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1. Introduction

Fast-growing technological development imposes a need for new functional materials with improved physical and mechanical properties. Since their first synthesis in 1960 [1], amorphous alloys, also known as metallic glasses, have been a focus of numerous investigations due to their advanced mechanical, electrical, magnetic, and anti-corrosion properties, related to their isotropic structure and short-range atomic arrangement [2–6].

Generally speaking, metallic glasses are multi-component systems involving different metals ($M_I$-$M_{II}$) or metal and non-metal, i.e., metalloid (M-NM) components [7–9]. For the $M_I$-$M_{II}$ systems, the metals belong to the groups of transition, rare-earth or alkaline metals, or are uranium, neptunium, or plutonium [2, 10, 11]. The M-NM systems can be represented by the general formula $M_{75–85}NM_{15–25}$ (at.%), where M is one or more metal elements, usually the transition or noble one, and NM is one or more metalloid or non-metal elements, most commonly B, Si, Ge, C, or P.

The metallic glasses are solid materials without structural translational periodicity, characteristic for a crystalline structure. From the atomic aspect, the structure of metallic glasses is analogous to the structure of liquids, characterized by macroscopic isotropy, nonexistence of the long-range atomic ordering, but existence of a short-range ordering at the atomic level. The short-range ordering of the atoms means that each atom is surrounded by the same atoms positioned at similar distances, where the lines drawn between the atom centers form similar angles, as a consequence of chemical bonds keeping the atoms together in solid state. Variation in inter-atomic distances and angles means the variation in the strength of chemical bonds, causing the softening of material in defined temperature interval instead of melting at defined temperature [12].

The ability of a liquid alloy to transform into the metallic glass is called the glass-forming ability (GFA). The GFA is determined by structural, thermodynamic, and kinetic parameters characterizing the system, i.e., chemical composition, geometrical arrangement of atoms, bonding and atomic size effects, cooling rate, and crystallization kinetics [5]. So far, many empirical criteria were proposed with the aim of predicting and explaining the GFA [5, 13–15]. The empirical criteria for easier glass formation can be expressed in five points as follows:

1. alloy is multi-component containing at least three elements, two of which are metals;

2. atomic radii difference among the three constituent elements should be at least 12%;

3. heats of mixing among the main three elements should be negative;
Metallic Glasses

4. total content of non-metals (metalloids) amounts to around 20 at.%; and

5. heteronucleants (oxide crystal inclusions) must be removed.

Generally speaking, the metallic glasses are solid materials exhibiting all the important features of the solid state. However, the short-range ordered glassy structure is manifested by broad halo peaks in XRD patterns. Due to the macroscopic isotropy of amorphous materials, for the description of their atomic structure, radial distribution function can be used. It represents the average number density of atoms as a function of the distance from the chosen atom.

In order to explain the amorphous structure of metallic glasses, different models were proposed [16–20]. Bernal introduced the model of dense random packing of hard spheres (DRPHS) [16, 17], which includes the presence of only metal atoms in the structure. The Polk’s modification of the Bernal’s model positioned the metalloid atoms at the larger holes of the DRPHS structure, but gave satisfactory results only for B and C as non-metallic components [18]. On the other hand, according to Gaskell’s model [19], the alloy structure is built from the ordered structural units composed of 200–400 atoms, identified as trigonal prisms, tetrahedra, or octahedra, forming random long-range structures. In spite of a relatively large number of the proposed models and their modifications, many details related to the structure of amorphous alloys still remain unclear.

The term “metallic glasses” denotes those amorphous alloys obtained by rapid quenching techniques. During fabrication of a glassy alloy, the crystallization, including the steps of nucleation and growth of the formed nuclei, must be avoided. This can be achieved in different ways, involving very fast cooling of an alloy melt, often at a rate of $10^6$ K min$^{-1}$. The most frequently used amorphization procedures aimed at preparation of amorphous alloys include rapid quenching of a melt of appropriate chemical composition, most commonly on a cold rotating metal disc [21]. Cooling rate necessary for amorphization is determined by the chemical composition, i.e., by the nature of the components forming a melt [8, 14]. Other methods used to obtained amorphous alloys include vapor deposition [22], spray deposition [23], ion implantation [24], laser processing [25], chemical reduction [26], electrodeposition [27], mechanical alloying [28], etc.

Glassy state is structurally and thermodynamically metastable and prone to transformations under the conditions of elevated pressure or temperature, or even during prolonged usage at moderate temperature. They could occur through the processes of relaxation, partial or complete crystallization, and recrystallization, changing the microstructure of a material, providing a simple procedure for production of polycrystalline and composite materials with targeted properties. Crystallization process can be [6, 12]:

- polymorphous crystallization (amorphous phase transforms into a single crystalline phase without a change in composition);

- primary crystallization (composition of the first crystalline phase formed from the glass differs from that of the amorphous matrix, and then the crystals of the phase formed primarily serve as the sites of secondary and tertiary crystallization);

- eutectic crystallization (two different phases crystallize simultaneously, in a coupled fashion, and their overall composition does not differ from that of the glassy matrix).
The microstructural transformations show a significant impact on physical properties of the materials changing their functionality. Structural relaxation process preceding the crystallization, characteristic of metallic glasses, includes rearrangement of individual species on the atom level and decrease in free volume, changing the short-range order and influencing primarily their electrical and magnetic properties. Additionally, as a result of relaxation, density, elastic modulus, Curie temperature, and viscosity grow, while thermal resistivity, diffusivity, and fracture toughness decrease [12]. The relaxation process can be achieved by low-temperature annealing at temperatures below the crystallization temperature.

