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Synthesis of Fe-based bulk metallic glasses with low purity materials by multi-metalloids addition

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Abstract

Bulk metallic glasses (BMGs) $Fe_{61}Co_7Zr_{10}Mo_5W_2\ M_{(15+X)}$ ($X=0$, 0.15, 0.30, 0.45, 0.60, 0.75 and 1.2) (M contains B, Al, Si, C and P) were prepared with low purity of raw materials by copper mould cast. X-ray diffraction and differential thermal analyzer results show that the glass forming ability (GFA) as well as the thermal stability of the Fe-based alloy made from low purity raw materials can be much improved by adding small amount of multi-metalloids. The positive effect of metalloids addition on the formation of the bulk metallic glasses is discussed.

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Keywords: Metalloid addition; Bulk metallic glasses; Glass forming ability; Confusion principle

1. Introduction

Since the finding of excellent soft magnetic properties for the Fe-based metallic glasses, the materials in forms of sheet and wire prepared by melt spinning method have been applied in many power transformer fields. However, extended application of the Fe-based metallic glasses was still limited because of their small size. Recently, Fe-based bulk metallic glasses (BMGs) systems, such as Fe–TM(TM = IV–VIII group transition metal)–B [1], Fe–(Co, Ni)–M–B [2] (M = Zr,Hf,Nb,Ta,Mo,W), Fe–Ni–P–B [3] and Fe–Al–Ga–P–C–B–Si [4], were obtained by copper mold cast or water quench methods. The formation and properties studies of multicomponent Fe-based BMGs have attracted increasing attention because of their fundamental interests and industrial application potential. However, high vacuum (at least 10^{-3} Pa), high purity of elements (oxygen content should be less than 400 ppm) are generally required for the fabrication of this kind of BMGs [3], even traces of oxygen and other impurities would induce the heterogeneous

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nucleation and reduce the glass forming ability (GFA) drastically. To prepare the Fe-based BMGs, some special methods such as fluxing, levitation melting and cycling melting are employed to deal with the master Fe-based alloys. The high purity of raw materials and the strict processing cause a high cost for production of BMGs, and restrict their applications. Previous work shows that suitable pure element addition is an effective way to improve the glass forming ability and properties of Zr-based [5–8] and Fe-based BMGs [9]. In this work, we choose the $Fe_{61}Co_7Zr_{10}Mo_5W_2B_{15}$ as a representative iron-based alloy and try to prepare the Fe-based BMGs more economically by the means of addition of a small amount of metalloids. Our experiments results demonstrate that a small amount of multi-metalloids addition is effective to improve the formation ability of $Fe_{61}Co_7Zr_{10}Mo_5W_2B_{15}$ alloy even though the raw materials are in low purity.

2. Experiments

Multi-component master alloys with compositions of $Fe_{61}Co_7Zr_{10}Mo_5W_2M_{(15+X)}$, (at.%) where X is 0, 0.15, 0.30, 0.45, 0.60, 0.75 and 1.20, M contains B, Al, Si, C and P, were prepared by arc melting of raw materials under a titanium metal gettered argon atmosphere. These ingots were remelted several times to ensure the homogeneity of the samples, and then were cast into a water-cooled copper mould under argon atmosphere. The raw materials used in this experiment were industrial pure iron (purity is 99.5 wt.%), pure cobalt, zirconium, molybdenum, tungsten metals, and iron boron alloy which contains 79.8 wt.% of Fe, 18.3 wt.% of B and other constitutes, such as aluminum, silicon, carbon, sulfur, phosphor and their oxides in remainder. The content of boron and other metalloids in the cast alloy can be adjusted by adding different amount the iron–boron alloy, which is much cheaper than pure metalloid elements (e.g. adding pure B [9]). The structure of the as-cast alloys were identified by X-ray diffraction (XRD) using MAC Science M18AHF diffractometer with Cu K_α radiation, the thermal properties were measured by Perkin Elmer Differential Thermal Analyzer-7 (DTA-7) under argon atmosphere with a heating rate of 10 °C/min.

