Preparation and characterization of $Fe_{67}Cr_4Mo_4Ga_4P_{12}B_5C_4$ ferromagnetic bulk amorphous alloy

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Fe-based amorphous alloys have a high application potential due to their unique soft magnetic and mechanical properties, and high corrosion resistance. These alloys can be obtained in the final shape without making other processing operations, which makes them suitable for many electronic applications such as magnetic shielding, magnetic sensors, magnetic cores and other devices. Bulk $Fe_{67}Cr_4Mo_4Ga_4P_{12}B_5C_4$ amorphous alloys in rods form with the diameter of 1 mm and 35 mm in length were successfully prepared by copper mould casting. The samples obtained were structural investigated by X-Ray diffraction (XRD), differential thermal analysis (DTA), and magnetic characterized by conventional low frequency induction method. The mechanical properties such as hardness and bulk modulus were determined using micro indentation tests by analysing the load-depth curve. This study was made in order to use these bulk amorphous alloys in magnetic shielding applications.

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1. Introduction

The discovery of bulk amorphous alloys, also called bulk metallic glasses (BMG), has triggered new interest in research on glassy metals. Before the development of BMG materials there have been many limitations of using metallic glasses, mainly limitations of size and workability [1-3]. The problem of size and forming has been solved by discovery of bulk metallic glasses, which have a wide super-cooled liquid region and high glass-forming ability [4-6]. Formation of bulk amorphous materials depends on many internal factors, such as impurities and atomic size of the constituent elements or external factors, such as cooling rate [7]. Bulk amorphous alloys are a novel class of engineering materials, which exhibit unique mechanical, thermal, magnetic and corrosion properties, very attractive compared to conventional crystalline alloys and are very useful in a wide range of engineering applications. [2]

Fe-based bulk amorphous alloy have emerged as a novel class of BMGs having better properties than their crystalline counterparts. Their magnetic behaviour combined with good mechanical properties and high corrosion resistance make them very attractive for applications as micro-gears, welding elements, dental and medical implants, solders and brazing elements, power transformers, power supplies, advanced power devices, magnetic sensors, electronic articles and automotive magnets [8-10]. However, the use of Fe-based alloys as structural materials is still limited due to high cooling rates required for their production to avoid crystallization and high vacuum to overcome oxidation. Efforts are being devoted to enhance the glass-forming ability (GFA) of Fe-based alloys by improving the purity of constituent elements or by addition of metalloids.

The magnetic properties of BMGs have been investigated mostly in Fe-based alloys [1-3].The most desirable soft magnetic properties of the material include high magnetic susceptibility, low coercivity and high electrical resistivity [11, 12].

2. Experimental procedures

Taking into consideration the requirements imposed for magnetic shielding applications, soft magnetic properties and high corrosion resistance, the chemical composition of the alloy used in experimental investigations was chosen from Fe-Cr-Mo-Ga-P-B-C. Given the positive effect of molybdenum and gallium on amorphization, along with a maximum proportion of 21 atomic percent of metalloids P, B, C), it can be estimated a high glass forming ability [7]. Increasing the corrosion resistance and soft magnetic properties requires the presence of chromium in the chemical composition. Master alloy of the composition $Fe_{67}Cr_4Mo_4Ga_4P_{12}B_5C_4$ was prepared by induction melting a mixture of pure Fe, Cr and Ga metals and Feï C, Feï Mo, Feï B and Feï P powdered ferroalloys, under a boron oxide flux. The composition is expressed in atomic percentage. The master alloy was melted several times in order to ensure a compositional homogeneity. From the master alloy ingots, bulk amorphous alloys in rod form were prepared by copper mould casting method (Figure 1a).

The master alloy was introduced in a quartz crucible, endowed at the bottom with a 1mm diameter hole for melt ejection. After complete melting via high frequency induction heating, the alloy was injected into the copper mould by an argon pressure of 0.6 atm. Bulk metallic glass with the diameter of 1 mm, and 35 mm in length was obtained, as shown in Fig. 1b.

