Glass-forming ability and magnetic properties of CoFeMoYB bulk glassy alloys with large supercooled liquid region

Qikui Man[a], Huaijun Sun[a], Yaqiang Dong[a], Baolong Shen[a,*], Hisamichi Kimura[b], Akihoro Makino[b], Akihisa Inoue[b]

[a] Zhejiang Province Key Laboratory of Magnetic Materials and Application Technology, Key Laboratory of Magnetic Materials and Devices, Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, 519 Zhuanshi Road, Zhenhai District, Ningbo, Zhejiang 315201, China
[b] Institute for Materials Research, Tohoku University, Katahira 2-1-1, Sendai 980-8577, Japan

ARTICLE INFO

ABSTRACT

Co-based bulk glassy alloys with diameters up to 4 mm were formed in $Co_{41+x}Fe_{28}Mo_4Y_{5-x}B_{22}$ ($x = 0–1.5$) system. The effect of Y content on the glass-forming ability and soft-magnetic properties of the Co-based bulk glassy alloys was investigated. With an increase of Y content from 3.5 to 5 at%, in addition to slight increases of glass transition temperature from 843 to 847 K and supercooled liquid region increases from 73 to 94 K, the addition of Y was found to be effective in approaching alloy to a eutectic point. Except for high glass-forming ability, the Co-based bulk glassy alloys exhibit good soft-magnetic properties, i.e., high saturation magnetization of 0.80–0.87 T, low coercive force of 2.87–3.34 A/m, high effective permeability at 1 kHz of $1.26–1.74 \times 10^4$ under a field of 1 A/m.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Since the first syntheses of an Fe-based bulk glassy alloy (BGA) in FeAlGaPCB system in 1995 [1], Fe-based BGAs have been intensively studied due to the abundant natural resources, low material cost, and unique properties such as good soft-magnetic properties, superhigh fracture strength and high corrosion resistance, which are potential for using as functional and structural materials [2–11]. For the Co-based amorphous alloys, it was found in 1992 that the amorphous wires exhibit giant magneto-impedance (GMI) effect, which has been subsequently developed as high-sensitivity sensor materials [12–14]. However, it is known that $Co_{70.5}Fe_{4.5}B_{15}Si_{10}$ amorphous alloy with low Fe content cannot be prepared into a BGA form [15]. As its low glass-forming ability (GFA), Co-based amorphous wires only can be prepared by in-rotating-water spinning or glass-coated melt-spinning method [16,17], which has restricted to produce a large amount of high-quality Co-based amorphous wires. Therefore, it is demanded to develop new Co-based BGAs with both higher GFA and good soft-magnetic properties. In 2005, a new ternary $Fe_{72}Y_6B_{22}$ BGA in diameter up to 2 mm with excellent soft-magnetic properties was synthesized [6]. From then on, many Fe-based BGAs with high GFA were reported by adjusting the initial composition of $Fe_{72}Y_6B_{22}$ [18–21]. In this study, with

the aim of increasing the GFA of the Co-based glassy alloys, Mo was added and Fe was partial substituted for Co, and optimized the alloy compositions by modifying the Y content. As a result, Co-based BGAs $Co_{41+x}Fe_{28}Mo_4Y_{5-x}B_{22}$ ($x = 0–1.5$) with diameters up to 4 mm were synthesized. In addition, this glassy alloy system exhibits rather high saturation magnetization (I_s) of 0.80–0.87 T, low coercive force (H_c) of 2.87–3.34 A/m, high effective permeability (μ_e) of $1.26–1.74 \times 10^4$ at 1 kHz under a field of 1 A/m.

2. Experimental

Alloy ingots with nominal compositions were made by alloying high-purity elements in an arc furnace under an argon atmosphere. The cylindrical alloy rods with diameters up to 4.5 mm were produced by the copper mold casting method. Glassy structure was examined by X-ray diffraction with Cu Kα radiation. Thermal stability associated with glass transition temperature (T_g), crystallization temperature (T_x), and supercooled liquid region ($\Delta T = T_x - T_g$) was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. The liquidus temperature (T_l) was measured by cooling the molten alloy samples with DSC. To reduce the influence of undercooling, measurements were performed at a very low cooling rate of 0.067 K/s. Magnetic properties of I_s, H_c, and μ_e at 1 kHz were measured with a vibrating sample magnetometer (VSM) under an applied field of 400 kA/m, a B–H loop tracer under a field of 400 A/m, and an impedance analyzer under a field of 1 A/m, respectively. All the samples for magnetic property measurements were annealed for 300 s at the temperature of $T_g - 50$ K for improving soft-magnetic properties through structural relaxation.

