Chinese Science Bulletin 2005 Vol. 50 No. 3 205—207

Formation of $Fe_{56}Mn_5Cr_7$-$Mo_{12}Er_2C_{12}B_6$ amorphous steel

LUO Chongyang[1,2], PAN Mingxiang[1], KOU Shengzhong[2], ZHAO Deqian[1] & WANG Weihua[1]

1. Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China;
2. State Key Laboratory of Gansu Advanced Nonferrous Metal Materials, Lanzhou University of Technology, Lanzhou 730050, China

Correspondence should be addressed to Pan Mingxiang (e-mail: panmx@aphy.iphy.ac.cn)

Abstract **The $Fe_{48}Cr_{15}Mo_{14}Er_2C_{15}B_6$ amorphous steel can hardly be used as an engineering material because of its extreme brittleness and very low iron content. By changing the composition of the nonmagnetic amorphous steel, and using the relation between the reduced glass transition temperature T_{rg} and the glass forming ability, a new amorphous $Fe_{56}Mn_5Cr_7Mo_{12}Er_2C_{12}B_6$ alloy with good glass forming ability and high iron content was obtained. The diameter of the as-cast sample rod reached 8 mm. This new amorphous steel has lower manufacturing cost due to its high iron content, and thus it can have wider applications.**

Keywords: amorphous steel, glass forming ability, reduced glass transition temperature.

DOI: 10.1360/982004-132

Amorphous alloys, especially Fe-based bulk metallic glasses (BMGs), have attracted much attention. Fe-based BMGs have higher strength and hardness, better corrosion resistance[1—4] and better physical properties (such as soft magnetic properties) than other amorphous alloys and crystalline alloy materials. For a long time researchers have engaged in the improvement of the glass forming ability (GFA), i.e. achievement of Fe-based BMGs with larger diameter or thickness.

Fe-based BMGs including Fe–TM–B (TM=IV–VIII group transition metal)[1], Fe–(Co, Ni)–M–B (M = Zr, Hf, Nb, Ta, Mo, W)[2], Fe–Ni–P–B[3] and Fe–Al–Ga–P–C–B–Si have been extensively studied[4]. The studies are mostly focused on soft magnetic properties because of their low GFA and small sample sizes. Recently, $Fe_{75-x-y}Cr_xMo_yC_{15}B_{10}$[5] and $Fe_{43}Cr_{16}Mo_{16}(C, B, P)_{25}$[6] which exhibit high corrosion resistance and high GFA were developed. These Fe-based BMGs also are called nonmagnetic bulk amorphous alloys due to the absence of magnetic properties at room or higher temperature. However, the high purity of raw materials and the strict processing conditions cause high cost. Even traces of oxygen and other impurities would induce the heterogeneous nucleation and reduce the GFA drastically. These factors restrict their applications as structural materials.

A recent advancement in nonmagnetic Fe-base BMGs is the significant increase of the glass formability by microalloying with few atomic volume fractions of Y and Ln (lanthanides). The representative compositions are $(Fe_{44.3}Cr_{10}Mo_{13.8}Mn_{11.2}C_{15.8}B_{5.9})_{98.5}Y_{1.5}$[7] and $Fe_{48}Cr_{15}Mo_{14}Er_2C_{15}B_6$[8]. The maximum sample diameter up to 12 mm has been obtained by conventional copper mold casting. The Fe-based bulk amorphous metals are called non-ferromagnetic steel alloys or structural amorphous steels (SASs).

The SASs exhibit nonferromagnetism at room temperature, but higher hardness and better corrosion resistance, and can be prepared more economically. On the other hand, the superior GFA of the SASs enables a simple preparation procedure. Therefore, SASs have great industrial application potentials.

To further enhance the ductility and toughness and reduce manufacturing cost, it is necessary to increase iron content and reduce the contents of Cr, Mo, B and Er components. In this paper, we report the effects of Fe and Cr contents on the glass forming ability of the $Fe_{48}Cr_{15}Mo_{14}Er_2C_{15}B_6$ alloy. Based on previous work[9] a new amorphous steel of $Fe_{56}Mn_5Cr_7Mo_{12}Er_2C_{12}B_6$ alloy with good glass forming ability (up to 8 mm in diameter at least) and high iron content was synthesized successfully.

