Fe-based Bulk Metallic Glasses Used for Magnetic Shielding

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Abstract. The casting in complex shapes (tubular) and the main magnetic properties of bulk metallic glasses (BMG) alloys from the ferromagnetic Fe-Cr-Ni-Ga-P-Si-C system, with a small addition of Ni (3% ) were studied. Samples as rods and sockets having the thickness up to 1 mm were obtained from master alloys by melt injection by low cooling rates into a Cu mold and annealed in order to ensure adequate magnetic requirements. The structure was examined by X-ray diffraction (XRD) and the basic magnetic properties (coercivity, magnetic remanence, initial susceptibility, etc.) were determined by conventional low frequency induction method. The experimental investigations on producing of BMG ferromagnetic alloys with 3% Ni show the possibility to obtain magnetic shields of complex shape with satisfactory magnetic properties. The presence of Ni does not affect the glass forming ability, but reduce the shielding capacity.

1. Introduction

In the last decades the ferromagnetic amorphous alloys have shown a great applicative interest due to their excellent magnetic properties. Most of the amorphous alloy families developed for different practical applications are characterized by critical cooling rates, usually higher than 10⁵ K/s, which confines the products obtained from these alloys to shapes like stripes, wires or foils having thickness below 60 µm. Manufacturing of magnetic screens, magnetic filters, or valves from bulk metallic glasses (BMG) like bars, pipes, sockets, etc., having the thickness in the millimetres range, by using solidification techniques like copper mould casting, high pressure die casting, suction casting, etc., represents an actual challenge from the viewpoint of both technological and exploitation properties optimisation. In the case of Fe-based BMG alloys working as magnetic shields in corrosive environment, the soft magnetic properties are altered by the presence of the glass forming metalloids in a relatively large proportion and that of the alloying elements having an important role in the increase of resistance to corrosion [1,2]. When added in large proportions – exceeding 40% (atomic percents) – in Fe-based alloys, Ni leads to an increase of the magnetic permeability, coercivity, resistance to corrosion and also to a decrease of the magnetic saturation. In this context, it becomes of interest to examine the effect of this alloying metal at small percents (not exceeding 3 %).
2. Experiments concerning manufacturing of Bulk Metallic Glasses used for Magnetic Shielding

In order to obtain bulk amorphous alloys noted by BMGs, the critical amorphization rate of cooling must be very low (0.1...10^2 K/s). Its value depends on that chemical composition which leads to achievement of large GFA.

The Japanese researchers [1] have proposed the following three empirical rules:

1. multicomponent system consisting of more than three elements;
2. significant difference (beyond 12%) in atomic size ratios among the three main constituent elements;
3. negative heat of mixing among the three main constituent elements.

Having in mind these rules, the production of the bulk metallic glasses (BMGs), e.g. in socket-like form, Fe-based alloys require P, Si, C and Ga in certain proportions, as these elements favorise a large supercooled liquid region and, implicitly, a high glass forming ability (GFA), but this fact has a negative influence on the soft magnetic properties. Furthermore, sometimes the presence of some alloying elements like Cr and Ni is necessary, as such additions contribute to an enhancement of the resistance to corrosion and of some mechanical properties which are necessary in applications like magnetic screens, magnetic filters, or valves.

It is well known that in case of magnetic shields for microapplications their walls thickness not exceeds few tenth millimetres (less than 1 mm). So that, the investigations performed in this paper followed on the one side the producing of BMG rods having 1 mm diameter (as control sample) and of the other side the possibilities of obtaining tubular shape products (max. 1 mm walls thickness) similar with the magnetic screens.

Thus, from our experiments made on several amorphous alloy families, properties like GFA or saturation magnetization, coercivity, magnetic susceptibility, etc., are little affected by the fact that the raw materials were of technical or chemical purity. The main influence on the magnetic properties is due to the internal stress pattern, which is usually controlled by annealing.