3. Results and discussion

Fig. 1 shows DSC curves of melt-spun $Co_{41+x}Fe_{28}Mo_4Y_{5-x}B_{22}$ ($x = 0–1.5$) glassy alloy ribbons. Upon heating, all these amorphous

Fig. 1. DSC curves of melt-spun $Co_{41+x}Fe_{28}Mo_4Y_{5-x}B_{22}$ ($x=0$, 0.5, 1 and 1.5) glassy alloy ribbons.

Fig. 3. XRD patterns of the cast $Co_{41+x}Fe_{28}Mo_4Y_{5-x}B_{22}$ ($x=0$, 0.5, 1 and 1.5) glassy alloy rods with critical diameters of 3.5 mm, 4 mm, 3.5 mm and 3 mm, respectively.
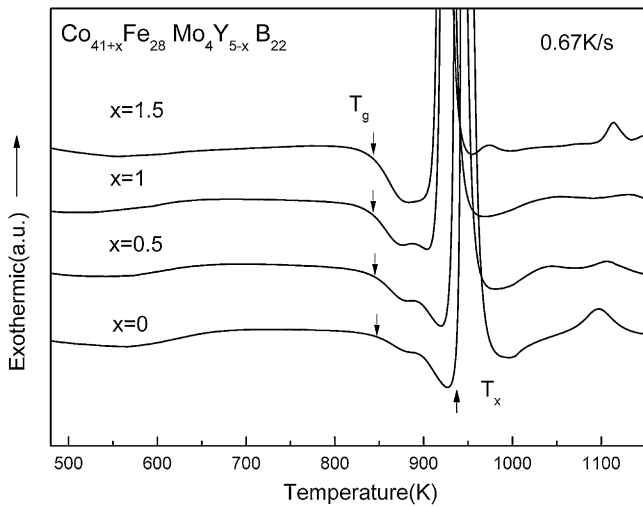
alloys exhibit distinct endothermic events characteristic of the glass transition, and three-stage exothermic event characteristic of crystallization for $x=0$, one-stage exothermic event for $x=0.5$ and 1, two-stage exothermic event for $x=1.5$. It is seen that T_g increases slightly from 843 to 847 K as x decreases from 1.5 to 0, combined with an obvious increase of ΔT_x from 73 to 94 K. Thus, it is considered that thermal stability of the supercoooled liquid against crystallization decreases with the decreasing of Y content. The previous data indicate that the largest ΔT_x for Co-based glassy alloys is 98 K for $Co_{40}Fe_{22}Nb_6Zr_2B_{30}$ alloy, while the critical diameter of the alloy is 1.5 mm [22]. The present results of the $Co_{41+x}Fe_{28}Mo_4Y_{5-x}B_{22}$ ($x=0$–1.5) glassy alloy system could form a single glassy phase in the 4 mm cylindrical sample, in combination with the large ΔT_x of over 90 K. In the supercooled liquid region, the second inflection event is observed for all samples except for $x=1.5$, which could be caused by the strong affinity between B and other constituent elements Co, Fe, Y and Mo as well as the repulsion between Mo and Y in amorphous alloys [23]. Fig. 2 shows DSC curves of $Co_{41+x}Fe_{28}Mo_4Y_{5-x}B_{22}$ ($x=0$–1.5) glassy alloys showing the cooling behaviors of this Co-

based alloy system. With increasing x from 0 to 1.5, T_l decreases from 1373 to 1356 K. All alloys exhibit a main exothermic peak of C_1 about 1300 K, and another small exothermic peak of C_2 can be detected in DSC curves of $x=0$ and 1.5, indicating the alloys of $x=0.5$ and 1 lie in the vicinity of a eutectic point rather than $x=0$ and 1.5. These behaviors indicate that the Y content is crucial in improving the thermal stability of the supercooled liquid as well as the alloy composition approaching a eutectic point. The reduced glass transition temperature (T_g/T_l) of the $Co_{41+x}Fe_{28}Mo_4Y_{5-x}B_{22}$ ($x=0$–1.5) glassy alloy lies in the range from 0.617 to 0.622.

