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Preparation and Properties of FeZrB Amorphous-Nanocrystalline Soft Magnetic Alloy

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Abstract: $Fe_{68}Zr_{20}B_{12}$ amorphous alloy was prepared by mechanical alloying(MA) method and annealed at different temperatures. Microstructures and magnetic properties of $Fe_{68}Zr_{20}B_{12}$ alloys as-milled and annealed at 693, 843, 943 and 993 K were studied. The raw powders(Fe, Zr, B) formed *b. c. c.* α-Fe solid solution at early stages of MA and then transformed into amorphous alloy. Grain size(D) of $Fe_{68}Zr_{20}B_{12}$ alloys increases with increasing annealing temperature and keeps at nanometer level. The specific saturation magnetization(σ_s) increases with increasing annealing temperature from 300 K to 943 K, and then decreases with annealing temperature at 993 K because of the precipitation of Fe_3B.

Key words: FeZrB amorphous-nanocrystalline alloy; grain size; specific saturation magnetization

1 Introduction

Fe-Zr-B amorphous-nanocrystalline alloy characterized by low coercive and high saturation magnetization[1] is one of the most extensively studied soft magnetic materials. Many researchers attach importance to the study of crystallization mechanism, thermal stabilization and magnetic properties[2-4]. However, the preparation of Fe-M-B (M=Zr, Nb, Hf) alloys usually adopts melt spinning, and study on magnetic property of Fe-M-B alloys focuses on coercivity.

In the present work, $Fe_{68}Zr_{20}B_{12}$ amorphous alloy was prepared by mechanical alloying(MA) and annealed at 693, 843, 943 and 993 K for 1 h. The formation of $Fe_{68}Zr_{20}B_{12}$ amorphous alloy was studied, and the influence of annealing on grain size (D) and specific saturation magnetization was investigated.

2 Experimental

Samples with nominal composition of $Fe_{68}Zr_{20}B_{12}$ were prepared by mechanical alloying (MA) technique. Fe, Zr and B powders with a purity of more than 99.5% were mixed and milled under an argon atmosphere using GN-2 planetary ball mill. The ball-to-power weight ratio was 30:1. After different milling times (5 h, 15 h, 45 h, 60 h), the mechanical attrition was interrupted and a small quantity of powder was taken out for further characterization. The $Fe_{68}Zr_{20}B_{12}$ alloy milled for 60 h was annealed at 693, 843, 943 and 993 K for 1 h at heating-up rate of 10 K/min under Ar atmosphere.

The microstructure of the samples was analyzed by X-ray diffraction (XRD, Rigaku D/max 2500/PC CuKα) and transmission electron microscopy (TEM, JEM-2100E, 200 kV). The crystallization temperature was measured by differential thermal analysis (DTA, PE TG/DTA-6300). The magnetic property was measured by vibrating sample magnetometer (VSM, Lake Shore M7407).

3 Results and Discussion

Fig.1 shows the XRD patterns of $Fe_{68}Zr_{20}B_{12}$ alloy after different milling time. The diffraction peaks decrease in intensity and become broader with the increase of milling time, which is related to the gradual refinement of grains and the increase of lattice strain[5]. When the milling time reaches 15 h, the diffraction peaks of Zr and B vanish, which confirms the forming of α-Fe solid solution. After 60 h of milling, a broad diffraction hump appears, which confirms the formation of amorphous phase. Based on the above-mentioned analysis, the formation of $Fe_{68}Zr_{20}B_{12}$ amorphous alloy experiences two distinct stages raw powders(Fe, Zr, B) → b. c. c. α-Fe solid solution→amorphous.

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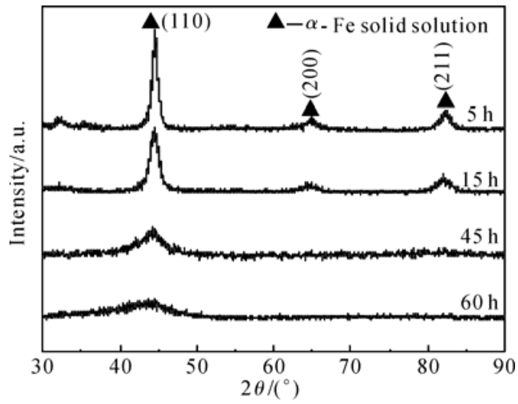

