Crystallization processes and magnetic properties of FeCoZrMB (M=Nb, V, Cr, Ti) amorphous alloys

W Q Yu¹² and L P Lu¹³

¹School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun 130022, China
²National Demonstration Center for Experimental Physics Education, Jilin Normal University, Siping 136000, China

E-mail: luliping771219@126.com

Abstract. A series of Fe₄₀Co₇₉Zr₄₆M₆B₁₀ (M=Nb, V, Cr, Ti, W, Al) alloys were prepared using melt-spinning. The thermal curve, structure and magnetic property of alloys are examined. Because of different negative heat of mixing between elements, only Fe₄₀Co₇₉Zr₄₆M₆B₁₀ (M=Nb, V, Cr, Ti) alloys form amorphous structure. These amorphous alloys are annealed at different temperatures under vacuum conditions. The crystallization processes of four amorphous alloys are similar. In the primary stage of crystallization process, only α-Fe(Co) phase precipitates and Co element mainly distributes in the residual amorphous. For the four alloys after annealing at 550°C, there is a few differences in saturation magnetization (Mₛ) and coercivity (Hₘ) due to their different microstructures.

1. Introduction

Since the excellent soft magnetic properties, Fe-based nanocrystalline soft magnetic materials have been attracted lots of attentions for a long time. Among the Fe-based nanocrystalline soft magnetic alloys, Hitperm FeCoMB(Cu) alloys as competitive materials for high temperature soft magnetic applications have been developed and attracted lots of attentions in recent years [1-4]. The magnetism of the materials is closely related to their microstructures composed by α-FeCo nanocrystals embedded in amorphous matrix. Grain size is one of the important factor affecting the properties of nanocrystalline soft magnetic materials. Within the exchange correlation length, coercivity (Hₑ) of nanocrystalline alloys with the two-phase structure follows a D⁶ power law [5]. Moreover, Hₑ is also related to the grain-size distribution of α-Fe nanograins [6].

In order to improve the performance of alloys, a wide variety of elements have been added into Fe-based alloy system. Adding transition metal can greatly improve and adjust their microstructure and performance, such as Nb [7-9], V [10,11], Cr [12-14], Ti [15,16], W [17,18] and Al [19-22] element. Nb and W are the most effective elements which can refine the grain size during annealing treatment [17]. The addition of V can improve the amorphous forming ability and the bending ductility of the alloys [10]. Minor Cr addition significantly improves the corrosion resistance [14]. Doping Ti can decrease core loss mainly by reducing its hysteresis loss [16]. Al doping results in the reduction of grain size and coercivity [22].

In this paper, the Fe₄₀Co₇₉Zr₄₆M₆B₁₀ (M=Nb, V, Cr, Ti, W, Al) alloy system is based on the addition of different transition metals to a conventional Hitperm-like amorphous alloy system. The crystallization processes and magnetic properties of Fe₄₀Co₇₉Zr₄₆M₆B₁₀ alloys with different transition
metal will be discussed in detail.

2. Experimental

2.1. Preparation

Ingots of Fe$_{40}$Co$_{40}$Zr$_{8}$M$_{2}$B$_{10}$ (M=Nb, V, Ti, W, Al) alloys were prepared by arc melting the mixtures of the pure metals above 99.9% and pure B (99.999%), and the ingots were remelted with the magnetic stirring for 4 times to ensure the homogeneity under vacuum conditions. Then alloy ribbons were prepared using a single roller melt-spinning equipment with copper wheel rotating at a surface velocity of 38 m/s. Ribbons were 1 cm in width and about 30 μm in thickness. Fe$_{40}$Co$_{40}$Zr$_{8}$M$_{2}$B$_{10}$ [M=Nb(#1), V(#2), Cr(#3), Ti(#4)] amorphous alloys were post-annealed at 500, 550, 600, 650 and 700°C for 1h under vacuum conditions, respectively.

2.2. Measurements

Thermal curves were performed by differential scanning calorimetry (DSC, Diamond) instrument. Structures of alloys were identified by transmission electron microscopy (TEM, JEM-2100E) and X-ray diffraction (XRD, D/max 2500/PC, 40 kV, 200 mA, Cu-Kα, λ=1.5406 Å). Thin-film TEM specimens were prepared by rgon ion beam thinning technique. Magnetic hysteresis loops were examined by vibrating sample magnetometer (VSM, Lake Shore M7407).

