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Amorphous-crystalline transition layers formation during quenching of $Fe_{61}Co_7Zr_{10}Mo_5W_2B_{15}$ melt①

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Abstract: New Fe-based multicomponent amorphous alloys have been developed recently based on empirical rules for large glass forming ability(GFA). In the present investigation, the master alloy ingot with the nominal composition of $Fe_{61}Co_7Zr_{10}Mo_5W_2B_{15}$ (mole fraction, %) was prepared by arc-melting under Ti-gettered Ar atmosphere. The Fe-based buttons with different transverse cross sections were fabricated by arc-melting method, and the d 2.5 mm Fe-based rods were manufactured by injection technique. Characterization of the ingots and the parameters associated with the thermal stability were carried out by X-ray diffractometry (XRD) and high temperature differential scanning calorimeter(DSC), respectively. The interval of the supercooled liquid region is 39 K for the Fe-based alloy. The GFA of Fe-based alloys is relatively lower, to the buttons obtained are all crystallized. The Fe-based rod exhibites a high Vickers hardness up to HV 1 329. In addition, an amorphous-crystalline transition layers are observed in the rod. This transition zone is caused by unhomogeneous temperature distribution and relatively lower GFA for Fe-based alloys.

Key words: bulk amorphous alloy; metallic glass; GFA(glass forming ability); quenching; crystallization

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1 INTRODUCTION

Metallic glasses fabricated by rapid quenching from melt were first discovered in 1960[1, 2], but because of the high quench rate requirements(10^4-10^6 K/s), only thin ribbons and sheets with a thickness less than 0.1 mm could be fabricated. The synthesis of bulk metallic glasses (with thickness > 1 mm) was successfully achieved by Chen in 1970s, but it was limited to those containing noble elements(such as Pd, Pt)[3]. Recently, it was discovered that certain metallic glasses can be fabricated from the liquid state at critical cooling rate from 0.1 K/s to several hundred K/s[4, 5]. This enables the production of bulk amorphous alloys with a thickness of the order of mm or even cm. Based on the achievements obtained in the research field of bulk amorphous alloys, three empirical rules have been proposed: (1) multicomponent systems consisting of more than three elements, (2) atomic size mismatch above 12% among the main constituent elements, and (3) negative heats of mixing among their elements[6-8]. It is well known that good magnetic properties can be achieved from amorphous alloys fabricated by ferromagnetic materials Fe, Co and Ni, but extremely high cooling rate is needed and consequently bulk forms are unavailable[9]. From 1995, a serials Fe-based bulk amorphous alloys with relatively large sizes and excellent magnetic properties have been developed, e.g., Fe-(Al, Ga)-(P, C, B, Si, Ge), Fe-(Nb, Mo)-(Al, Ga)-(P, B, Si), Fe-(Zr, Hf, Nb)-(Cr, Mo)-B, Fe-(Nb, Cr, Mo)-(P, C, B), Fe-Co-(Zr, Nb)-(Mo, W)-B, Fe-Nb-Nd-B. Among these Fe-based amorphous alloys, it has been found that the GFA of $Fe_{61}Co_7Zr_{10}Mo_5W_2B_{15}$ (mole fraction, %) composition is the highest, and the t_{max} is evaluated about 6 mm in diameter in the shape of rod. But this important empirical result has not been confirmed by else researchers[10-15].

In this paper, the glass forming ability of Fe-based alloy is investigated and the amorphous-crystalline transition layers formed during the melt quenching are discussed. The supercooled liquid region of this alloy is also studied. In addition, the glass forming ability of alloys is discussed on the structural and processable point of view.