Starting from Fe-P, Fe-Si pre-alloys and pure Cr, Ni, Ga; Fe-Cr-Ni-Ga-P-Si-C ingots were prepared as master alloys by induction melting in Ar atmosphere. BMGs sockets having Fe70 Cr2 Ni3 Ga4 P13 Si5 C3 composition, 1 mm wall thickness, 6 to 7 mm diameter and 15 mm length were then produced by means of a laboratory-made installation [4] using a special Cu mould (figure 1); the Ar overpressure was kept to 0.35 Bar. The products (figure 2) were obtained in a shape consistent with a good magnetic shielding capacity. Their surface was smooth and homogeneous and no spots of corrosion were observed. The same parameters were used in order to manufacture the BMG rods of 1 mm diameter.

The difficulties in ensuring some high quality amorphous products result, on one side, from the casting process optimization (casting temperature, pressure, working environment, mould form) and, on the other side, from the obtaining of a minimum cooling rate which offers the formation of the desired structural state at the as-chosen chemical composition.

In order to increase the magnetic performances of the investigated alloys an annealing treatment at 340°C for 10 minutes in a silicon oil bath was performed.
3. Structural and magnetic characterization of the obtained alloys

The structure of the prepared samples (for all molten alloys) was examined by XRD method using the Mo-Kα radiation (figure 3). The diffraction pattern of the as-quenched sample reveals typical halos with no evidence of crystalline Bragg peaks. It may be observed that in the case of the annealed samples (for different temperatures) the onset of the crystallization process is proved by the occurrence of the ferrite peaks; as the annealing temperature increases, the crystalline fraction of the ferrite increases.

![Figure 3. The X-Ray patterns diffraction of Fe₇₀Cr₄Ni₃Ga₄P₁₃Si₅C₃](image3.png)

Because it is common practice to perform magnetic measurements (either under closed or open magnetic circuit) on samples having some standard shapes (ring, rectangular frame, rod, ribbon, wire), the basic magnetic properties were examined (using the low frequency conventional induction method \[3\]) on the control sample in the as-quenched and annealed state; the results are shown in figures 4-5. The main values of the measured magnetic properties are summarized in table 1. The saturation magnetization ($M_{\text{sat}}$) was estimated to $676 \text{ kA m}^{-1}$ ($\mu_0M_{\text{sat}}=0.85 \text{ Tesla}$).

![Figure 4. Minor hysteresis loops of the sample in the as-quenched (left) and in the annealed state (right)](image4.png)
Figure 5. Normal magnetization curves (left) and the field dependence of the magnetic susceptibility (right) of the samples in the as-quenched state and subsequent to annealing.

Table 1. Values of the measured magnetic properties

| Magnetic properties                  | as quenched | annealed  |
|--------------------------------------|-------------|-----------|
| coercivity ($H_C$)                   | 106 Am$^{-1}$ | 102 Am$^{-1}$ |
| magnetic remanence ($M_r$)           | 95.5 kAm$^{-1}$ | 175 kAm$^{-1}$ |
| initial magnetic susceptibility ($\chi_a$) | 900         | 1500      |

From the as-measured quantities it follows that the examined samples exhibit soft magnetic behaviour, comparable to that of low Ni content Fe-based alloys or that of non-oriented grains Fe-3%Si; these results are somewhat under expectations. However, the magnetic remanence and initial susceptibility were substantially improved subsequent to annealing, presumably by thermally activated relaxation of some native internal stresses inherently occurring in the casting process (the role of the internal stresses in hindering the magnetization processes like domain wall movement and magnetization vector rotation is well known).

4. Conclusions

The experimental investigations on producing BMGs by mould casting have shown the possibility to obtain magnetic shields of complex shape. The preliminary researches regarding the utilization of Ni in small percents for enhancing the soft magnetic properties (especially the magnetic susceptibility) lead to satisfactory results, however less than expected. Annealing improves the soft magnetic properties. The optimization of the chemical composition (even with Ni-free alloys and small amount of Cr and/or P in order to improve the resistance to corrosion) and of the annealing technological parameters (even in transverse magnetic fields) are expected to lead to much better results for magnetic shielding purposes.

References
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