3. Results and discussion

Fig. 1 exhibits the picture of columned samples $Fe_{61}Co_7Zr_{10}Mo_5W_2M_{(15+X)}$ ($X=0$, 0.15, 0.30, 0.45, 0.60, 0.75, 1.20) alloys with diameter of 1 and 2 mm prepared by arc-melt and copper mould casting method. All the samples have metallic luster, indicating that the argon atmosphere can prevent the alloys from being oxidized effectively. Fig. 2 shows the XRD patterns for the as cast $Fe_{61}Co_7Zr_{10}Mo_5W_2M_{(15+X)}$ ($X=0$, 0.15, 0.30, 0.45, 0.60, 0.75, 1.20) alloys (exhibited in Fig. 1) with different metalloids additions. Without metalloids addition ($X=0$ in Fig. 2), only partially amorphous structure was formed, as demonstrated by a few of Bragg peaks superimposed on the diffused diffraction maxima, which means that the alloy contains crystalline phases. The crystalline phases are identified as Fe_2B, Mo_2B and Fe. The result demonstrates that without metalloid addition, full amorphous can not be obtained in the alloy. GFA of the alloy can be considerably improved by addition of metalloids, when $X=0.15$, the crystalline peaks nearly disappear, and the cast alloy shows an apparent amorphous structural characteristic within the detect limit of XRD. For $X=0.45$ and 0.60, no crystalline peaks at all can be detected in the XRD curve characterizing the fully amorphous structure of the

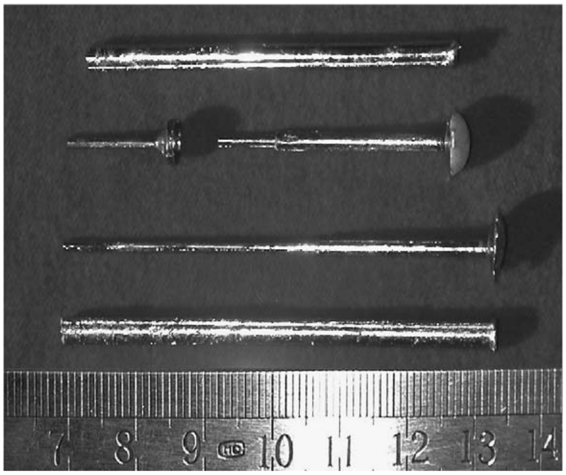

Fig. 1. The outer morphology and surface appearance of cast $Fe_{61}Co_7Zr_{10}Mo_5W_2M_{(15+X)}$ ($X=0$, 0.15, 0.30, 0.45, 0.60, 0.75, 1.20) columned alloys with diameters 1 and 2 mm.

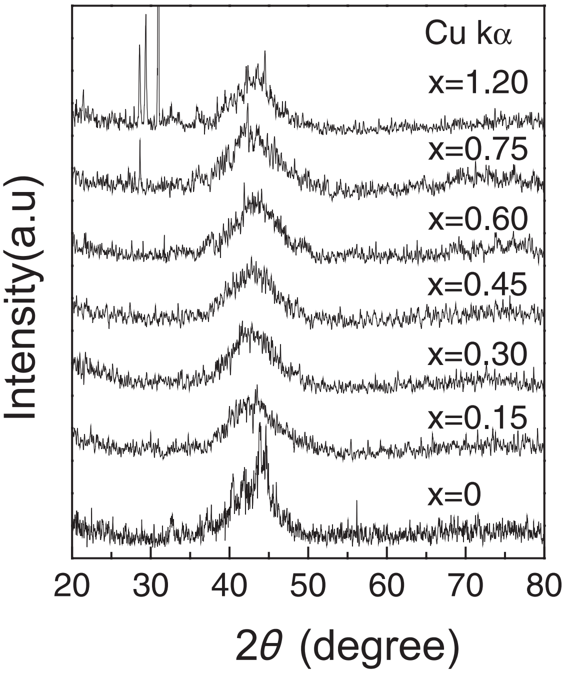

Fig. 2. The X-ray diffraction patterns for the cast $Fe_{61}Co_7Zr_{10}Mo_5W_2M_{(15+X)}$ ($X = 0$, 0.15, 0.30, 0.45, 0.60, 0.75, 1.20).