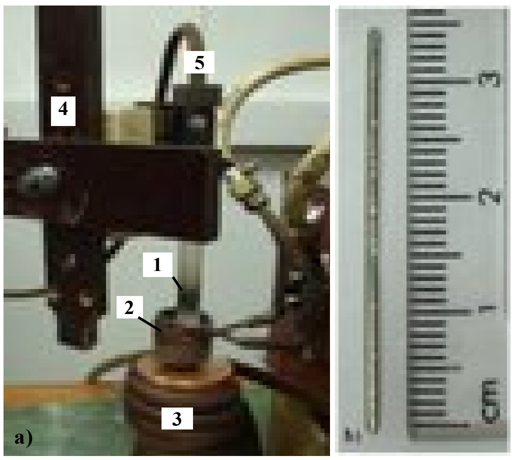

Fig.1. a) The copper mould casting setup b) The rod obtained by copper mould casting 1 - crucible; 2 - coil; 3 – copper mould; 4 – guiding device of the crucible; 5 – Ar pressure

The cast rod has a cylindrical shape with smooth outer surfaces and good metallic luster.

The amorphous structure of the final products was examined by X-ray diffraction (XRD) using a BRUKER AD8 ADVANCE diffractometer, with the Cu-KŬ radiation. The thermal behaviour was studied in the range from 200°C to 1200°C, at a heating rate of 20 °C/min, by means of differential thermal analysis; a Baehr DTA 703 device was used.

The magnetic properties of the obtained alloys (as-cast and annealed at 450°C) were examined in open magnetic circuit, using a conventional ac measuring stand [13] operating at a frequency of 9 Hz. The equipment allows recording (in ASCII format) of the magnetic hysteresis loop and determination of the normal magnetization curve $M = M(H)$, and of the field dependence of the magnetic susceptibility $\chi = \chi(H)$. An AF oscillator generates a sinewave signal of adjustable frequency and amplitude, which is fed to a power amplifier whose load (serial) includes the primary magnetization circuit, composed from a field coil (151 Oe/A), a tuning capacitor (of capacitance of the order of tens of μF, depending on the working frequency) and a non-inductive precision resistor (3.80 Ω). A current $i(t)$ injected in the field coil will generate an axial magnetic field $H(t)$, whose direct measure is the voltage $u_H(t)$ across the ends of the precision resistor; in SI units, the numeric relation is:

$$H(t) = 3160 \times u_H(t) \quad (1)$$

By means of a compensated search coil (7500 turns, 0.08 mm diameter Cu wire) a signal $e_M(t)$ directly proportional to the time derivative of the magnetic flux from the inside of sample is collected, amplified and, finally, subjected to analogue time integration. Accordingly, the magnetization of the sample results as:

$$M(t) = \frac{\alpha}{\mu_0 s(1-N_D)} u_M(t) \quad (2)$$

where α is a factor which depends on construction details (including the number of turns of the search coil, the gain of the amplifier and the time constant of the integrator), μ_0 is the vacuum permeability, s is the cross sectional area of the sample and N_D is the demagnetization factor (fluxmetric). On the other hand, the signals $u_H(t)$ and $e_M(t)$ are also transmitted to a pair of precision AC/DC converters, of output voltages directly proportional, for a given magnetization cycle, to the amplitudes H_{max} and M_{max} of field and magnetization, respectively. Thus, the normal magnetization curve is obtained by stepwise varying H_{max}.

In order to increase the magnetic performances of the alloy, *in vacuum* annealing at 450 °C for 1 h was performed.

The mechanical properties such as hardness and bulk modulus were determined by instrumented indentation tests. The indentation tests consist of performing a print on the surface of a material by the penetration of an indenter at a specified load. The mechanical properties mentioned before were determined by analysing the load-depth curve [14].

Before micro indentation testing can be performed, it is necessary to create a high-quality surface in order to ensure both accuracy and repeatability of the tests. The samples have been metallographically mounted, ground and polished.

To get more accurate values, twenty measurements with the applied load ranging from 100 to 10000 mN were performed on a CSM Micro Indenter. The indentation indents are presented in Fig. 2.

