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Aspects regarding certain technological parameters corresponding to thermal treatments applied to amorphous materials

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Abstract. Amorphous metals, which are produced in the form of strips, fibers, and wires, exhibit internal stresses in their structure, generated by the matrix-reinforcement interface. The study of load transfers that occur at the interface, as well as the adhesion between the two components, is influenced by the treatment of the reinforcing fibers or filler particles.. These will have a strong negative impact during operation. Since these materials are created to serve well-defined purposes, it is necessary that their structure be stable over time or present certain properties specific to the requirements, for which the application of thermal treatments is imposed. The synthesis of various studies from the specialized literature emphasizes that the purpose of these treatments is to induce specific magnetic properties.

1. Introduction

The importance of these materials for military and aerospace applications, as well as their usage in current industrial equipment, household appliances, and sports and recreational equipment, has been highlighted when it was observed that certain properties, such as high tensile strength or lower density, make them superior to traditional materials. The properties of composite materials are determined by both the matrix and the form, dimensions, and orientation of the fibers, as well as their reinforcement method [2]. Whether the matrix and reinforcement are similar or not, the essential aspect is the stress state characterizing the amorphous material.

Amorphous metals can be applied to them simple or special annealing treatments as well as aging treatments.

Simple or special annealing treatments aim to relieve stress or improve certain magnetic properties, but they are accompanied by a decrease in chemical or mechanical properties. Special annealing treatments are carried out under mechanical stress or in magnetic fields.

In the first working variant, it is recommended to apply a tensile force of approximately 600-700 MPa, taking care not to exceed the elastic limit, at the operating temperature.

In the second working variant, the value of the magnetic field intensity and its orientation relative to the sample axis are important. Therefore, it is recommended to use a range of 80-800 A/m in the longitudinal magnetic field and values tens of times higher for the transverse magnetic field.

The aging treatment applied to amorphous materials aims to stabilize their magnetic properties.

2. The technological parameters required for the application of heat treatments

The selection of these parameters is based on the nature of the amorphous material and the desired objectives, namely obtaining high values of physical, chemical, and mechanical properties [3].

2.1. Heating temperature

In the case of annealing treatments, the temperature is chosen to be lower than the crystallization temperature, i.e.:

$$T_h = T_c - (60\ldots200)°C, \quad (1)$$

where Th is the heating temperature and T_c is the crystallization temperature.

The value of the crystallization temperature can be determined through various methods, such as differential thermal analysis, differential dilatometric analysis, electrical analysis, magnetic analysis, and X-ray analysis. The last method provides good accuracy in determining this parameter.

The influence of increasing the heating temperature on the structure of Fe-C-O amorphous metal was investigated (Fig. 1 [9]), and it is observed that at temperatures of 20-45°C, diffraction loops are evident (Fig. 1a). At a heating temperature of 200°C for 1 hour, the development of new Feα centers is favored, and a peak is observed on the diagram (Fig. 1b). At a heating temperature of 300°C for 1 hour, Fe_3C crystals begin to form, and multiple peaks are observed on the diagram (Fig. 1c). The conclusion drawn is that the heating temperature should be stopped at 120°C to prevent any adverse effects on the material's structure.

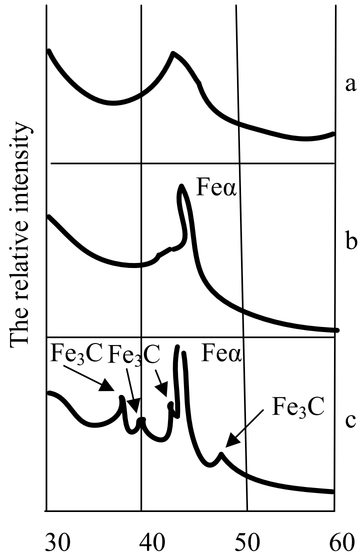


Fig. 1 The influence of heating temperature on the structure of Fe-C-O amorphous metal [9]