alloys. The results demonstrate that the Fe-based BMGs can be fabricated by using low purity raw Fe element through addition of amount of multi-metalloids. The possible reason is that metalloids addition can suppress the precipitation of the Fe_2B, Mo_2B and Fe crystalline compounds during the cast process. However, with more metalloids addition ($X > 0.75$), the crystalline peaks occur again, but the positions of crystalline peaks are different from those in the alloy without addition ($X = 0$), they can be indexed as Fe_3B crystalline compound. This means that new crystallines is formed with excess metalloids. As a result, a proper metalloids addition can greatly improve the GFA of the $Fe_{61}Co_7Zr_{10}Mo_5W_2M_{15}$ alloy, and too much (more than $X = 0.75$) addition also leads to the precipitation of crystalline phase.

The thermal stability of these alloys was examined by differential thermal analyzer (DTA) at a heating rate of 10 °C/min under a flow of purified argon. Fig. 3 shows DTA traces of the cast alloys (the inset gives enlarged example for the sample processing). All the DTA traces exhibit obvious endothermic characteristic of a glass transition followed by two exothermic crystallization reactions at higher temperatures. It is found that the glass transition temperature T_g changes a little with the increasing of additional metalloids. The first crystallizing peaks move toward high temperature region when metalloids amount increases from $X = 0-0.60$, and then shifts to low temperatures with more metalloids content. However, glass transition temperature T_g and the second crystallization temperature T_{x2} almost remained unchanged with increase of the metalloids content. Changes in the onset of first exothermic peak with the metalloids content are shown in Fig. 4, the alloy with $X = 0.60$ exhibit s the highest T_{x1}, implying this alloy is of best glass forming ability.

The positive effects of multi-metalloids addition on GFA and thermal stability can be understood from

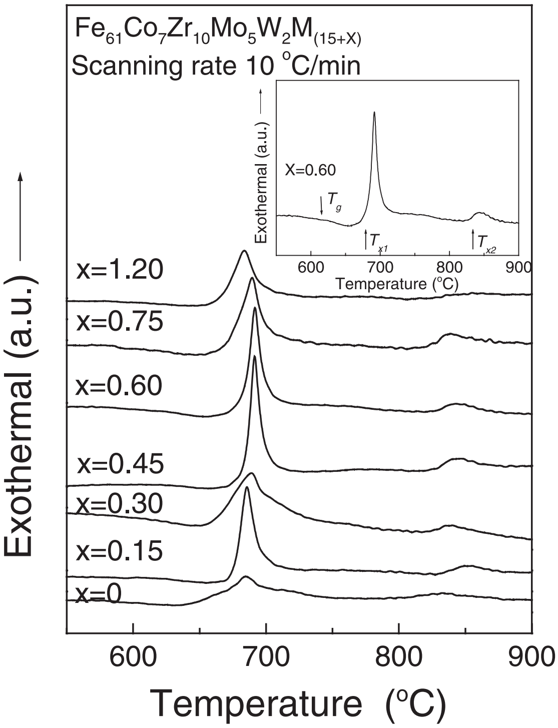

Fig. 3. The differential temperature analyzer curves of $Fe_{61}Co_7Zr_{10}Mo_5W_2M_{(15+X)}$ ($X = 0$, 0.15, 0.30, 0.45, 0.60, 0.75, 1.20). The inset plot is an enlarged curve for $X = 0.60$ with the position of T_g, T_{x1} and T_{x2} indicated, where T_g represents the beginning temperature of glass transition, T_{x1} represents the first crystallization temperature, T_{x2} represents the second crystallization temperature.