Fig.1 XRD patterns of $Fe_{68}Zr_{20}B_{12}$ alloy as a function of MA time

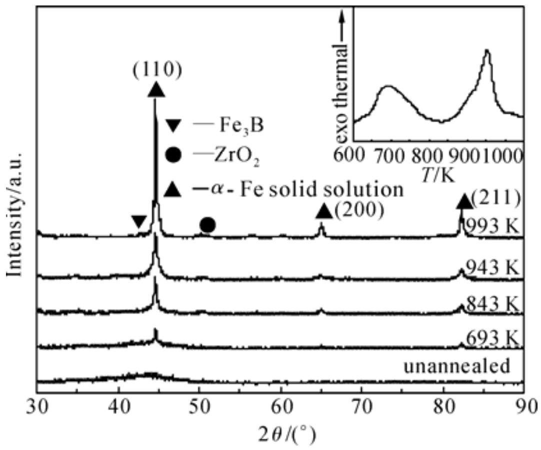

Fig.2 XRD patterns of $Fe_{68}Zr_{20}B_{12}$ alloy milled for 60 h and annealed at 693, 843, 943 and 993 K for 1h. Insert shows the DTA curve of $Fe_{68}Zr_{20}B_{12}$ alloy milled for 60 h

According to the DTA curve of amorphous alloy, as inserted in Fig.2, the amorphous sample was annealed at 693, 843, 943 and 993 K. The XRD patterns of the samples milled for 60 h and annealed at different temperatures are shown in Fig.2. When the annealing temperature reaches 693 K, α -Fe phase precipitates from the amorphous matrix. Further increase of annealing temperature results in the more precipitation of crystalline phase and the gradual disappearance of amorphous matrix. When annealing temperature reaches 993 K, Fe_3B and ZrO_2 precipitate. The appearance of ZrO_2 may be due to the oxidation during milling[6].

Fig.3 shows the TEM images and the selected area electron diffraction (SAED) patterns of the sample annealed at 843 K. It can be seen that nanocrystalline phases are formed. The SAED pattern indicates that the sample annealed at 843 K contains amorphous and precipitated phases. The precipitated phases contain α-Fe together with other phases.

Fig.4 shows the microstructure of $Fe_{68}Zr_{20}B_{12}$ alloys annealed at 693, 843, 943 and 993 K. It can be seen that grain size increases with increasing annealing temperature.

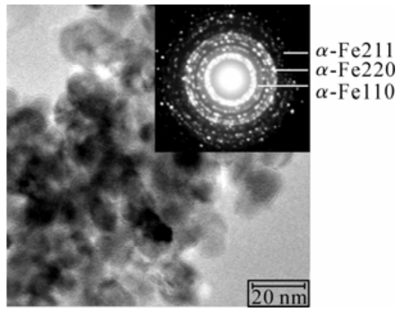

Fig.3 TEM image and selected-area electron diffraction pattern of the sample annealed at 843 K

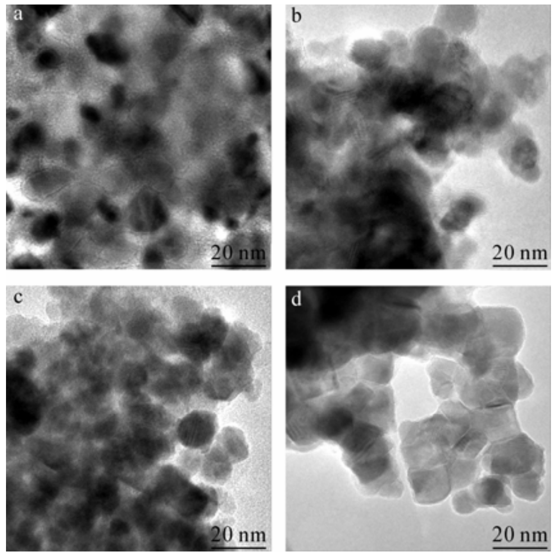

Fig.4 Microstructure of $Fe_{68}Zr_{20}B_{12}$ alloys annealed: (a) at 693 K; (b) at 843 K; (c) at 943 K; (d) at 993 K

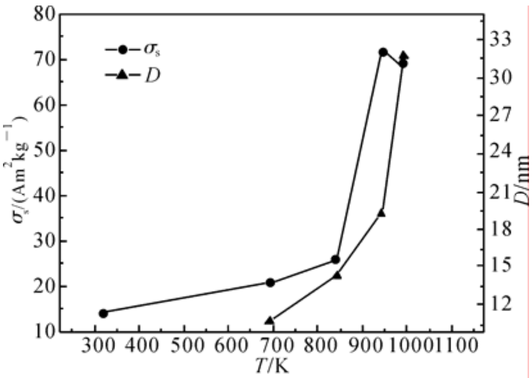

Fig.5 Variation of grain size (D) and specific saturation magnetization(σ_s) of $Fe_{68}Zr_{20}B_{12}$ alloy milled for 60 h as a function of annealing temperature

Fig.5 shows the variation of grain size (D) and specific saturation magnetization(σ_s) of $Fe_{68}Zr_{20}B_{12}$ amorphous alloys as a function of annealing temperature. The grain size increases with increasing temperature and keeps at nanometer level. The variation of σ_s is more complicated with the increase of annealing temperature. σ_s increases slowly in the initial stage, then increases sharply and reaches 72.3 Am^2/kg at 943 K. However, it decreases at 993 K.