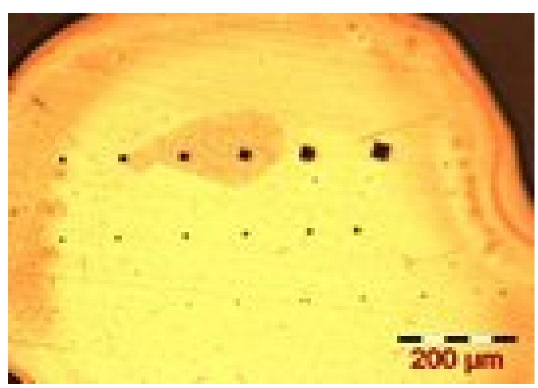

Fig.2. The micro indentation indents

The four key parameters needed to determine the hardness and the bulk modulus from the load-depth curves are the maximum load, P_{max}, the maximum depth, h_{max}, the contact depth, h_c and the elastic unloading stiffness, also called the contact stiffness $S = dP/dh$, defined as the slope of the upper portion of the unloading curve during the initial stages of unloading [15].

The accuracy of hardness and bulk modulus measurement depends on how well these parameters can be measured experimentally [16].

3. Results and discussions

The X-ray diffraction patterns of the obtained rods (in the as-quenched state and after heat treatment) as shown in Figure 3, are typical for an amorphous structure. The two patterns consist only of a broad incipient peak centred at 2θ =~45°, where the (110) diffraction line of ŬFe is expected.

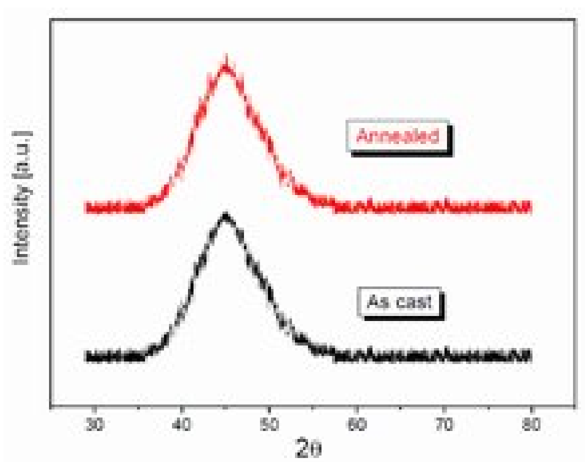

Fig.3. XRD patterns of the as-cast and annealed bulk $Fe_{67}Cr_4Ga_4P_{12}B_5Mo_4C_4$ alloy samples

The thermal behaviour of the $Fe_{67}Cr_4Mo_4Ga_4P_{12}B_5C_4$ bulk amorphous alloy is shown in Figure 4. The DTA curve exhibits three exothermic peaks representing the first stage of crystallization (the first peak), the formation of a second crystalline phase (the second peak) and the transformation of crystalline phases (third peak). The endothermic peak represents the melting of the alloy. The glass transition temperature (T_g), the crystallization temperature (T_x) and the melting temperature (T_m) were found to be 436 °C, 471 °C and 938 °C, respectively. The super-cooled liquid region, given by φT_x = T_xï T_g, extends over 35 °C, prior to crystallization. Accordingly, it can be said that this alloy shows a good glass forming ability [2].

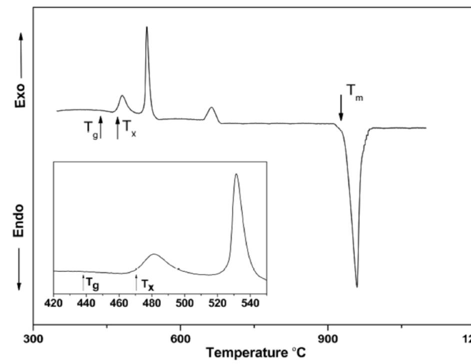

Fig. 4. DTA curve for the cast bulk $Fe_{67}Cr_4Mo_4Ga_4P_{12}B_5C_4$ amorphous alloy.

