Bulk Fe-Co-Ni-Zr-Nb-B Amorphous Materials

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(Fe,Co,Ni)-(Zr,M)-B (M=Nb,Ta,Ti) amorphous alloys exhibit a large supercooled liquid region (ΔTₜ) up to 90 K that have allowed us to prepare bulk amorphous samples with thickness up to 2 mm by mould casting method. These alloys have also good soft magnetic properties, i.e. saturation magnetisation (Bₛ) up to 1.1 T, coercive field (H_c) of 3 A/m and permeability of about 10000 at 500 Hz in the as-cast state. The Curie temperatures (T_C) of these amorphous alloys are between 513 and 573 K. The thermal and thermomagnetic annealing applied to (Fe,Co,Ni)-(Zr,M)-B₃₀ (M=Nb,Ta,Ti) amorphous samples cause the change of their amorphous structure and magnetic properties. The obtaining of these bulk amorphous alloys with soft magnetic properties will allow using them in many engineering applications.

Key words: large glass-forming ability, thermal stability, amorphous ferromagnetic alloys, sample thickness, soft magnetic properties

1. Introduction

Recently, it has been found some bulk amorphous alloys with good soft magnetic properties obtained by melt spinning and mould casting methods in multicomponent Fe-(Al,Ga)-(P,C,B,Sm,Ge), Co-(Al,Ga)-(P,C,B,Sm) and (Fe,Co,Ni)-(Zr,Nb)-B²⁻¹⁻³⁻⁻⁻ systems. The large glass-forming ability of these alloys that allowed their obtaining in bulk amorphous forms with thickness up to 1.5 mm, with low critical cooling rates between 10⁻² and 10⁻⁶ K/sec, is due to the high thermal stability of their supercooled liquid region. Comparatively, conventional Fe-B-Si and Co-Fe-B-Si amorphous alloys with soft magnetic properties require high critical cooling rates of about 10⁻³⁻¹⁻⁰⁻⁶ K/sec and can be obtained in amorphous state under the shape of ribbons with thickness up to 0.050 mm and wires with diameters up to 0.120 mm. It was found that (Fe,Co,Ni)-(Zr,Nb)-B⁴⁻⁻⁻⁻ amorphous alloys have a large supercooled liquid region (ΔTₜ), defined by the difference between crystallisation temperature (Tₙ) and glass transition temperature (Tₐ), of about 85 K. This supercooled liquid region is about 20 K and 40 K higher than ΔTₜ of the Fe-(Al,Ga)-(P,C,B,Sm,Ge) and Co-(Al,Ga)-(P,C,B,Sm) amorphous alloys, respectively. One can observe that all the systems, in which were prepared these bulk amorphous alloys contain more than three components with different atomic sizes and large negative heats of mixing. As a result of lower atomic mobility of the components, the nucleation processes are delay. The critical cooling rates required to obtain amorphous phase are directly related to electrical and magnetic properties of the samples. It is known that Fe-based amorphous magnetic alloys exhibit high saturation magnetisation, low core losses and high electrical resistivity, while Co-based amorphous magnetic alloys have near zero magnetostriction and the highest permeability. Subsequently, we present our recent results on the preparation and study of the soft magnetic properties of the (Fe,Co,Ni)-(Zr,M)-B (M=Nb,Ta,Ti) amorphous alloys. We also discuss the dependence of the thermal stability and soft magnetic properties on the composition of amorphous samples and the changes of the atomic structure and of electric and magnetic properties of the samples having different dimensions after various annealing.