1 Experimental procedures

Multicomponent master alloys with compositions of $Fe_{(48+x)}Cr_{(15-x)}Mo_{14}C_{15}B_6Er_2$, where x is 0, 5, 10, and 15 at.%, were prepared by arc melting of raw materials under a molten titanium gettered argon atmosphere, and then were cast in water-cooled copper molds under argon atmosphere. The raw materials used in this experiment were industrial pure iron (purity is 99.5 wt.%), chromium (99.8%), molybdenum (99.95%), boron (99.8%), carbon (99.5%), erbium (99.5%) and manganese (99.0%). The structure of the as-cast alloys samples was identified by X-ray diffraction (XRD). The thermal properties were measured by a Perkin Elmer Differential Thermal Analyzer-7 (DTA-7) under argon atmosphere (99.999%) with a heating rate of 10 K/min.

2 Results and discussions

Figure 1 shows XRD patterns of the as-cast $Fe_{(48+x)}Cr_{(15-x)}Mo_{14}C_{15}B_6Er_2$ (x = 0, 5, 10 and 15 at.%) alloy samples. The amorphous $Fe_{48}C_{r15}Mo_{14}C_{15}B_6Er_2$ and $Fe_{53}C_{r10}Mo_{14}C_{15}B_6Er_2$ alloys up to 8 mm in diameter have been obtained. For comparison, all the samples were prepared in the 5 mm diameter rods. As shown in Fig. 1, broad peak presents in the vicinity of $2\theta = 43°$ indicating the amorphous structure of the alloys. With the increase of Fe and decrease of Cr, the position of the peak is unchanged, but crystalline peaks gradually appear on the XRD curve suggesting that this sample is partially amorphous with considerable crystalline fraction. The GFA declines markedly when Fe content is further increased to 63 at.%.

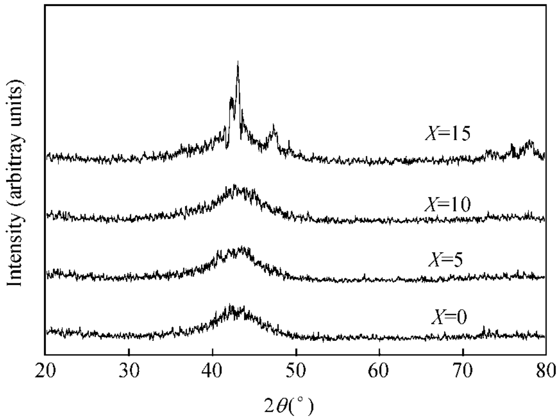

Fig. 1. X-ray diffraction patterns for the as-cast $Fe_{(48+x)}Cr_{(15-x)}Mo_{14}C_{15}B_6Er_2$ (x = 0, 5,10, 15).

To investigate the effect of composition variation on the GFA, Fig. 2 shows the DTA curves of these samples. All the DTA traces exhibit obvious endothermic characteristics at high temperatures and at lest two exothermic crystallization peaks, showing that the these alloys have amorphous structure due to the existences of obvious glass transition and crystallization processes.

As a general rule, the width of supercooled liquid region ΔT_x (the temperature difference between the onset crystallization temperature T_x and the glass transition temperature T_g) is used as a criterion of supercooled liquid stability[10]. A large ΔT_x value may indicate that the supercooled liquid can exist in a wide temperature range without crystallizing, and has a high resistance to the nucleation and growth of crystalline phases and the alloy has a better GFA. With the increase of Fe (or decrease of Cr), the glass transition temperature T_g and the liquidus temperature T_l decrease with the increase of Fe content, but the crystallization temperature T_x changes only a little. Therefore, the ΔT_x has an increasing trend. However, with the increasing ΔT_x the critical section thickness of the sample decreases, indicating the decrease of GFA of the alloy. The experimental result is contrary to the general

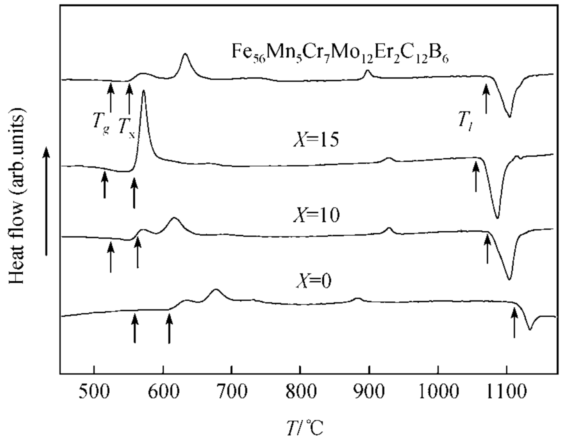

Fig. 2. Differential thermal analysis curves of $Fe_{(48+x)}Cr_{(15-x)}Mo_{14}C_{15}B_6Er_2$ (x = 0, 10, 15) alloy samples. The curve at top is for $Fe_{56}Mn_5Cr_7Mo_{12}Er_2C_{12}B_6$ sample.