The rod shape and magnetic hardness of the obtained alloys determined the choice of open magnetic circuit type. The results are shown in Figures 5-8. The main values of the measured magnetic quantities are summarized in Table 1.

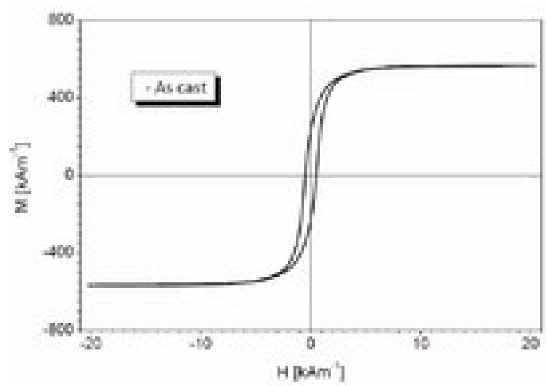

Fig.5. The hysteresis loop of the sample in the as-cast state.

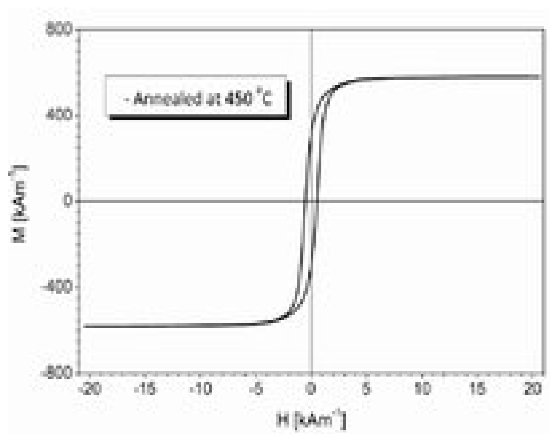

Fig.6. The hysteresis loop of the sample in the annealed state.

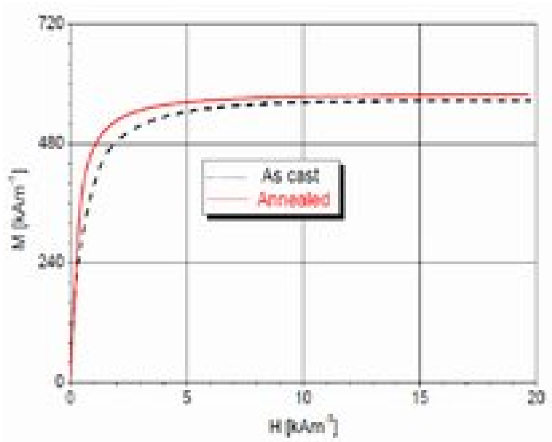

Fig.7. Normal magnetization curves of the samples

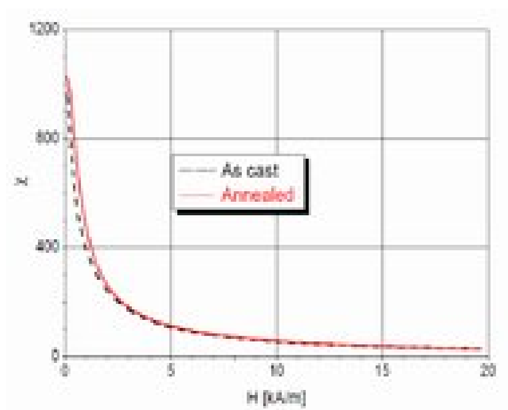

Fig.8. The field dependence of the magnetic susceptibility.

Table.1. Values of the measured magnetic quantities.

magnetic property	as cast	450°C annealed
technical saturation magnetization	566 kAm^{-1}	580 kAm^{-1}
coercivity	400 Am^{-1}	340 Am^{-1}
magnetic remanence	288 kAm^{-1}	303 kAm^{-1}
initial magnetic susceptibility	977	1027

From the measured values of the magnetic properties it follows that the examined samples exhibit soft magnetic behaviour. A slight improvement of the soft magnetic properties was observed after the heat treatment, which led to structure relaxation and reduction in the native internal stresses occurred during the casting process.