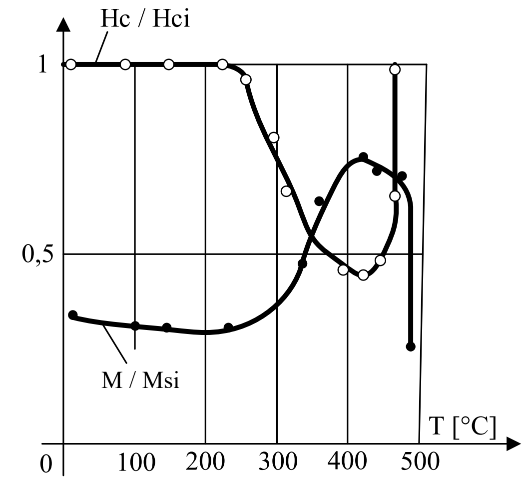


Fig. 2 The determination of the crystallization temperature in the case of the amorphous alloy $Fe_{76,5}B_{17}Si_5C_{1,5}$ [9]

The determination of the crystallization temperature was studied in the case of $Fe_{76,5}B_{17}Si_5C_{1,5}$ amorphous alloy using magnetic analysis (Fig. 2 [9]). The variation of Hc/Hci and M/Msi ratios with heating temperature was analyzed, where Hc represents the coercive field of the heat-treated samples, Hci is the coercive field of the untreated samples, M represents the longitudinal variations of sample magnetization, and Msi is the saturation magnetization of the untreated samples.

From the diagram, it can be observed that starting from 420°C, the Hc/Hci ratio increases while the M/Msi ratio decreases. This can be explained by the formation of crystals, which exhibit mechanisms for blocking Bloch walls. Therefore, this amorphous metal has a crystallization temperature of 420°C and a crystallization interval of (420-500)°C. By analyzing the values of the temperature and crystallization interval, it was observed that the lowest values of the recrystallization temperature are 170-190°C below T_c, while the highest values are 58-68°C above T_c.

The choice of the recrystallization temperature should result from laboratory trials on different materials and take into account the following observations:

• A value higher than the crystallization temperature leads to the formation of a metal with a crystalline structure and negates the effects achieved through ultra-rapid cooling.

• A value significantly below the crystallization temperature can cause embrittlement of the amorphous metal.

Therefore, Equation (1) provides a guideline only to avoid the crystallization of the amorphous metal.

2.2. Heating rate

To avoid the occurrence of thermal stresses in the structure, heating rates of 20-40°C/min are recommended.

2.3. Holding time

This parameter is chosen based on several factors, such as the nature of the material, dimensions of the component, annealing temperature value, and desired objectives, namely stress relief and improvement of specific properties. The duration of annealing holding time is determined experimentally to avoid the occurrence of brittleness. The recommended minimum duration is 15-20 min/mm of the component's width. The value of holding time influences various property values. In this regard, the influence of holding time (at an annealing temperature of 300°C) on the magnetic induction B[T] and magnetic field intensity H[A/cm] of $Fe_{80}P_{16}B_4$ amorphous metal was observed (Fig. 3 [4]; 3a) untreated amorphous alloy; 3b) 1 - hour holding time; 3c) 3 - hours holding time; 3d) 30 - hours holding time). The variation of these magnetic properties is attributed to the oxidation of the strip's surface, which generates compressive stresses along the axis.

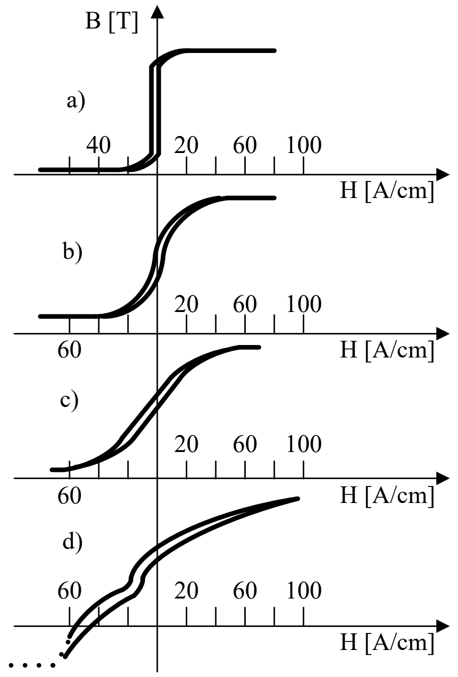


Fig.3 The influence of annealing duration on the magnetic properties [4]