viewpoint that the GFA of alloy is relative to the ΔT_x. Table 1 summarizes the thermal parameters of $Fe_{(48+x)}Cr_{(15-x)}Mo_{14}C_{15}B_6Er_2$ (x = 0, 10, 15) alloys. Liu et al, proposed γ [$\gamma = T_x/(T_g + T_l)$][11] as a criterion of GFA, and a large γ predicates a high GFA. But for this alloy system, the change of parameter γ does not accord with that of the GFA. However, the reduced glass transition temperature T_{rg}($T_{rg}=T_g/T_l$)[12] changes according to the GFA of the alloys. The higher T_{rg} value, the more reliable GFA should be sustained in the $Fe_{(48+x)}Cr_{(15-x)}Mo_{14}C_{15}B_6Er_2$ alloys. Therefore, the key to the problem is how to increase the Fe content without significantly deteriorating the GFA of the alloys.

To optimize glass formability, the $Fe_{58}Cr_5Mo_{14}Er_2C_{15}B_6$ is chosen as a starting composition because of its high iron content and relative high GFA. Element Mn has been used to depress T_l, and B has been added to obtain high T_g and high viscosity of the melt, thus enhancing the GFA of Fe-based amorphous forming alloys[13]. By adding 5 at.% Mn and keeping the content of B unchanged, the $Fe_{56}Mn_5Cr_7Mo_{12}Er_2C_{12}B_6$ bulk amorphous rod with 8 mm diameter has been successfully obtained.

The DTA curve for the as-cast $Fe_{56}Mn_5Cr_7Mo_{12}Er_2C_{12}B_6$ SAS sample is shown at the top of Fig. 2. The T_g of the amorphous sample is almost unchanged compared with that of the $Fe_{58}Cr_5Mo_{14}Er_2C_{15}B_6$ amorphous alloy,

Table 1 Thermal properties for $Fe_{(48+x)}Cr_{(15-x)}Mo_{14}C_{15}B_6$ Er2(x = 0, 10 and 15) SASs

Composition	Maximum size (mm)	T_g (K)	T_x(K)	T_m(K)	T_l (K)	ΔT_x (K)	T_{rg}	γ
$Fe_{56}Mn_5Cr_7Mo_{12}Er_2C_{12}B_6$	≥ϕ8	793	832	1354	1401	39	0.566	0.379
$Fe_{63}Mo_{14}Er_2C_{15}B_6$	ϕ3	771	830	1337	1389	59	0.555	0.384
$Fe_{58}Cr_5Mo_{14}Er_2C_{15}B_6$	ϕ6	793	829	1344	1416	36	0.560	0.375
$Fe_{48}Cr_{15}Mo_{14}Er_2C_{15}B_6$	ϕ8 ~ 12	844	880	1378	1446	36	0.584	0.384

but it has a lower T_l, thus higher T_{rg} of 0.566. High GFA is obtained despite a narrow supercooled liquid region of 39 K.

Figure 3 is a camera photo of as-cast $Fe_{48}Cr_{15}Mo_{14}Er_2C_{15}B_6$ (Fig. 3(a)) and $Fe_{56}Mn_6Cr_7Mo_{12}Er_2C_{12}B$ (Fig. 3(b) and (c)) SAS samples. All the samples have luster surface. Fig. 3 (c) shows the fracture appearance of $Fe_{56}Mn_5Cr_7Mo_{12}Er_2C_{12}B_6$ sample. A shiny fracture typical of a bulk glassy alloy can be seen on the fracture surface.

