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Structural and magnetic properties of $Fe_{76}P_5(Si_{0.3}B_{0.5}C_{0.2})_{19}$ amorphous alloy

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ABSTRACT

Recently, bulk amorphous alloys were produced in the Fe–B–Si–P–C system with high glass forming ability, excellent magnetic properties and the advantage of containing no expensive glass-forming elements, such as Ga, Y, Cr or Nb, having, therefore, a good perspective of commercial applications. In the present work, the $Fe_{76}P_5(Si_{0.3}B_{0.5}C_{0.2})_{19}$ amorphous alloy prepared by two quenching techniques has been studied. Amorphous ribbons of about 40 μm thick were obtained by planar-flow casting together with cylinders having 1 and 2 mm diameter produced by copper mold injection casting. All the samples appear fully amorphous after X-ray diffraction analysis. A comprehensive set of thermal data (glass, crystallization, melting and liquidus temperatures) were obtained as well as a description of the melting and solidification processes. Mechanical microhardness tests showed that the samples have a hardness of 9.7 ± 0.3 GPa. Good soft-magnetic properties were obtained, including a high magnetization of 1.44 T and a low coercivity (4.5 A/m for ribbons and 7.5 A/m in the case of 1 mm rod samples, both in as-cast state). Thermomagnetic studies showed a Curie temperature around 665 K and the precipitation of new magnetic phases upon temperatures of 1000 K. Furthermore, the frequency dependence of magnetic losses at a fixed peak induction was studied. The results suggest the occurrence of a fine magnetic domain structure in bulk samples. The good soft magnetic properties of the bulk metallic glass obtained by copper mold casting for this particular Fe-based composition suggests possible applications in transformer cores, inductive sensors and other devices.

1. Introduction

Ferromagnetic metallic glasses sheets have shown an interesting combination of magnetic, mechanical and chemical properties. These materials have been produced since 1967 [1], but their thickness was limited to the range of few micrometers because of the high cooling rate required during solidification to hinder crystallization (about 10^6 K/s). Nowadays, the use of ferromagnetic amorphous alloys in efficient transformer cores is becoming more widespread, as they are the magnetically softest commercially available materials. However, cores made of thin sheets (usually about 40 μm thick) present some difficulties associated with the lack of self-sustainability. In addition, great core sizes are necessary, due to the gap between sheets that, added to after-annealing brittleness and sensitivity to mechanical stresses [2], make desirable the development of bulk amorphous alloys.

The first ferromagnetic bulk metallic glass alloy was obtained in 1995 [3] using a copper mold, with cooling rates lower than 100 K/s. Since then, much research effort has been devoted to enhance the saturation magnetization and to reduce the coercive field of ferromagnetic bulk metallic glasses. Such a goal is not an easy task, as tailoring the alloy composition with the goal of improving magnetic properties must preserve the requirements of a high glass forming ability (GFA).

Recently, bulk amorphous alloys with Fe–B–Si–P–C composition, containing no other metallic element than iron usually necessary to reach an adequate GFA, have been developed by Inoue et al. [4,5]. In this case, the saturation magnetization is not reduced by the addition of glass forming elements and reaches a value of 1.44 T. In particular, the developed alloys are based on the well-known Fe–B–Si system, where B has been partially replaced by non-metallic P and C, allowing the formation of amorphous rods with diameter up to 3 mm.

This paper is focused on the study of the alloy $Fe_{76}P_5(B_{0.5}C_{0.3}Si_{0.2})_{19}$ whose composition was found to be the optimum in the mentioned system [4]. Combining measurements of thermal stability and magnetic properties, including magnetic losses and temperature dependence of magnetization, a full picture on glass formation and possible applications was obtained.