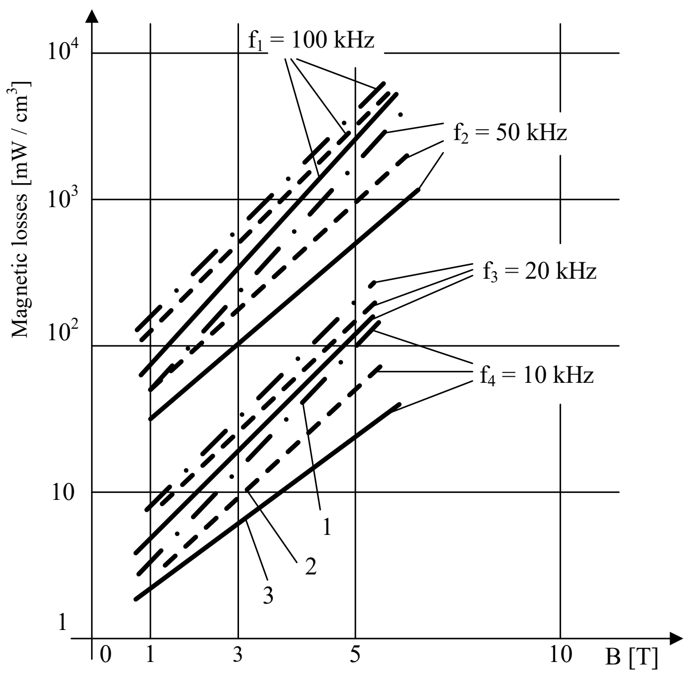


Fig.4 The influence of heating environment on the magnetic losses of an amorphous metal [9]

2.4. Heating medium

Heating in the annealing treatment can be carried out in air (curve 3), in a protective atmosphere (Ar, N - curve 2), or in high vacuum - curve 1 (10^{-4} torr). These environments influence the mechanical and magnetic properties of the amorphous metal. Different strips of $(Fe_{80.5}Ni_{10.5}Nb_9)_{83}Si_5B_{12}$, with a length of 10mm, thickness of 20μm, and magnetostriction λs of $4\cdot 10^{-6}$, were subjected to annealing treatment at 480°C for 20 minutes in various heating atmospheres. It was observed that the lowest core loss was recorded for the nitrogen atmosphere (Fig. 4 [9]).

The choice of this environment is crucial as it can lead to degradation of the amorphous material.

2.5. Cooling medium

The cooling medium after the annealing treatment can be air, water, or oil. The amorphous material $Co_{67}Fe_4Ni_2Mo_2B_{15}Si_{10}$ was studied, which was annealed for one hour at 150°C and then cooled in two different conditions: first in air and then in water. The influence of the cooling rate of the respective medium on the magnetic permeability was observed (Fig. 5 [9]; curve 1 - annealed for one hour at 150°C and cooled in water; curve 2 - annealed for one hour at 150°C and cooled in air). An increase in permeability is observed with an increase in cooling rate; however, this is accompanied by a decrease in the long-term stability of the amorphous metal (i.e., aging). Faster aging was observed when cooled in water, and if the cooling duration increases significantly, even lower permeability is recorded compared to slow cooling. Similar results were obtained when working with other types of amorphous metals, showing that cooling rate and aging time influence their magnetic properties [7].

In conclusion, a slow cooling is preferable as it ensures better long-term preservation of the magnetic properties of the amorphous metal.

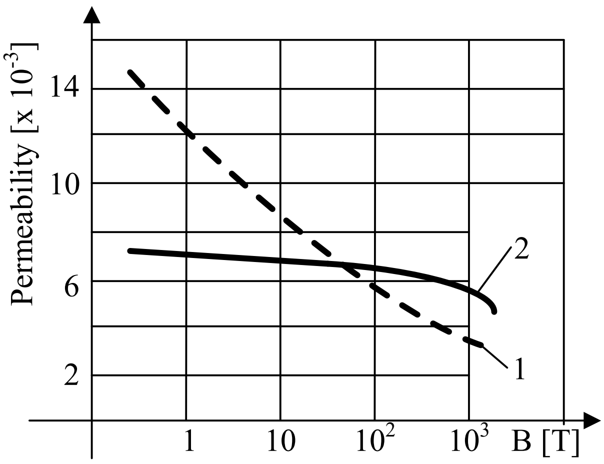


Fig. 5 Variation of magnetic permeability as a function of cooling rate during aging of an amorphous metal [9]

2.6. The use of temperature-time-transformation diagrams

These diagrams, commonly referred to as Temperature-Time-Transformation (TTT) diagrams in the specialized literature, enable the correct selection of technological parameters for thermal treatments applied to amorphous metals. Fig. 6 ([1], [5]) presents a general form of the TTT diagram obtained for a metal-metalloid type amorphous metal. Metalloids play a role in promoting the formation of the amorphous state. It can be observed that with prolonged heating, exceeding 103s, at a temperature of 400°C, the structure becomes predominantly crystalline. This structure consists of microcrystals with dimensions of 50-100Å and represents a supersaturated solid solution with the same chemical composition as the amorphous matrix.