Based on the results obtained from DSC measurements, it is expected that this alloy system, especially for the alloy with the compositions of $x=0.5$ and 1, exhibits a high GFA. We tried to form cylindrical glassy rods with different diameters up to 4.5 mm. The critical diameter for formation of a single glassy phase was 3.5, 4, 3.5, and 3 mm at $x=0$, 0.5, 1, and 1.5, respectively. Fig. 3 shows X-ray diffraction patterns for these cast alloy rods. Only broad peak without any crystalline peaks can be seen for every sample, indicating the formation of a glassy phase with diameters in the range up to 4 mm.

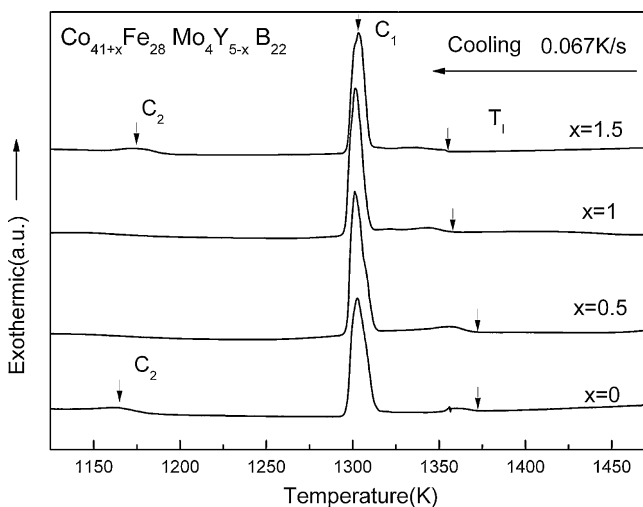**Fig. 2.** DSC curves of $Co_{41+x}Fe_{28}Mo_4Y_{5-x}B_{22}$ ($x=0$, 0.5, 1 and 1.5) alloys showing the cooling behaviors of this Co-based alloy system.
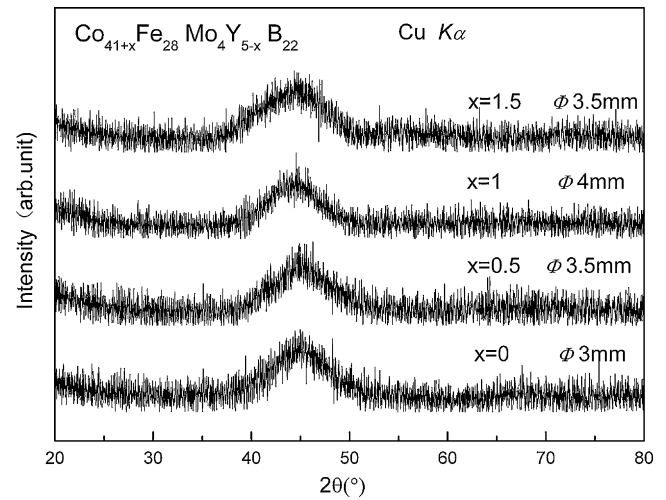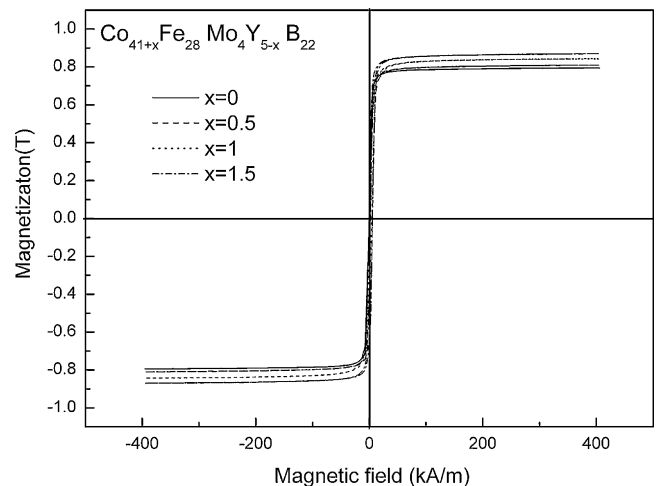

Fig. 4. M–H hysteresis loops of the cast $Co_{41+x}Fe_{28}Mo_4Y_{5-x}B_{22}$ ($x=0$, 0.5, 1 and 1.5) glassy alloy ribbons.