2 EXPERIMENTAL

The master ingot was prepared by arc melting the mixture of pure Fe and other metals on a magnetic stirring water-cooled crucible under a Ti-gettered Ar atmosphere. The crystalline boron in the shape of needles was applied in order to prepare Fe-based master ingot. The purity of

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all the elements used was more than 99.5%. The alloy compositions of $Fe_{61}Co_7Zr_{10}Mo_5W_2B_{15}$ represented the nominal atomic percentage of the mixture. The Fe-based little buttons with different transverse cross sections were prepared in the same arc furnace. The Fe-based rods were fabricated by injecting the melts into copper mould under Ar atmosphere. The buttons and rods achieved were cut off using diamond wheel machine and by means of spark-erosion. The structure was studied by X-ray diffractometry (RIGAKU, D/max-rB, Cu K_α). The parameters associated with the thermal stability were carried out by NETZCH 404 high temperature differential scanning calorimeter (DSC) at a heating rate of 0.33 K/s. The microhardness was measured under a load of 9.8 N by FM-7 Vickers hardness tester (SUZUKI, loading time 15s). The metallographical structures were observed by optical microscopy (OM, Olympus BH).

3 RESULTS AND DISCUSSION

In order to investigate the GFA of the Fe-based alloy with the composition of $Fe_{61}Co_7Zr_{10}$-$Mo_5W_2B_{15}$, several buttons with various transverse cross sections were prepared by arc melting technique under a Ti-gettered Ar atmosphere. These buttons have shining surface, but the XRD results (Fig. 1) show that only sharp-peak spectra obtained, that is, no amorphous phase existed in the buttons. It can also be seen that the less the size of the buttons, the less the crystalline fraction in it.

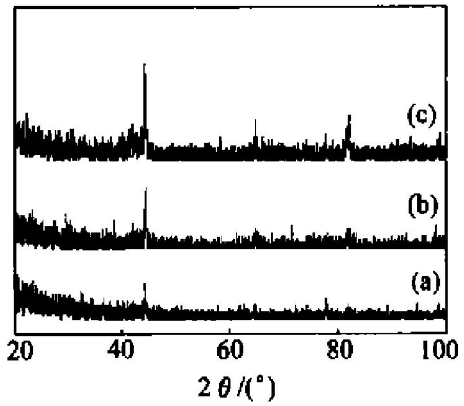

Fig. 1 XRD spectra corresponding to transverse cross sections of Fe-based buttons with diameter of 3.1 mm(a), 4.0 mm(b) and 4.7 mm(c)

The Fe-based rods with d 2.5 mm were fabricated by injecting the melts into copper mould. They also have shining metallic luster. The schematic of the buttons and rods as well as the positions selected for special study of structure are shown in Fig. 2. The rectangle (Fig. 2(d)) corresponds to the part for optical microscopy (OM) in Fig. 3. The Vickers hardness testing for Fe-based rods corresponded to the rectangle is shown in Fig. 2(b). The parts used for DSC testing are shown in Fig. 2(c) (3# and 5#). Table 1 shows the XRD and microhardness results of the rods (1# in Fig. 2(c)), buttons (B1-B3), and master alloy ingot (MAI). It should be noted that the less the transverse cross section is, the higher the microhardness could be achieved due to diminshing the structure scale of eutectic microstructure.

Table 1 XRD and HV results of rods, buttons and MAI

Shape	D/mm	H/mm	Mass/g	XRD results	HV
Rod	2.5	50.0	4.00	a+ c	1 175 - 1 329
B1	4.3	3.1	0.30	c	630 - 740
B2	5.5	4.0	0.56	c	720 - 800
B3	7.0	4.7	1.01	c	650 - 690
MAI	–	–	86.00	c	570 - 610