From instrumented indentation test, which allow the plot of a load-depth curve (Figure 9), the calculation of the bulk modulus can be done by Oliver and Pharr method (1992). They proposed that the bulk modulus can be calculated from the total compliance, of the specimen and of the instrument, which results from the contribution to the depth measurement deflections of the load frame, added to the displacement into the material [15].

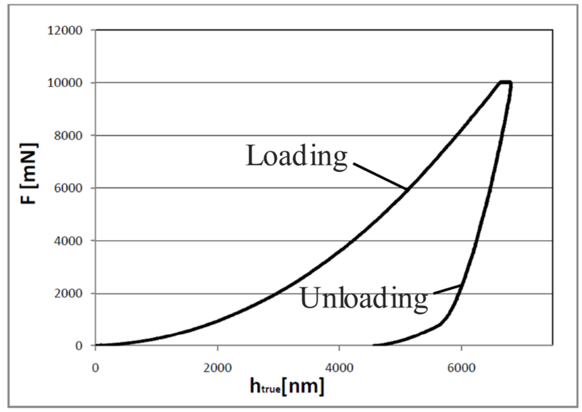

Fig.9. Indentation load-depth curve performed on the bulk $Fe_{67}Cr_4Ga_4P_{12}B_5Mo_4C_4$ amorphous alloy

When a load is applied, the reaction force is taken up by deflection of the load frame and added to the depth registration. The correction is made using the formula:

$$h = h_m - C_f \cdot P \qquad (3)$$

where h is the indentation depth into material, h_m is the measured indentation depth, C_f is the instrument compliance and P is the load applied [16,17].

The contact stiffness is very important since it is required to calibrate the indentation depth prior to the calculations. The contact stiffness is given by:

$$\frac{1}{S} = C_f + \sqrt{\frac{\pi}{24{,}5}} \cdot \frac{1}{2 \cdot \beta \cdot \gamma \cdot E_R} \cdot \frac{1}{h_c} \qquad (4)$$

where β is a correction factor which depends on the shape of the indenter, h_c is the contact depth and E_R is the reduced modulus defined as:

$$\frac{1}{E_R} = \frac{1-\nu_m^2}{E_m} + \frac{1-\nu_i^2}{E_i} \qquad (5)$$

where E_m and ν_m are the bulk modulus and Poissonôs ratio of the material and E_i and ν_i are the same parameters for the indenter [16,17].

Fig. 10 represents the inverse of the contact stiffness as a function of the inverse of the contact indentation depth obtained from the indentation test. The representation is linear, the slope is directly linked to the bulk modulus of the material according to Equation 4.

By considering the elastic properties of the indenter, 1140 GPa for the bulk modulus and 00.7 for the Poissonôs ratio and by taking 0.3 for the Poissonôs ratio of the material and 1.067 for the correction factor γ we obtain a value of 147.24 GPa for the reduced modulus. Therefore, the bulk modulus of the bulk $Fe_{67}Cr_4Mo_4Ga_4P_{12}B_5C_4$ rod is 153.76 GPa.

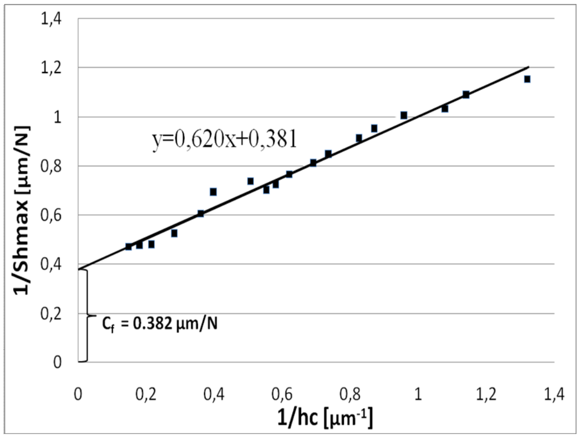

Fig.10. 1/S as a function of $1/h_c$ for the indentation test performed on the bulk $Fe_{67}Cr_4Ga_4P_{12}B_5Mo_4C_4$ rod

The hardness is estimated from:

$$H = \frac{P}{A_C} = \frac{P}{26.43 h_c^2} \quad (6)$$

Using the contact depth for calculation, an average value of 9.41 GPa was obtained for the Martens hardness.