3. Results and discussion

3.1. Glass forming ability of alloys

Figure 1 gives the XRD patterns of Fe$_{40}$Co$_{40}$Zr$_{8}$M$_{2}$B$_{10}$ (M=Nb, V, Cr, Ti, W, Al) alloys as-quenched. Fe$_{40}$Co$_{40}$Zr$_{8}$W$_{2}$B$_{10}$ alloy has large negative heats of mixing between Al element and other elements. However, the (200) diffraction peak of α-Fe(Co) phase can be observed. It should be that Al has a large saturation vapor pressure and evaporates during the smelting process. For Fe$_{40}$Co$_{40}$Zr$_{8}$M$_{2}$B$_{10}$ (M=Nb, V, Cr, Ti) alloys, the negative heat of mixing between M=M=Nb, V, Cr, Ti) and other elements are bigger and form amorphous structure in the as-quenched state.
For the as-quenched alloys which is not fully amorphous, the existing grains will increase rapidly after heat treatment, resulting in the great difference in grain size. Relatively uniform grains can be obtained by annealing amorphous alloys. Therefore, we mainly study the crystallization processes and magnetic properties of Fe₄₀Co₄₀Zr₈M₂B₁₀ (M=Nb, V, Cr, Ti) amorphous alloys. DSC traces of Fe₄₀Co₄₀Zr₈M₂B₁₀ (M=Nb, V, Cr, Ti) alloys as-quenched are shown in figure 2. The glass forming ability (GFA) can be calculated by the temperature span of the supercooled liquid region ΔTx (difference between Tg and To) [24]. The glass transition temperature(Tg), onset crystallization temperature (To), supercooled liquid region ΔTx and crystallization peak temperature (Tp) can be obtained by DSC.

Table 1. The values of heat of mixing between M and other elements (kJ/mol).

| M   | Fe  | Co  | Zr  | B   |
|-----|-----|-----|-----|-----|
| Nb  | -16 | -25 | 4   | -54 |
| V   | -7  | -14 | -4  | -42 |
| Cr  | -1  | -4  | -12 | -31 |
| Ti  | -17 | -28 | 0   | -58 |
| W   | 0   | -1  | -9  | -31 |
| Al  | -11 | -19 | -44 | 0   |

Table 2 gives a list of Tg, To, ΔTx and Tp of four kinds of amorphous alloys. The wider the ΔTx is, the greater the GFA is. Both ΔTx and Tp of the alloys have the following relations: ΔTx₈₃>ΔTx₈₂>ΔTx₈₁>ΔTx₉₄ and Tp₉₄>Tp₈₂>Tp₈₁>Tp₉₃. The GFA of four amorphous alloys has the following relations: GFA₈₄>GFA₈₃>GFA₈₂>GFA₉₃. The negative heat of mixing between M(M=Nb, V, Cr, Ti) and other elements have the following relations: H₄₃>H₄₃>H₄₂>H₄₁. Therefore, the GFA of four kinds of alloy presents the results above.

Table 2. Tg, To, ΔTx and Tp of Fe₄₀Co₄₀Zr₈M₂B₁₀ (M=Nb, V, Cr, Ti) amorphous alloys.

|                | Fe₄₀Co₄₀Zr₈Nb₂B₁₀ (#1) | Fe₄₀Co₄₀Zr₈V₂B₁₀ (#2) | Fe₄₀Co₄₀Zr₈Cr₂B₁₀ (#3) | Fe₄₀Co₄₀Zr₈Ti₂B₁₀ (#4) |
|----------------|------------------------|-----------------------|------------------------|------------------------|
| Tg/°C          | 505.0                  | 505.5                 | 506.3                  | 496.8                  |
| To/°C          | 540.1                  | 524.7                 | 522.2                  | 532.6                  |
| ΔTx/°C         | 35.1                   | 19.2                  | 15.9                   | 35.8                   |
| Tp/°C          | 558.3                  | 543.0                 | 539.6                  | 551.7                  |
3.2. Crystallization processes of alloys

XRD patterns of Fe₄₀Co₄₀Zr₃MₓB₁₀ (M=Nb, V, Cr, Ti) alloys after annealing are shown in figure 3. The crystallization processes of these four amorphous alloys are similar. After annealing at 500°C, only α-Fe(Co) phase is formed. The lattice constants of α-Fe(Co) of Fe₄₀Co₄₀Zr₃MₓB₁₀ (M=Nb, V, Cr, Ti) alloys after annealing at 550°C are 2.860, 2.859, 2.860 and 2.862, respectively. The lattice constants of pure α-FeCo and α-Fe are 2.8550 and 2.8664 Å [25], respectively. It is deduced that Co element in the alloys mainly distributes into the remained amorphous. It is attributed to the big heat of mixing between Co element and Zr element (-41 kJ/mol). More and more α-Fe(Co) nanocrystals precipitate and the diffraction peaks intensity increases with the increase of annealing temperature. After annealing at 650°C, ZrCo₃B₂ phase forms. The precipitation of ZrCo₂B₂ phase at high temperature is due to that the Co element in residual amorphous matrix reacts with the Zr and B elements distributed in the residual amorphous matrix [26]. The crystalline phases of alloys precipitated at the final annealing stage are the same and identified to be α-Fe(Co), ZrCo₂B₂ and Fe(Co)₃Zr phases. The crystallization processes of these four amorphous alloys are similar: amorphous→remained amorphous+α-Fe(Co)→α-Fe(Co)+ZrCo₂B₂+Fe(Co)₃Zr.