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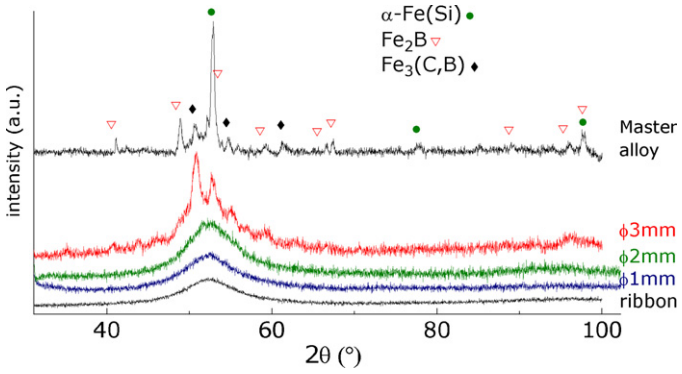

Fig. 1. XRD patterns of master alloy, ribbons and rods samples with different diameters.

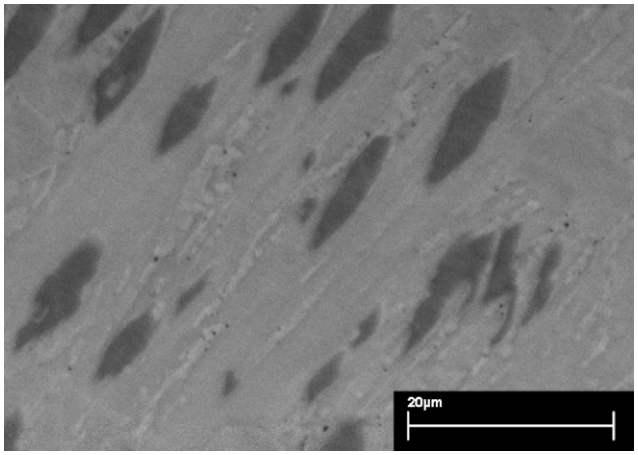

Fig. 2. Back-scattering SEM image of the master alloy.

2. Experimental

A master alloy of composition $Fe_{76}P_5(Si_{0.3}B_{0.5}C_{0.2})_{19}$ was prepared using Fe, Si and C pure elements (>99.9%) and Fe–B and Fe–P (>98.9%) ferroalloys in an arc melting furnace under Ar atmosphere. In order to optimize the C content and avoid mass losses during the melting process, a Fe–C alloy was previously prepared and its composition was evaluated by a calorimetric analysis of melting. The master alloy was remelted at least five times to get chemical homogeneity and the mass loss resulted to be less than 0.2%. Then, 40 μm thick and 4 mm width ribbons were produced by planar-flow casting, and cylindrical rods of 1, 2 and 3 mm diameter were obtained by injection copper mold casting technique.

X-ray diffraction (XRD) was employed to study the structure of the samples (Philips PW1830 diffractometer with Co-Kα radiation, λ = 1.7897 Å). Differential scanning calorimetry (DSC) studies were conducted in a Perkin Elmer Diamond – DSC device at a heating rate of 0.33 K/s and high temperature measurements were performed in a Setaram HTDSC at a heating rate of 0.083 K/s.

The microstructure of the obtained samples was examined with an optical microscope and with a scanning electron microscope (SEM-LeicaStereoscan 420). In addition, energy dispersive spectroscopy (EDS) was employed to verify the chemical composition of the samples. The density of bulk samples was measured by the Archimedes' technique using deionized water and, in the case of ribbon samples, the density was estimated by numerous size-weight measurements. Hardness measurements were performed using a Buehler Vickers microhardness tester at an applied load of 300 g for 15 s.

Magnetization vs. temperature experiments (at an applied field of 80 kA/m and a heating rate of 0.083 K/s), and saturation magnetization measurements (at a maximum field of 800 kA/m) were carried out in a Lake Shore 7400 Vibrating Sample Magnetometer (VSM). Inductive hysteresis loops and magnetic losses in the material were measured using a digital feedback wattmeter under sinusoidal induction waveform [6] in the frequency range from 1 to 500 Hz at a fixed magnetic induction of 0.6 T [7].