The hardness values could be independent of load, it could increase or deacrease with load, and it could show a complex variation with load changes depending on the material. The hardness-load dependence is known as the Indentation Size Effect. The phenomenon has been associated with various causes such as roughness, varying composion or shape of the indenter [18].

When studying the indentation size effect it is observed that the fitting parameters and the theoretical ones change without clear justification. To explain the difference, Chicot suggested the use of a hardness-length scale factor [16].

The relation between the hardness and the indentation depth is:

$$\left(\frac{H}{H_0}\right)^2 = 1 + \left(\frac{h^*}{h}\right) \quad (7)$$

where H_0 is the macro-hardness and h^* is the characteristic scale-length representing the hardness-load dependence.

Chicot suggested the study of the indentation behaviour by expressing the square of the hardness versus the reciprocal of the indentation depth. The slope, expressed as a function of the macro-hardness and the characteristic scale-length, is then proportional to an indentation toughness expressed in $MPa.m^{1/2}$ [16,18]. This parameter is called the hardness length scale factor, H_{LSF}, which is equivalent to:

$$H_{LSF} = H_0\sqrt{h^*}\text{, cand } H^2 = H_0^2 + \frac{\left(H_0\sqrt{h^*}\right)^2}{h} \quad (8)$$

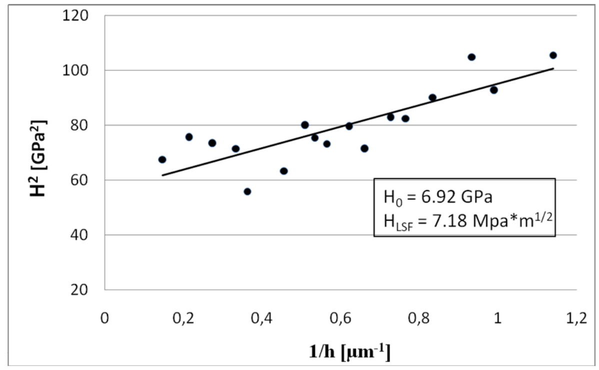

Fig.11. Indentation size effect of the bulk $Fe_{67}Cr_4Ga_4P_{12}B_5Mo_4C_4$ amorphous alloy

4. Conclusions

Bulk $Fe_{67}Cr_4Mo_4Ga_4P_{12}B_5C_4$ amorphous alloy in form of rods of 1 mm diameter and 35 mm in length have been successfully obtained by copper mould casting method. It was found from DTA measurements that the glass transition temperature of the alloy is 436 °C, the crystallization temperature is 471 °C and the melting temperature is 938 °C.

The quasistatic (9 Hz) ac magnetic measurements indicated 400 Am^{-1} coercivity, 566 kAm^{-1} saturation magnetization (technical), 288 kAm^{-1} remanence and 977 the initial magnetic susceptibility in the as-cast state, values characteristic to the soft magnetic materials.

A slight improvement (due to internal stress relaxation) of these values was observed subsequent to vacuum annealing 450 °C for 1h, as follows: 340 Am^{-1} coercivity, 580 kAm^{-1} saturation magnetization (technical), 303 kAm^{-1} magnetic remanence and 1027 initial magnetic susceptibility.

The instrumented indentation test was useful for determining the mechanical properties, but the results were calibrated in order to obtain a good interpretation. From the instrumented micro indentation tests we can say that the bulk $Fe_{67}Cr_4Mo_4Ga_4P_{12}B_5C_4$ amorphous alloy exhibit good mechanical properties given the values obtained for the bulk modulus of 153.76 GPa and of 9.41 GPa for Martens Hardness.

Future research work will be dedicated to the improvement of the magnetic properties, in order to develop bulk ferromagnetic amorphous alloys families for magnetic shielding applications.

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