![XRD patterns of four kinds of alloys after annealing at different temperatures.](image)

**Figure 3.** XRD patterns of four kinds of alloys after annealing at different temperatures. (a) Fe₄₀Co₄₀Zr₃Nb₂B₁₀, (b) Fe₄₀Co₄₀Zr₃V₂B₁₀, (c) Fe₄₀Co₄₀Zr₃Cr₂B₁₀, (d) Fe₄₀Co₄₀Zr₃Ti₂B₁₀.

Figure 4 shows the TEM images, SAED patterns and PSD of the alloys after annealing at 550°C. For the four kinds of alloys after annealing at 550°C, the nanocrystals are surrounded by a residual amorphous matrix. SAED patterns all show the crystallization phase is only α-Fe(Co). They all form a typical two-phase structure characterized by bcc α-Fe(Co) nanocrystalline grains embedding in the amorphous matrix. The volume fraction of Fe₄₀Co₄₀Zr₃Nb₂B₁₀ alloy is the lowest and the crystallization volume fraction of Fe₄₀Co₄₀Zr₃Cr₂B₁₀ alloy is the biggest. The crystallization volume fraction of Fe₄₀Co₄₀Zr₃MₓB₁₀ (M=Nb, V, Cr, Ti) alloys have the following relations: V₃Nb > V₃V > V₃Cr > V₃Ti. According to the grain size distribution, the grain size [α-Fe(Co)] of Fe₄₀Co₄₀Zr₃MₓB₁₀ (M=Nb, V, Cr, Ti) alloys are 7.8, 7.2, 6.9 and 8.2 nm, respectively. Furthermore, Fe₄₀Co₄₀Zr₃V₂B₁₀ and Fe₄₀Co₄₀Zr₃Ti₂B₁₀ alloys nanocrystals distribute inhomogeneously. During the annealing process of
amorphous alloy, the transition metal will reject from α-Fe particles and accumulate in the residual amorphous matrix, thus reducing the growth of α-Fe particles. The difference in the atomic radius and electronegative between elements leads to the differences in grain refinement.

Figure 4. Left is the transmission electron microscope (TEM) images and selected-area electron diffraction (SAED) patterns of the alloys after annealing at 550°C; Right is the grain size distribution (PSD) of the alloys after annealing at 550°C. (a, a’) Fe$_{40}$Co$_{40}$Zr$_8$Nb$_2$B$_{10}$, (b, b’) Fe$_{40}$Co$_{40}$Zr$_8$V$_2$B$_{10}$, (c, c’) Fe$_{40}$Co$_{40}$Zr$_8$Cr$_2$B$_{10}$, (d, d’) Fe$_{40}$Co$_{40}$Zr$_8$Ti$_2$B$_{10}$
3.3. Magnetic properties of alloys

The magnetic hysteresis loops of Fe_{40}Co_{40}Zr_{8}M_{2}B_{10} (M= Nb, V, Cr, Ti) alloys are shown in figure 5. Four kinds of alloys all show good soft magnetic property from magnetic hysteresis loops. Table 3 gives the saturation magnetization ($M_s$) and coercivity ($H_c$) of Fe_{40}Co_{40}Zr_{8}M_{2}B_{10} (M= Nb, V, Cr, Ti) alloys annealed at 550°C.

![Figure 5. Magnetic hysteresis loops of Fe_{40}Co_{40}Zr_{8}M_{2}B_{10} (M= Nb, V, Cr, Ti) alloys annealed at 550°C.](image)

**Table 3.** $M_s$ and $H_c$ of Fe_{40}Co_{40}Zr_{8}M_{2}B_{10} (M= Nb, V, Cr, Ti) alloys annealed at 550°C.

|          | $M_s$(emu/g) | $H_c$(Oe) |
|----------|--------------|-----------|
| Fe_{40}Co_{40}Zr_{8}Nb_{2}B_{10} (#1) | 135.4       | 22.4      |
| Fe_{40}Co_{40}Zr_{8}V_{2}B_{10} (#2) | 159.0       | 24.6      |
| Fe_{40}Co_{40}Zr_{8}Cr_{2}B_{10} (#3) | 169.0       | 22.5      |
| Fe_{40}Co_{40}Zr_{8}Ti_{2}B_{10} (#4) | 158.3       | 24.5      |

There is a little difference in Coercivity ($H_c$) among alloys, which is due to the different grain size and different nanocrystals distribution of α-Fe(Co) phase. The differences in saturation magnetization ($M_s$) among alloys is due to the differences of crystallization volume fraction of α-Fe(Co) phase. $M_s$ of the alloys has the following relations: $M_{s\#3}>M_{s\#2}>M_{s\#4}>M_{s\#1}$.