a —Amorphous; c —Crystalline

The amorphous-crystalline transition layers could be identified through metallographical observation. This zone located in the cone-shape head (Fig. 2(d)) of the rod. The zone with gray color was crystalline, yet the zone with light color was the transition layer from amorphous to crystalline structure, which means that amorphous phase was formed in this region. Thermal stability parameters associated with glass transition, supercooled liquid region, and crystallization were examined by high temperature DSC for the Fe-based rods (Fig. 4). The values of T_g, T_x, T_m (where T_m is the melting temperature) and ΔT_x for Fe-based rods were 634.5 ℃, 673.5 ℃, 1 191.9 ℃ and 39 ℃, respectively. It has been pointed out that there is close relation among supercooled liquid region ΔT_x, reduced glass transition temperature T_{rg} ($= T_g/T_m$) and glass forming ability of bulk amorphous alloys, that is, a clear tendency for GFA to increase with increasing ΔT_x and T_g/T_m[16-19]. Good bulk glass formers are alloys with deep eutectics and a high T_{rg} up to 2/3[20]. For this Fe-based alloy, the value of T_{rg} was 0.53. Maybe this value was different from other researchers' results, but it corresponded the poor GFA in these experiments. Moreover, other samples cut from upper part of the rod (5# in Fig. 2 (c)) did not show any exothermal peak in the testing temperature range. It indicated that this rod has layered structure and the amorphous phase is concentrated near bottom transverse cross section.

This fact can be confirmed by Vickers hardness testing of orthogonal and longitudinal sections performed for the samples (Fig. 2(b) and (d)). Bottom part of the rod has hardness of HV 1 329

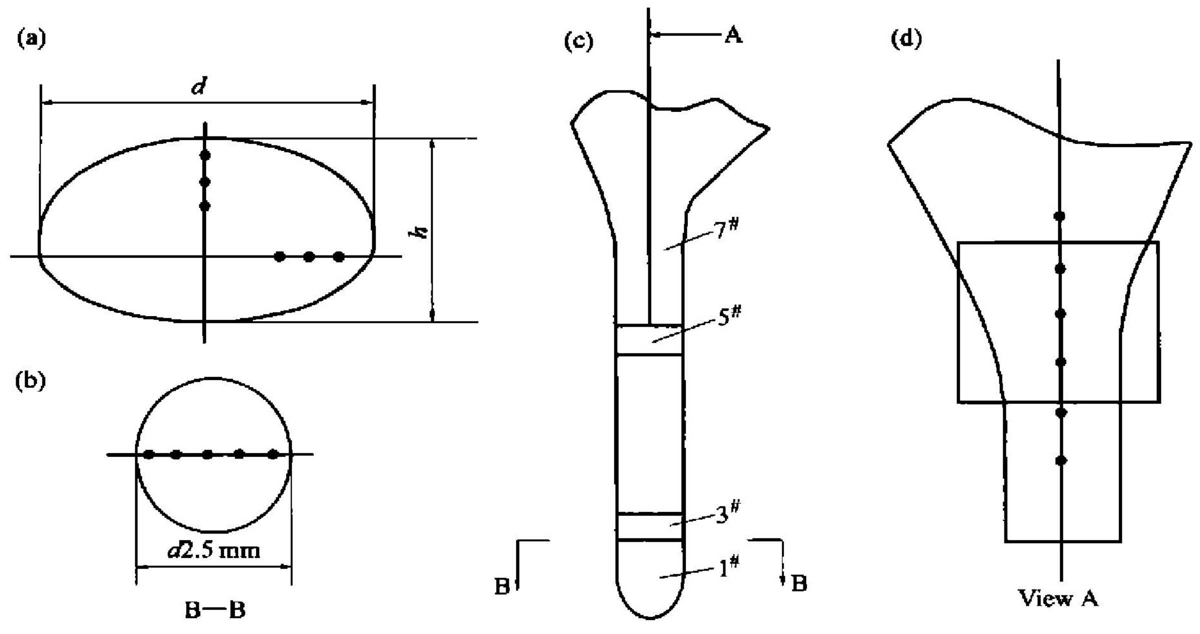

Fig. 2 Schematic of Fe-based button and rod and parts selected for testings
(Arabic numerals 1, 3, 5, 7 in Fig. 2(c) represent respectively testing parts)