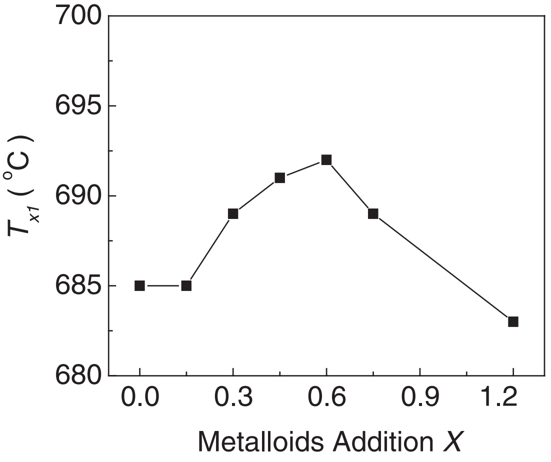

Fig. 4. The changes of T_{x1} with the increasing of metalloid addition in $Fe_{61}Co_7Zr_{10}Mo_5W_2M_{(15+X)}$ at.% M ($X=0$, 0.15, 0.30, 0.45, 0.60, 0.75, 1.20) alloys, T_{x1} represents the first crystallization temperature.

structural viewpoint. There is more than one kind of metalloid with different atomic size in the alloy, it is expected to obtain a larger dense random packing in the supercooled liquid than only a kind of metalloid in alloy does, which makes the redistribution of atoms on a large range scale in cooling process difficult. On the other hand, the mobility of atoms in cooling process is a key for the nucleation and growth of a crystalline phase. The present work can be explained by the so-called "confusion principle" [10–13].

4. Conclusions

$Fe_{61}Co_7Zr_{10}Mo_5W_2M_{(15+X)}$ ($X=0$, 0.15, 0.30, 0.45, 0.60, 0.75, 1.20) Fe-based bulk metallic glass is obtained from low purity of raw materials by a small amount of boron and other metalloids addition using a conventional copper mould-casting method. The multi-metalloid addition is demonstrated to have positive effect on glass forming ability and thermal stability of the Fe-based alloy. The multi-metalloid addition method is an effective way to prepare Fe-based BMG with low purity raw materials and simple preparation technical procedure.

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References

[1] A. Inoue, T. Zhang, A. Takeuchi, Appl. Phys. Lett. 71 (1997) 464.
[2] A. Inoue, T. Zhang, H. Koshiba, J. Appl. Phys. 83 (1998) 6326.
[3] T.D. Shen, R.B. Schwarz, Acta Mater. 49 (2001) 837.
[4] T. Mizushima, K. Ikarashi, S. Yoshida, A. Makino, A. Inoue, Mater. Trans., JIM 40 (1999) 1019.
[5] Y. Zhang, M.X. Pan, D.Q. Zhao, R.J. Wang, W.H. Wang, Mater. Trans., JIM 41 (2000) 1410.
[6] W.H. Wang, Q. Wei, H.Y. Bai, Appl. Phys. Lett. 71 (1997) 58.
[7] Y.H. Kim, A. Inoue, T. Masumoto, Mater. Trans., JIM 32 (1991) 599.
[8] W.H. Wang, H.Y. Bai, J. Appl. Phys. 84 (1998) 5961.
[9] X.M. Wang, A. Inoue, Mater. Trans., JIM 40 (1999) 634.
[10] R. Busch, A. Peker, W.L. Johnson, Mater. Sci. Forum 235–238 (1997) 327.
[11] A.L. Greer, Metallic glasses, Science 267 (1995) 1947.
[12] A.L. Greer, Confusion by design, Nature 366 (1993) 303.
[13] P.J. Desré, Mater. Sci. Forum 179–181 (1995) 713.