Curve Ms_1 corresponds to the nucleation and growth process of crystals within the amorphous matrix. These crystals consist of pure metallic elements. Curve Ms_2 corresponds to the nucleation and growth process of crystals of an intermetallic phase formed by metal and metalloid atoms.

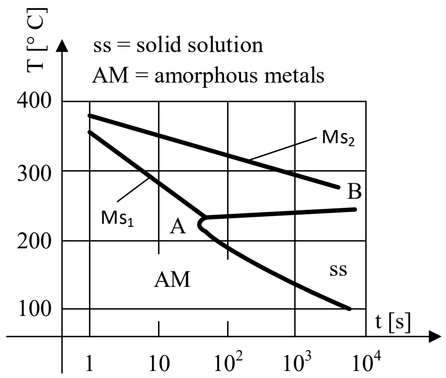


Fig. 6 General shape of a TTT diagram for metal-metalloid type amorphous metals ([1], [5])

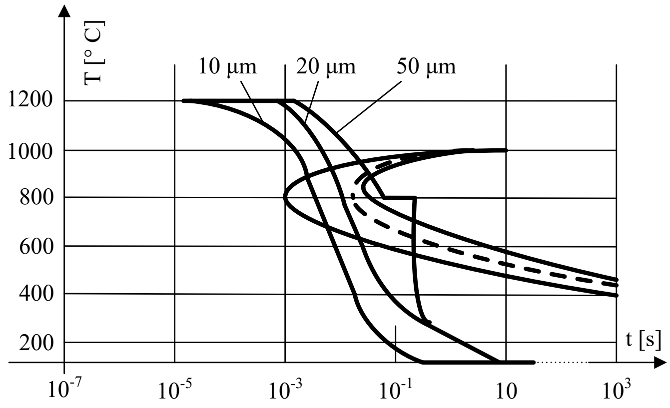


Fig. 7 TTT diagram for amorphous metal $Fe_{83}B_{17}$ ([1], [5])

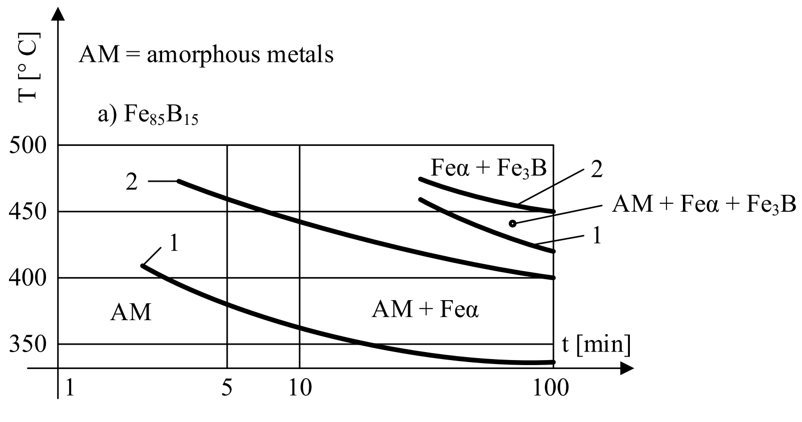
There is no clear distinction between the Ms_1 phase and the solid solution, as they represent limiting cases of crystallization for the metallic element within the amorphous metal. Curve AB could be considered as a boundary between these crystalline phases, without being an interfacial limit. If this diagram were obtained for an Fe-B amorphous metal, Ms_1 would correspond to the formation of Feα crystals, and Ms_2 would correspond to the formation of Fe_3B crystals. Boron promotes the formation of the amorphous structure and enhances the long-term stability of the alloy.

In Fig. 7, the TTT diagram for the $Fe_{83}B_{17}$ amorphous metal has been depicted ([1], [5]). It is evident that heating slightly above 10^{-3}s at a temperature of 667°C promotes the formation of crystallization centers, and maintaining this temperature for one second will result in the transformation of the amorphous structure into a crystalline one.