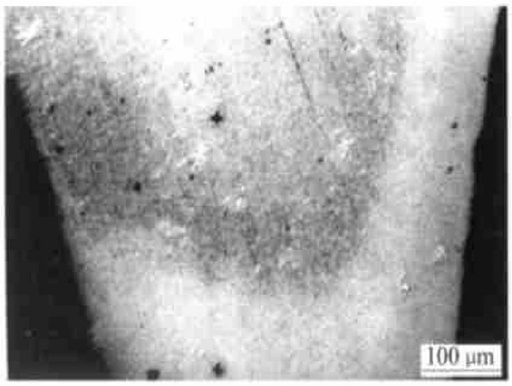

Fig. 3 Amorphous-crystalline transition layers at cone-shaped head of Fe-based rod with d 2.5 mm

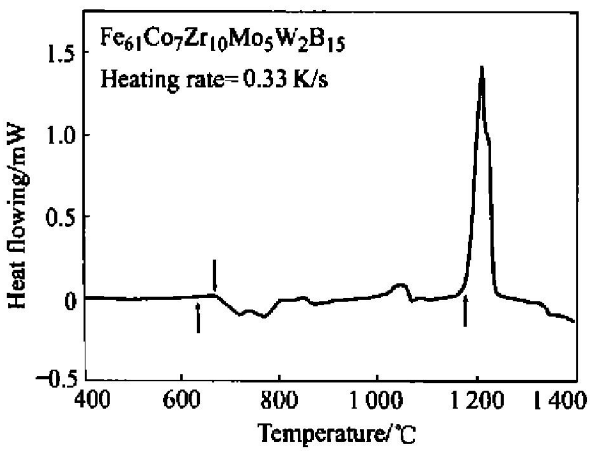

Fig. 4 DSC curve for Fe-based rod(3# in Fig. 2(c)) with d 2.5 mm

near the surface whose hardness being HV 1 200 at the center of the rod(1#). However, at the upper part of the rod only HV 928 is received for the light color area(7#). The microhardness is decreased to HV 650 in the cone-shaped head of the sample(gray crystalline zone in Fig. 3).

From that discussed above, we can conclude that the critical thickness of fully amorphous rods fabricated by injection technique is less than 2.5 mm for this composition. Although the rod has more mass than the buttons, yet the conditions with respect to amorphous forming were better than the latter. This results caused by the extremely steep temperature distribution in the melt during melting by arc. The temperature of the melt is over 3 000 ℃ near the arc but lower at the bottom contacting with the water-cooled copper mould. As we reported before, only a limited temperature range, which we called undercoolable melts(UCM), can produce good conditions for glass forming in the Zr-based alloys[21]. It is expected the same condition in the Fe-based amorphous forming. The melt of the rod was prepared by magnetic levitation followed by even cooling of copper mould through injection technique, so the temperature distribution is more homogeneous by means of magnetic levitation induction melting than arc melting. As a result, the injection technique has an advantage over arc melting method for preparing bulk amorphous alloys.

4 CONCLUSION

The alloys with the glass-forming composition $Fe_{61}Co_7Zr_{10}Mo_5W_2B_{15}$(mole fraction, %) was prepared using elements with high purity. The XRD spectra indicate that all the Fe-based buttons have no amorphous phase, but the crystalline fraction decreases with decreasing transverse cross sections. Different part of the rod with d 2.5 mm exhibits various structure, which leads to different microhardness and thermal stability. The rods prepared by injection technique have layered structure and the amorphous phase is concentrated near bottom transverse cross section. The interval of the supercooled liquid region is 39 K for the Fe-based alloy. Homogeneous temperature distribution can result in good conditions for amorphous forming. The critical thickness of fully amorphous rods fabricated by injection technique is less than 3 mm for a composition of $Fe_{61}Co_7Zr_{10}Mo_5W_2B_{15}$.

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