4. Conclusions

Fe_{40}Co_{40}Zr_{8}M_{2}B_{10} (M= Nb, V, Cr, Ti, W, Al) alloys were prepared by melt-spinning. Among of them, Fe_{40}Co_{40}Zr_{8}M_{2}B_{10} [M= Nb(#1), V(#2), Cr(#3), Ti(#4)] alloys have large negative heat of mixing and form amorphous. The GFA of the four kinds of alloy has the following relations: GFA_{#4}> GFA_{#3}> GFA_{#2}> GFA_{#1}. Only α-Fe(Co) phase precipitates in the primary stage of crystallization process and Co element mainly distributes into the residual amorphous. They all form a typical two-phase structure characterized by bcc α-Fe(Co) nanocrystalline grains embedding in the amorphous matrix. For the four amorphous alloys after annealing at 550°C, there is a few differences in saturation magnetization ($M_s$) and coercivity ($H_c$) due to their different microstructures.
References

[1] Han B-K, Kim Y K and Choi-Yim H 2014 Curr. Appl. Phys. 14 685-7
[2] Arvindha Babu D, Majumdar B, Sarkar R, Manivel Raja M and Akhtar D 2011 J. Mater. Res. 26 2065-71
[3] Sun Y, Zhong L and Bi X F 2009 Scripta Mater. 60 814-7
[4] Radoň A, Patryk W, Lukasz H, Mariola K G, Piotr G, Ryszard N and Rafał B 2018 J. Alloy. Compd. 763 141-52
[5] Herzer G 1990 IEEE Trans. Magn. 26 1397-402
[6] Bitoh T, Makino1 A, Inoue A and Masumoto T 2003 Mater. Trans. 44 2011-9
[7] Li X L, Liu J B, Qu C R, Song K K and Wang L 2017 J. Alloy. Compd. 694 643-6
[8] Alleg S, Souilah S, Younes A, Bensalem R, Suñol J J and Greneche J M 2012 J. Alloy. Compd. 536 S394-7
[9] Silveyra J M and Illeková E 2014 J. Alloy. Compd. 610 180-3
[10] Ji L, Zheng Z G, Qiu Z G, Zeng D C, Yu H Y and Xu B 2018 J. Alloy. Compd. 766 391-7
[11] Liu L, Yang Y R, Qiu M, Pi Y M and Yan G M 2015 J. Simul. 3 22-4
[12] Ma Y, Liu Y, Li J, Zhang H and Yang H 2016 J. Iron Steel Res. Int. 23 625-32
[13] Botta W J, Berger J E, Kiminami C S, Roche V, Nogueira R P and Bolfarini C 2014 J. Alloy. Compd. 586 S105-10
[14] Xu D D, Zhou B L, Wang Q Q, Zhou J, Yang W M, Yuan C C, Xue L, Fan X D, Ma L Q and Shen B L 2018 Corros. Sci. 138 20-7
[15] Liu W L, Wang Y G and Chen F G 2014 J. Mater. Sci-Mater. El. 25 5066-70
[16] Wang J, Liu X, Mo J, Mao X H, Fan X A and Luo Z G 2018 J. Alloy. Compd. 766 769-74
[17] Zhang Y, Yan B, Yang Y and Wang Y X 2013 J. Alloy. Compd. 574 556-9
[18] Liang D D, Wei X S, Chang C T, Li J W, Wang X M and Shen J 2017 J. Alloy. Compd. 731 1146-50
[19] Stepanov N D, Shaysultanov D G, Chernichenko R S, Tikhonovsky M A and Zherebtso S V 2019 J. Alloy. Compd. 770 194-203
[20] He J Y, Liu W H, Wang H, Wu Y, Liu X J, Nieh T G and Lu Z P 2014 Acta Mater. 62 105-13
[21] Duan H J, Wang Z and Jia Y R 2019 Mater. Res. Bull. 111 289-93
[22] Murugaiyan P, Abhinav A, Verma R, Panda A K, Mitra A, Baysakh S and Roy R K 2018 J. Magn. Magn. Mater. 448 66-74
[23] Takeuchi A and Inoue A 2005 Mater. Trans. 46 2817-29
[24] Inoue A 2000 Acta Mater. 48 279-306
[25] Yu W Q, Zeng H Q, Sun Y M, Sun Y J and Hua Z 2017 Phys. Lett. A 381 1573-6
[26] Yu W Q, Zeng H Q, Sun Y M and Hua Z 2017 Vacuum 137 175-82