The minimum time for the formation of crystallization centers and the duration of this process depend on factors such as the thickness of the amorphous material strip or wire and the heating temperature.

In Fig. 7, cooling curves have been overlaid on the TTT diagram for strips of the same width but different thicknesses, and it is observed that the formation of the crystalline structure is favored at thicknesses exceeding 50µm.

Just like in the case of TTT diagrams obtained for crystalline metals, the position and shape of the CC curves in the case of amorphous metals vary depending on their chemical composition and the coordinates of the eutectic (composition, temperature).



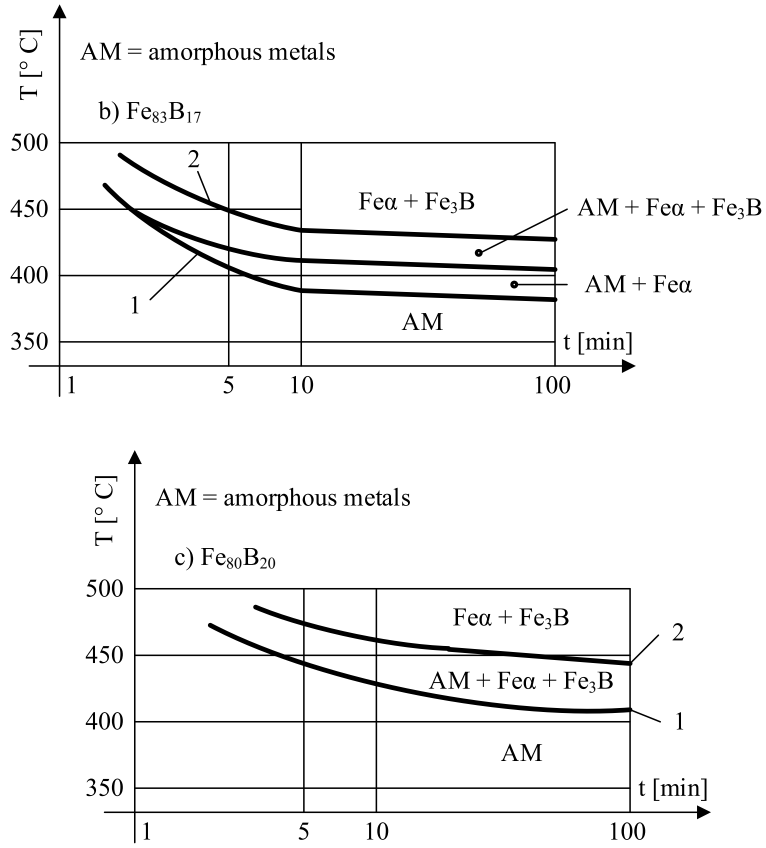


Fig. 8 TTT diagrams of alloys in the Fe-B system [9].

TTT diagrams have been developed for Fe-B amorphous alloys in hypoeutectic, eutectic, and hypereutectic compositions (Fig. 8 [9]). The starting transformation curve is labeled as 1, and the ending transformation curve is labeled as 2. It can be observed that as the metalloid content (B) increases, the amorphous state remains stable at temperatures above 400°C.

3. Conclusions

The heat treatments applied to amorphous metals aim to improve the stability of the amorphous structure, relieve stress, and enhance magnetic properties.

To achieve this, it is necessary to construct the TTT diagram for different grades of such materials, determine the heating temperatures that allow the preservation of the amorphous state, select the heating atmosphere, the duration of the holding time, as well as the cooling method.

The association of high mechanical properties ([2], [7], [8]) with remarkable electrical or magnetic characteristics allows the utilization of these materials across various economic sectors; in the field of electrotechnics, they are used in the fabrication of high-power electrical transformers, inductance coils that employ an amorphous wire alongside the conventional conductor, and current sensors; in physics, they find application in particle accelerators, while in electronics, they are employed in the manufacturing of magnetic heads for audio and video devices, torque transducers, switch-mode power supplies, and magnetometers; in the medical domain, they serve as displacement sensors for diagnostic and surgical procedures; in machine construction, their use enhances wear resistance, thus improving cutting properties; in the petrochemical industry, they increase the corrosion resistance of various markers and pipes; in the military sector, they are utilized in fire-resistant fabrics, bulletproof vests, and protective helmets; moreover, in the naval field, they are used in thick canvas for sail-making.

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