As can be seen from Fig.5, grain size increases slowly in the initial stage (below 843 K), then increases sharply with the increase of annealing temperature and reaches 31.7 nm at 993 K. Atom diffusion and nucleation rate are low in the initial stage of crystallization, so grain size increases slowly in the initial stage (below 843 K). With further increase of annealing temperature, the energy offered by outside can overcome the obstacle of nucleation. Therefore, a lot of crystal nucleuses come into being continuously, which makes nucleation quick and grain size increase.

The variation in specific saturation magnetization may be related to the competition between the ferromagnetic and antiferromagnetic exchange interaction. The specific saturation magnetization of the as-milled alloy is low, which may be due to the formation of antiferromagnetic coupling between Fe and Zr with long time milling[7]. When annealing temperature is below 843 K, a small amount of α-Fe crystalline will precipitate. The competition between ferromagnetic and antiferromagnetic exchange interactions causes the slight increase of σ_s. According to the nearest-neighbor coordination model, the magnetic moment of iron atoms is assumed to depend on the number of magnetic atoms and non-magnetic atoms in the first nearest-neighbor shell. Above 843 K, more α-Fe crystalline precipitates, and a Zr and B depleted environment are formed around Fe atoms[8]. This led to the sharp decrease of antiferromagnetic exchange interaction and the increase of ferromagnetic exchange interaction. Therefore, the σ_s increases sharply and reaches 72.3 Am^2/kg at 943 K. Due to the precipitation of Fe_3B compound, σ_s decreases at 993 K[9].

4 Conclusions

a) The formation of $Fe_{68}Zr_{20}B_{12}$ amorphous alloy experiences two stages: the raw powders(Fe, Zr, B) form the *b. c. c.* α-Fe solid solution and then transform to amorphous alloy.

b) Grain size increases continuously with the increase of annealing temperature, and reaches 31.7 nm at 993 K.

c) The variation of σ_s is complicated. With the increase of annealing temperature, σ_s increases slowly in the initial stage, then increases sharply and reaches 72.3 Am^2/kg at 943 K. Due to the precipitation of Fe_3B compound, σ_s decreases at 993 K.

References

[1] A Makino, T Hatanai, A Inoue, *et al*. Nanocrystalline Soft Magnetic Fe-M-B(M=Zr, Hf, Nb) Alloys and their Applications[J]. *Mater. Sci. Eng.,* 1997, A226-228: 594-602

[2] A Makino, K Suzuki, A Inoue, *et al*. Magnetic Properties and Microstructure of Nanocrystalline bcc Fe-M-B(M=Zr, Hf, Nb) Alloys[J]. *J. Magn. Magn. Mater,* 1994, 133: 329-333

[3] B G Shen, R F Xu, G J Zhao, *et al*. Effect of Composition on Curie Temperature, Magnetic Moment, and High-field Susceptibility of Amorphous $Fe_{90-x}M_xZr_{10}$ (M=V, Cr, Mn, Co, Ni, Cu, Si, and B) Alloys[J]. *Phys. Rev. B*, 1991, 43(13): 11005-11009

[4] M N Gona, S Yanase, S Hashi, *et al*. Magnetoimpedance Effect in Nanocrystalline FeZrNbB Ribbons[J]. *J. Magn. Magn. Mater.*, 2003, 254: 466-468

[5] A Grabias, M Kopcewicz, D Oleszak. Phase Transformations in the Fe(Co, Ni)ZrB Alloys Induced by Ball Milling[J]. *J. Alloys. Compounds,* 2002, 339: 221-229

[6] Y J Liu, I T H Chang, M R Lees. Influences of Oxide Phases on the Coercivity of Mechanically Alloyed Multicomponent Fe-based Amorphous Alloys[J]. *Scripta Mater.*, 2001, 44(12): 2729-2734

[7] S L He, K Y He. Magnetic Properties of $(Fe_{1-x}Co_x)_{84}Zr_{3.5}Nb_{3.5}B_8Cu_1$($x$=0-0.8) Amorphous Alloy at High and Low Temperature[J]. *Metallic Functional Materials*, 2002, 9(3): 34-37

[8] Y Hu, L Lin, K C Chan, M X Pan, *et al*. The Effect of Crystallization on Microstructure and Magnetic Properties of $Fe_{61}Co_7Zr_{9.5}Mo_5W_2B_{15.5}$ Bulk Metallic Glass[J]. *Materials Letters*, 2006, 60: 1080-1084

[9] Q Z Zhi, J J Wang, W Z Chen, *et al*. Structure and Magnetic Properties of Nanocrystalline Fe-Nb-B Alloys[J]. *Journal of Northeastern University*, 2004, 25(1): 1072-1075