Partial crystallization of metallic glasses leads to the formation of nanostructured or composite materials, involving nanocrystals embedded in amorphous matrix, with specific physical properties. All these together make the metallic glasses extraordinary precursors for the production of materials with targeted functionality. Properties of metallic glasses and nanocrystalline alloys obtained from the amorphous precursors are determined by both, the alloy chemical composition and microstructure.

Almost all the glassy alloys with favorable magnetic properties contain a high percentage of transition metals or rare earth elements. In this sense, iron, cobalt, and nickel-based metallic glasses are soft magnetic materials. Their excellent combination of magnetic properties including low coercivity, relatively high saturation magnetization, zero magnetostriction as well as their relatively high electrical resistivity allows their application in transformer cores, magnetic sensors, magnetic shielding, amplifiers, information handling technologies [6, 29, 30], etc. On the other hand, addition of Nd and Pr provides their hard magnetic properties [31].

Metallic glasses are considered, from a mechanical point of view, very hard and strong materials, with high wear resistance [2, 6]. The high strength of these materials is a consequence of the fact that they do not contain defects characteristic for crystalline structure. Advantageous mechanical properties are exhibited by the multi-component alloys based on Ti, Zr, Al, Mg, Fe, Co, or Ni [5, 32–40]. However, these materials are characterized by limited plastic strain in tension, while the inhomogeneous deformation occurs through the formation of shear bands [6]. Fracture toughness of metallic glasses is somewhat lower than that of crystalline materials, but two orders of magnitude higher than in the case of oxide glasses [12]. Metallic glasses based on Al and Mg possess high specific strength, due to their low density and mass [39, 40]. As a result of their favorable mechanical properties, including high strength and large elastic elongation limit, metallic glasses are used in reinforcing composites, for sporting goods, microgears, aircraft parts, brazing foils [6, 12, 41, 42], etc.

Good corrosion resistance, observed for the metallic glasses containing Cr, Zr, Ni, Nb, Mo, or V, is a particularly important characteristic of these materials from the aspect of their applicability in modern technology [43–46]. Some metallic glasses are suitable for being used as biomedical materials (such as the TiZrCuPdSn alloys [47]), while some other glassy alloys show superconducting properties (such as the TiNb-based ones [48]).

From a technological point of view, nanocrystalline alloys obtained by partial crystallization of the glassy alloys represent a particularly interesting class of functional materials. The iron-based nanocrystalline alloys with the composition Fe-R-B (where R is rare earth element, B is boron) possess hard magnetic properties [49]. However, the soft magnetic materials in this class are nanocrystalline materials with the composition Fe-Si-B-Nb-Cu (FINEMET), Fe-M-B-Cu (M is Zr, Hb or F) (NANOPERM), Fe-Co-M-B-Cu (M is Zr, Hb or F) (HITPERM) [50], etc. To maintain favorable functional properties, in this case the soft magnetic ones, crystal
size of the $\alpha$-Fe or $\alpha$-Fe(Si) in FINEMET or NANOPERM alloys must not exceed 15 nm [51]. To obtain nanocrystalline structure from the amorphous one, controlled fast nucleation and slow crystal growth are required. This can be achieved by an appropriate choice of the alloy composition and by thermal treatment as in the FINEMET-type alloys, where Cu is added to facilitate nucleation, while the Nb decreases the crystal growth rate [51–53].

In order to provide and maintain an amorphous or nanocrystalline structure of targeted functionality, thermal stability, thermodynamics, and kinetics of phase transformations thermally induced of amorphous and nanocrystalline materials should be known [8, 54–75]. This requires determination of the temperatures of all of the phase transformations as well as the kinetic triplets of these processes, consisting of Arrhenius parameters, activation energy, and pre-exponential factor, as well as kinetic model (conversion function). By determining the crystallization kinetic model, information about crystallization mechanism, including nucleation, crystal growth, and impingement effects can be obtained. In this way, the lifetime of specific microstructure, important for reliable applicability of materials, can be predicted.

Solid-state transformations are often complex processes, consisting of several concurrent or consecutive steps, manifested experimentally by compounded curve forms. In order to discuss all these steps and propose the most probable mechanisms, during the analysis, deconvolution of the compounded peaks (DSC, TG, or even XRD) by using different mathematical tools is required [76–84].

In view of the foregoing, metallic glasses have still been intriguing although studied for more than 50 years now, offering a wide range of practical applications either in the glassy or derivative form, and promising further technological improvement and development.
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