudinal magnetic field was carried out. The material treated in these conditions at 350°C is characterized by a narrow and symmetrical hysteresis loop, similarly as in “as quenched” state, and it has also a very high magnetic permeability about the value $\mu_{\text{max}} = 344810$ - the best obtained for the investigated alloy.

The detailed results of magnetic properties investigations are shown in Table 1 and Fig. 13.

The results of tensile strength, plasticity and cracking energy are presented in Fig. 15.

![Fig. 11. Structure of alloy after annealing at 400°C. In the amorphous matrix small spherical precipitations of crystallites Co and Co$_3$B, thin foil, 52 000 x](image1)

![Fig. 12. Electron diffraction to Fig. 11](image2)

![Fig. 13. Influence of annealing temperature on changes of remanence and coercive force of AMM type alloy (for annealing time 2 h)](image3)

![Fig. 14. Influence of the annealing temperature on resistivity changes](image4)
In the amorphous matrix small spherical precipitations of crystallites Co and Co$_3$B, thin foil, 52 000 x 153. Fig. 11. Structure of alloy after annealing at 400°C.

The investigations of influence of the thermal activation on the changes of mechanical, electrical and magnetic properties, phenomenon of crystallization and fracture morphology of amorphous ribbons produced from the AMM type (Co$_{70}$Fe$_{2.5}$Mn$_{2}$Mo$_{1}$Si$_{9}$B$_{15}$) alloy, showed that in the analysed heat treatment temperature range 100-400°C for 2 hours, changes of properties and alloy structure occur.

In “as quenched” state investigated alloy has the amorphous structure, high tensile strength, plasticity and cracking energy. The alloy undergoes relaxation processes in temperature above 100°C. This accompanied significant deterioration of soft magnetic properties. The loss of high plasticity follows after annealing at 250°C, however beginning of the crystallization process was found at 350°C. In this state, the ribbons is characterized by high brittleness, low tensile strength and electrical resistance. The best magnetic properties obtained in “as quenched” state and after annealing of the alloy at 350°C in the longitudinal magnetic field.

4. Conclusions

The investigations of influence of the thermal activation on the changes of mechanical, electrical and magnetic properties, phenomenon of crystallization and fracture morphology of amorphous ribbons produced from the AMM type (Co$_{70}$Fe$_{2.5}$Mn$_{2}$Mo$_{1}$Si$_{9}$B$_{15}$) alloy, showed that in the analysed heat treatment temperature range 100-400°C for 2 hours, changes of properties and alloy structure occur.

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