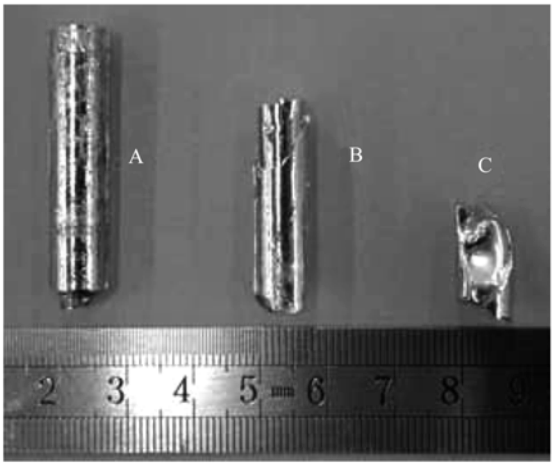

Fig. 3. A camera photo of as-cast $Fe_{48}Cr_{15}Mo_{14}Er_2C_{15}B_6$ (A) and $Fe_{56}Mn_6Cr_7Mo_{12}Er_2C_{12}B$ (B) SAS samples. (C) is the fracture appearance of $Fe_{56}Mn_5Cr_7Mo_{12}Er_2C_{12}B_6$ sample.

3 Conclusions

A new bulk amorphous steel $Fe_{56}Mn_5Cr_7Mo_{12}Er_2C_{12}B_6$ alloy rod with 8 mm diameter has been successfully synthesized by adding Mn and adjusting the ratios of element Fe, Cr and Mo. The bulk amorphous forming alloy has higher iron content, good glass forming ability and high thermal stability at the same time, and thereby reduces the contents of noble metals Cr and Mo. The new amorphous steel has lower manufacturing cost owing to its high iron content, and it has more engineering application potential.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Grants No. 50371098 and 50321101) and the Key Project of the Beijing Science and Technology Program (Contract No. H02040030320).

References

1. Inoue, A., Zhang, T., Takeuchi, A., Bulk amorphous alloys with high mechanical strength and good soft magnetic properties in Fe–TM–B (TM=IV–VIII group transition metal) system, Appl. Phys. Lett., 1997, 71: 464—466. [DOI]
2. Inoue, A., Zhang, T., Koshiba, H., New bulk amorphous Fe–(Co,Ni)–M–B (M = Zr, Hf, Nb, Ta, Mo, W) alloys with good soft magnetic properties, J. Appl. Phys., 1998, 83: 6326—6328. [DOI]
3. Shen, T. D., Schwarz, R. B., Bulk ferromagnetic glasses in the Fe-Ni-P-B system, Acta. Mater., 2001, 49: 837—847. [DOI]
4. Mizushima, T., Ikarashi, K., Inoue, A., Soft magnetic properties of ring shape bulk glassy Fe-Al-Ga-P-C-B-Si alloy prepared by copper mold casting, Mater. Trans. JIM., 1999, 40 (9): 1019—1022.
5. Pang, S. J., Zhang, T., Katsuhiko, A., Inoue, A., Formation of bulk glassy $Fe_{75-x-y}Cr_xMo_yC_{15}B_{10}$ alloys and their corrosion behavior, J. Mater. Res., 2002, 17: 701—704
6. Pang, S. J., Zhang, T., Katsuhiko, A., Inoue, A., Synthesis of Fe–Cr–Mo–C–B–P bulk metallic glasses with high corrosion resistance, Acta. Mater., 2002, 50: 489—497. [DOI]
7. Lu, Z. P., Liu, C. T., Tompson, J. R., Structural amorphous steels, Phys. Rev. Lett., 2004, 92: 245503. [DOI]
8. Ponnambalam, V., Poon, S. J., Fe-based bulk metallic glasses with diameter thickness larger than one centimeter, J. Mater. Res., 2004, 19: 1320—1326.
9. Pan, M. X., Hu, Y., Wang, W. H. et al., Formation of Fe-based bulk metallic glasses with low purity elements by component addition and substitution, J. Metastable and Nanocrys. Mater., 2003, 15-16: 99—104.
10. Inoue, A., High strength bulk amorphous alloys with low critical cooling rates, Mater. Trans. JIM., 1995, 36(7): 866—875.
11. Lu, Z. P., Liu, C. T., A new glass-forming ability criterion for bulk metallic glasses, Acta. Mater., 2002, 50: 3501—3512. [DOI]
12. Turnbull, D., Under what condition can a glass be formed?, Contemp Phys., 1969, 10(5): 473—488.
13. Ponnambalam, V., Poon, S. J., Synthesis of iron-based bulk metallic glasses as nonferromagnetic amorphous steel alloys, Appl. Phys. Lett., 2003, 83: 131—1133.

(Received August 4, 2004)