Table 1
Maximum diameter, thermal stability and magnetic properties of cast $Co_{41+x}Fe_{28}Mo_4Y_{5-x}B_{22}$ (x = 0, 0.5, 1 and 1.5) glassy alloys.

Alloy	D_{max} (mm)	T_g (K)	ΔT_x (K)	T_l (K)	T_g/T_l	I_s (T)	H_c (Am^{-1})	μ_e (1 kHz)
$Co_{41}Fe_{28}Mo_4Y_5B_{22}$	3.5	847	94	1373	0.617	0.80	3.34	12 600
$Co_{41.5}Fe_{28}Mo_4Y_{4.5}B_{22}$	4	845	90	1372	0.616	0.81	3.27	14 300
$Co_{42}Fe_{28}Mo_4Y_4B_{22}$	3.5	843	77	1359	0.620	0.84	3.13	15 500
$Co_{42.5}Fe_{28}Mo_4Y_{3.5}B_{22}$	3	843	73	1356	0.622	0.87	2.87	17 400

Typical M–H loops of the $Co_{41+x}Fe_{28}Mo_4Y_{5-x}B_{22}$ (x = 0–1.5) glassy alloys measured at room temperature are shown in Fig. 4. The saturation magnetization slightly decreases from 0.87 T to 0.80 T with the increasing of Y content from 3.5 to 5 at%. Table 1 summarizes the maximum diameter, thermal stability and magnetic properties of the $Co_{41+x}Fe_{28}Mo_4Y_{5-x}B_{22}$ (x = 0–1.5) glassy alloys. As shown in the table, this BGA system exhibits good soft-magnetic properties, i.e., high I_s of 0.80–0.87 T, low H_c of 2.87–3.34 A/m, high μ_e of 1.26–1.74 × 10^4 at 1 kHz under a field of 1 A/m.

Here we discuss the reasons why the $Co_{46}Fe_{20}B_{22+x}Si_{6-x}Nb_6$ glassy alloy system exhibits a high GFA and good soft-magnetic properties. First, as shown in Fig. 2, the $Co_{41+x}Fe_{28}Mo_4Y_{5-x}B_{22}$ (x = 0–1.5) alloy compositions are close to the eutectic composition resulting in the increase of the thermal stability of the supercooled liquid. On the other hand, in the Co–Fe–Mo–Y–B alloy system, the atomic radii of Co, Fe, Mo, B and Y are 0.125, 0.124, 0.136, 0.09 and 0.182 nm [24]. It has been pointed out that the large (L) and small (S) atoms may form a strong L–S percolating network or reinforced 'backbone' in the amorphous structure [25]. Thus, the increase of Y content could reinforce the backbone structure of supercooled liquid of the alloys lead to the increases of GFA. Besides, it has been pointed out by Ponnambalam et al. that the role of yttrium may be oxygen scavenging effect leading to suppression of heterogeneous nucleation [19,25]. Y atom has a stronger affinity for the oxygen atom compared with other elements in the system (Y_2O_3 = −1904 kJ/mol, Fe_2O_3 = −820.5 kJ/mol, B_2O_3 = −1273 kJ/mol) result in the formation of yttrium oxide during melting and casting processes [26]. An oxygen scavenging effect is believed to be another important factor for the enhancement of the GFA by Y addition [27].

4. Summary

In conclusion, a BGA system of $Co_{41+x}Fe_{28}Mo_4Y_{5-x}B_{22}$ with high GFA and good soft-magnetic properties was synthesized. The Co-based glassy alloy system could form a single glassy phase in the 4 mm cylindrical sample, in combination with the large ΔT_x of over 90 K. This Co-based ferromagnetic bulk glassy alloy system is promising for future applications new structural and functional materials.