2. Experiment

Fe₆₀Co₃₀Ni₁₀Zr₁₅Nb₂₅B₅₀, Fe₆₀Co₃₀Ni₁₀Zr₁₅Nb₂₅Ta₁₅B₅₀ and Fe₆₀Co₃₀Ni₁₀Zr₁₅Nb₂₅Ta₁₅B₅₀ alloys were prepared by arc melting a mixture of pure Fe, Co, Ni, Zr, Nb, Ta, Ti and B crystals in argon atmosphere. We obtained amorphous ribbons with thickness ranging from 0.025 mm to 0.120 mm by melt-spinning method in argon atmosphere. The partially vitrified bulk samples, with thickness up to 2 mm, were obtained by mould casting and suction casting in vacuum or argon atmosphere. The structure of all samples was examined by X-ray diffractometry (XRD). The glass transition temperature (Tₙ), crystallisation temperature (Tₙ) and supercooled liquid region (ΔTₜ) were determined from differential thermal analysis (DTA) curves at a heating rate of 20 K/min. The magnetic behaviour of the ribbons and bars was measured with a vibrating sample magnetometer (VSM) under a maximum applied field of about 1200 kA/m and by an a.c. fluxmetric method. The dependence of the saturation magnetisation on temperature for the as-cast state and after crystallisation was plotted also with the VSM. The permeability at 500 Hz, electrical resistivity and the variation of electrical and magnetic properties during and after different annealing were evaluated with the same a.c. fluxmetric equipment. The saturation magnetostriction constant (λₜ) was measured by small angle magnetisation rotation (SAMR) method.

3. Results and discussion

In figure 1 the DTA curves are plotted for (Fe,Co,Ni)-(Zr,M)-B₃₀ (M=Nb,Ta,Ti) amorphous alloys. One can observe that Tₙ ranges from 728 K to 768 K for Fe₆₀Co₃₀Ni₁₀Zr₁₅Nb₂₅Ta₁₅B₅₀ and Fe₆₀Co₃₀Ni₁₀Zr₁₅Nb₂₅B₅₀ amorphous alloys, respectively, while the crystallisation temperature (Tₙ) is ranging between 818 K and 848 K. The DTA curves exhibit only one endothermic peak according to the glass transition and one sharp exothermic peak corresponding to the crystallisation. This behaviour
indicates that the crystallisation is due to the simultaneous precipitation of all crystalline phases, which explains the large glass-forming ability of these alloys. The substitution of 1.5 % at Zr with Ti or Ta in Fe<sub>56</sub>Co<sub>7</sub>Ni<sub>7</sub>Zr<sub>7</sub>Nb<sub>6</sub>B<sub>20</sub> amorphous alloy leads to the increase of supercooled liquid region. Therefore, the supercooled liquid region is of about 80 K, 85 K and 90 K for Fe<sub>56</sub>Co<sub>7</sub>Ni<sub>7</sub>Zr<sub>7</sub>Nb<sub>6</sub>B<sub>20</sub>, Fe<sub>56</sub>Co<sub>7</sub>Ni<sub>7</sub>Zr<sub>7</sub>Nb<sub>6</sub>Ta<sub>7</sub>B<sub>20</sub> and Fe<sub>56</sub>Co<sub>7</sub>Ni<sub>7</sub>Zr<sub>7</sub>Nb<sub>6</sub>Ti<sub>7</sub>B<sub>20</sub> amorphous alloys, respectively. These are due to the atomic sizes of the different atomic components which increase in the following order: Ta>Zr>Ti>Nb, and lead to the extension of the short-range order in amorphous structure. As a consequence the crystallisation is suppressed in the supercooled liquid region. The large glass-forming ability due to the large values of supercooled liquid region shows that these alloys can be obtain as bulk amorphous samples in the as-cast state. The amorphous structure of the samples was confirmed by X-ray diffractometry. The X-ray diffraction patterns show only one main halo peak and no sharp peak specific to the crystalline phase, even for the ribbons with thickness above 0.100 mm.

The changes of the samples’ dimensions and basic composition of Fe<sub>56</sub>Co<sub>7</sub>Ni<sub>7</sub>Zr<sub>7</sub>Nb<sub>6</sub>B<sub>20</sub> alloy, lead to the variation of the magnetic characteristics. Thus, the saturation magnetisation exhibits different values depending on the composition and dimensions of the samples. For Fe<sub>56</sub>Co<sub>7</sub>Ni<sub>7</sub>Zr<sub>7</sub>Nb<sub>6</sub>B<sub>20</sub> amorphous alloy, the value of the saturation magnetisation increases from 0.97 T for amorphous ribbons with thickness of about 0.090 mm obtained by melt-spinning method up to 1.06 T for partially vitrified bars with thickness of about 2 mm prepared by suction casting method. For Fe<sub>56</sub>Co<sub>7</sub>Ni<sub>7</sub>Zr<sub>7</sub>Nb<sub>6</sub>Ta<sub>7</sub>B<sub>20</sub> amorphous ribbons with thickness of 0.120 mm, the saturation magnetisation has the value of about 0.89 T, while for Fe<sub>56</sub>Co<sub>7</sub>Ni<sub>7</sub>Zr<sub>7</sub>Nb<sub>6</sub>Ti<sub>7</sub>B<sub>20</sub> amorphous ribbons with thickness of 0.030 mm, the value of the saturation magnetisation is about 1.06 T.