3. Results and discussion

X-ray diffraction patterns of master alloy, ribbon and bulk samples are shown in Fig. 1. Three different phases can be identified in the master alloy: an α-Fe(Si) solid solution, together with Fe_2B and $Fe_3(C,B)$ compounds. No crystalline phases were detected in as-quenched ribbon, 1 and 2 mm bulk samples. The 3 mm diameter bulk sample presents some crystalline peaks superimposed to the amorphous halo. These peaks correspond to the same phases present in the master crystalline alloy, as it can be noticed when comparing the two spectra.

A back-scattering SEM image of the master alloy is shown in Fig. 2. It reveals a primary phase that corresponds to Fe_2B compound and an eutectic mixture, likely formed by the α-Fe(Si) solid solution and the $Fe_3(C,B)$, as detected by XRD. In the case of bulk samples, back-scattering SEM images of the 1 mm diameter rod does not reveal any contrast and confirms the presence of a single amorphous phase, as shown in Fig. 3(a). In the case of 2 mm diameter sample, microcrystalline phases are observed on the surface of the rod (Fig. 3(b) and (c)). Some defects along the surface of the mold could have promoted the formation of nucleation sites and the successive growth of crystalline phases, but it is noteworthy that the core of the rod resulted fully amorphous in all samples. The optical micrograph of the 3 mm diameter sample (Fig. 3(d)) reveals an amorphous matrix (as observed by XRD) with some crystallites distributed in the inner region of the cylinder.

DSC traces of the ribbon and of 1 and 2 mm diameter rods are shown in Fig. 4(a). It can be seen that all samples show a similar behavior with the crystallization occurring in a single exothermic signal. The values of Curie, glass transition and crystallization temperatures (Tc, Tg, Tx, respectively) were determined and the results are reported in Table 1. The results confirm the formation of a glassy phase in the three different samples. However, the 2 mm rod presents a significantly lower heat of crystallization (ΔH_X) in comparison to the other samples; this fact is probably due to a partial crystallization during the casting process, as reported in Fig. 3(b). The sample shows a supercooled liquid region ($\Delta T_x = T_x - T_g$) of about 50 K, in good agreement with results obtained previously [4]. The HTDSC traces of the melting and solidification of the master alloy are reported in Fig. 4(b). The melting and liquidus temperatures (T_m and T_l, respectively) remain constant during continuous heating as well as during continuous cooling, indicating that no significant undercooling phenomenon occurs. The melting reaction ($T_m = 1232$ K) involves a mixture of phases presumably with the presence of the Fe_2B compound and is followed by a barely visible liquidus point at higher temperature. The DSC trace of solidification reveals a small exothermic peak due to the liquidus ($T_l = 1422$ K) followed by a broad shoulder and by partially overlapped exothermic reactions. This result suggests the formation of a complex structure far from eutectic. It is worth noting that compositions most favorable for glass formation are usually close to eutectics, even if, for multicomponent alloys, high GFA off-eutectic compositions have been reported. Combining the results obtained with the thermal analysis, the value of γ parameter, which is taken as an indicator of the GFA of the alloy [8], can be calculated. It turns out equal to 0.37, confirming the high GFA for this alloy composition.

Bulk amorphous samples showed a Vickers hardness value of about 9.7 ± 0.3 GPa, which was obtained after averaging several measurements, in good agreement with the high strength measured by compressive test [4]. Density was determined to be 7100 ± 50 kg/m^3 for bulk samples and 7000 ± 100 kg/m^3 for ribbons.

The magnetic hysteresis loops for the studied alloys are shown in Fig. 5. The differences in the susceptibility are due to the presence of a non-negligible demagnetizing field in the case of cylinders samples. All samples show the same value of saturation magnetization ($M_s \sim 1.44 \pm 0.02$ T) listed in Table 1. Inductive measurements at 1 Hz revealed a coercive field value, H_c, of 4.5, 7.5 and 20.5 A/m