References

[1] A. Inoue, Y. Shinohara, G.S. Gook, Mater. Trans. JIM 36 (1995) 1427–1433.
[2] W.L. Johnson, JOM 54 (2002) 40–43.
[3] T. Zhang, A. Inoue, Mater. Trans. 43 (2002) 708.
[4] A. Inoue, B.L. Shen, H. Koshiba, H. Kato, A.R. Yavari, Nat. Mater. 2 (2003) 661.
[5] Z.P. Lu, C.T. Liu, J.R. Thompson, W.D. Porter, Phys. Rev. Lett. 92 (2004) 245503.
[6] C.Y. Lin, H.Y. Tien, T.S. Chin, Appl. Phys. Lett. 86 (2005) 162501.
[7] C.T. Chang, B.L. Shen, A. Inoue, Appl. Phys. Lett. 89 (2006) 051912.
[8] D.H. Kim, J.M. Park, D.H. Kim, W.T. Kim, J. Mater. Res. 22 (2007) 471–477.
[9] V. Ponnambalam, S.J. Poon, G.J. Shiflet, V.M. Keppens, R. Tayloy, G. Petculescu, Appl. Phys. Lett. 83 (2003) 1131.
[10] J.H. Yao, J.Q. Wang, Y. Li, Appl. Phys. Lett. 92 (2008) 251906.
[11] H.X. Li, S.L. Wang, S. Yi, Z.B. Jiao, Y. Wu, Z.P. Lu, J. Magn. Magn. Mater. 321 (2009) 2833–2837.
[12] K. Mohri, K. Kawashima, T. Kozhawa, Y. Yoshida, L.V. Panina, IEEE Trans. Magn. 28 (1992) 3150–3152.
[13] L.V. Panina, K. Mohri, T. Uchiyama, M. Noda, IEEE Trans. Magn. 31 (1995) 1249–1260.
[14] H.Q. Guo, H. Kronmuller, T. Dragon, Z.H. Cheng, B.G. Shen, J. Appl. Phys. 89 (2001) 514.
[15] K.I. Arai, N. Tsuya, M. Yamada, T. Masumoto, IEEE Trans. Magn. 12 (1976) 939–941.
[16] A.V. Ulitovskiy, Prekory Tech. Eksper. 3 (1957) 115.
[17] T. Masumoto, I. Ohnaka, A. Inoue, M. Hagiwara, Scripta Metall. 15 (1981) 193.
[18] D.S. Song, J.H. Kim, E. Fleury, W.T. Kim, D.H. Kim, J. Alloys Compd. 389 (2005) 159–164.
[19] C.Y. Lin, M.C. Lee, T.S. Chin, J. Phys. D: Appl. Phys. 40 (2007) 310–314.
[20] M.T. Liu, S.C. Ray, H.M. Tsai1, C.W. Pao, D.C. Ling, W.F. Pong, J.W. Chiou, M.H. Tsai, L.Y. Jang, T.W. Pi, J.F. Lee, C.Y. Lin, T.S. Chin, J. Phys.: Condens. Matter. 20 (2008) 465105.
[21] X.M. Huang, C.T. Chang, Z.Y. Chang, X.D. Wang, Q.P. Cao, B.L. Shen, A. Inoue, J.Z. Jiang, J. Alloys Compd. 460 (2008) 708–713.
[22] T. Itoi, A. Inoue, Mater. Trans. JIM 41 (2000) 1256.
[23] X.M. Huang, X.D. Wang, Y. He, Q.P. Cao, J.Z. Jiang, Scripta Mater. 60 (2009) 152–155.
[24] Metals Databook. Tokyo, The Japan Institute of Metals, Maruzan, 2004, p. 8.
[25] S.J. Poon, G.J. Shiflet, F.Q. Guo, V. Ponnambalam, J. NonCryst. Solids 317 (2003) 1–9.
[26] O. Kubaschewski, C.B. Alcock, Metallurgical Thermochemistry, Pergamon, Oxford, 1979.
[27] J.M. Park, J.S. Park, J.H. Na, D.H. Kim, D.H. Kim, Mater. Sci. Eng. A 435–436 (2006) 425–428.