Figure 2 presents the thermomagnetic curves of Fe<sub>56</sub>Co<sub>7</sub>Ni<sub>7</sub>Zr<sub>7</sub>Nb<sub>6</sub>Ti<sub>7</sub>B<sub>20</sub> amorphous ribbons. From these curves we determined the Curie temperatures of the amorphous and crystalline phases as about 560 K and 1100 K respectively. From Fig. 2 one can observe that the saturation magnetisation of the amorphous ribbons starts to increase with the crystalline phase’ precipitation, than reaching a maximum value of about 1.06 T, which is the same with that obtained for the partially vitrified bars having up to 2 mm in thickness.

Figure 3 shows the changes of the magnetisation after 300 s of thermal annealing at different temperatures for Fe<sub>56</sub>Co<sub>7</sub>Ni<sub>7</sub>Zr<sub>7</sub>Nb<sub>6</sub>Ti<sub>7</sub>B<sub>20</sub> amorphous ribbon of about 35 µm in thickness. One can see from the figure that the profile of the thermomagnetic curves is changing after annealing at temperatures above 753 K due to the nucleation process.

The thermal annealing applied to the amorphous samples at temperatures below 753 K leads to the structural relaxation of the ribbon and, in the same time, to a slight improvement of their soft magnetic properties. The highest degree of structural relaxation is obtained after performing the thermal annealing at 753 K for 300 s, this being also confirmed by the maximum value of the permeability, as it can be seen in Fig. 4.
The magnetic permeability, which has the value of 10000 in as-cast state, increases with about 10% at the highest structural relaxation, and then exhibit a decrease as the result of the crystalline phase precipitation.

For amorphous samples with larger dimensions the structural relaxation is reached in the as-cast state. In these samples can occur slight movements of the atoms from their initial positions due to their large dimensions. The structural relaxation in the thick samples is mainly due to their obtaining process at low critical cooling rates.

Figure 5 presents the changes of the electrical resistance of FeCoNiZr3Nb3B20 amorphous samples, for successive heating at different temperatures. The thermal annealing at 873 K, above the temperature at which begin the process of crystallisation determines a decrease of the electric resistance.

From the determined value of the electrical resistance of FeCoNiZr3Nb3B20 amorphous alloy, we calculated the electrical resistivity as about 1.85 $\mu\Omega$-m. This value is much greater than that calculated for the conventional soft magnetic Fe-Si-B amorphous alloys.

The value for the saturation magnetostriction constant ($\lambda_s$), determined experimental by the small angle magnetisation rotation method is of about $7 \times 10^{-6}$, while the $\lambda_s$ value obtained for amorphous Fe-Si-B alloy is $36 \times 10^{-6}$. This value is relatively low comparatively with those reported for these kinds of alloys and is in agree with the small value of coercive field of 5 A/m and the high value of permeability obtained for these amorphous alloys.

4. Conclusions

The (FeCoNi)(Zr,M)-B (M=Nb,Ta,Ti) amorphous alloys obtained in different bulk forms and under the shape of ribbons with different thickness exhibit a large glass-forming ability due to their large supercooled liquid region. The highest value for the supercooled liquid region ($\Delta T_L$) of about 90K was obtained for the FeCoNiZr5Nb3Ti3B20 amorphous alloy, which also exhibit good soft magnetic properties in as-cast state. Thus, this amorphous alloy has saturation magnetisation of about 1.06 T, coercive field up to 5 A/m, Curie temperature up to 573 K and permeability between 10000 and 15000 at 500 Hz. The induced structural relaxation in the amorphous samples with thickness up to 0.100 mm leads to the improvement of their magnetic properties. By thermal annealing at temperatures over a certain value, a decrease of soft magnetic properties is obtained due to the precipitation of the crystalline phases and, therefore, to the decrease of the glass-forming ability.

The obtaining of amorphous multicomponent alloys with large glass-forming ability and good soft magnetic properties makes possible the development of the engineering applications that require bulk amorphous samples in different forms.

References