Prominent Fe-based bulk amorphous steel alloy with large supercooled liquid region and superior corrosion resistance

P.H. Tsai a, A.C. Xiao b, J.B. Li b, J.S.C. Jang a,b,⇑, J.P. Chu c, J.C. Huang d

a Institute of Materials Science and Engineering, National Central University, Jhongli City, Taoyuan 32001, Taiwan
b Department of Mechanical Engineering, National Central University, Jhongli City, Taoyuan 32001, Taiwan
Department of Materials Science and Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan
c Department of Materials and Optoelectronic Science, National Sun Yat-Sen University, Kaohsiung 804, Taiwan

A R T I C L E   I N F O

Article history:
Received 29 July 2013
Received in revised form 27 September 2013
Accepted 27 September 2013
Available online 10 October 2013

Keywords:
Bulk amorphous steel
Metallic glass
Thermal properties
Corrosion resistance
Sharpness test

A B S T R A C T

A prominent Fe-base bulk amorphous steel (BAS) alloy which presents high glass forming ability (GFA), good corrosion resistance, superior mechanical properties and relative lower cost. The Fe_{41}Cr_{15}Co_{7}Mo_{14}C_{21},B_{2}Y_{2} (x = 5–10) BAS rods with a diameter of 2–6 mm, can be fabricated by the suction casting method. The highest GFA value can be obtained by adjusting the ratio of boron/carbon, reaching to the value of \gamma = 0.4 and \gamma_{m} = 0.69 for the alloy composition of Fe_{41}Ce_{10}Co_{4}Mo_{14}C_{21}B_{2}Y_{2}. Meanwhile, this alloy also presents very large supercooled liquid region up to 81 K, favourable to be fabricated into micro-surgery tools by thermoplastic forming. In addition, the Fe-base BAS alloy exhibits extremely high hardness around 1200 Hv. The anodic polarization measurement of the Fe-based BAS exhibits a higher corrosion resistance than 304 SS and 316 SS in the Hank’s balanced salt solution. The sharpness test results reveal that the Fe-based BAS blade exhibits much higher sharpness because of its lower surface roughness and higher hardness. Moreover, the Fe-base BAS blade presents much better durability on cutting testing, it can remain relatively sharper edge-tip with a low blade sharpness index (BSI) value of 0.38 (in comparison with the BSI value of 0.59 for commercial blades) after the cutting testing over 50 cm length.

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1. Introduction

The Fe-based bulk metallic glass (BMG), also known as the Fe-based bulk amorphous steel (BAS), has drawn great attention due to the unique properties such as excellent magnetic properties, high fracture strength, high hardness, excellent corrosion resistance, superior thermal stability favorable for structural as well as functional applications [1–10]. In addition, the Fe-based BAS can be fabricated by using industrial ferrous-alloys, significantly reducing the production cost [11]. Recently, some researchers used BMGs to make surgical blades and revealed that the blade edge-tips are extremely flat and the surface roughness readings of the blade surfaces and edge-tips decrease down to nano-scales due to the amorphous nature. As a result, the cutting sharpness was enhanced significantly in comparison with the commercial surgical blades [12]. According to recent works of amorphous alloys, the Fe-based BAS can be an excellent choice for medical implants, surgical tools and other biomedical related parts.

According to previous researches, the Fe_{41}Cr_{15}Co_{7}Mo_{14}C_{21}B_{2}Y_{2} BAS [13,14] shows excellent glass forming ability (GFA), high fracture strength and hardness, but exhibits no plastic strain at room temperature. This makes it not easy to be fabricated into large sizes and thus limits their uses. Considering the factors in increasing the GFA of the Fe-based BAS, heats of mixing and atomic packing density are the keys to calibrate the character of Fe-based BAS alloy systems. For example, the heat of mixing of Fe–Mo, Fe–Cr, Fe–Co, Mo–Co, Mo–Cr, Fe–B, Mo–B, Cr–B and Co–B are –2, –1, –1, –5, 0, –26, –2, –31 and –24 kJ/mol, respectively, indicating boron would play an important role for adjusting the GFA in this alloy system.

The martensitic stainless steel is the most common material for medical tools and instrument parts, particularly in disposable surgical blades. Additionally, our previous work showed that the ZrCuA–La_{3}Si BMG blade exhibits flat edge-tip and lower surface roughness than the commercial one [12]. Moreover, the blade sharpness index (BSI) value of the Zr-based BMG blade is smaller than that of the commercial blade by 30%. A lower BSI value indicates a sharper blade (the BSI value typically varying between 0.2 for sharp blades and 0.5 for blunt blades), and a sharper blade can cut through rubber substrate with less energy. In clinical surgery, the surgery blades with better sharpness and durability can make a clean long distance cut and create a neat wound, resulting in faster healing.

In this study, the Fe_{41}Cr_{15}Co_{7}Mo_{14}C_{21}B_{2}Y_{2} alloy is selected as the base alloy for evaluating the effect of carbon/boron ratio on...
its GFA and thermal properties. In addition, the corrosion resistance of the Fe-based BAS, 304 SS and 316 SS is investigated by the anodic polarization measurement in simulated body fluids. Moreover, the surface and the edge-tip morphologies of blades before and after the cutting experiment were examined by scanning electron microscopy (SEM).

2. Experimental procedures

The Fe41Cr15-Co-Mo-C-B (x = 5–10) BASs were prepared by arc melting of the appropriate mixture of ferrous alloys and pure elements, such as cast iron (94.2 wt% Fe, 4.8 wt% C, 1 wt% Si), high boron ferrous alloy (77.45 wt% Fe, 21 wt% B, and 0.55 wt% C), chromium (99 wt% purity), cobalt (99.9 wt% purity), molybdenum (99 wt% purity), boron (99.99 wt% purity) and yttrium (99% purity), under a Ti-gettered argon atmosphere. The ingots were re-melted four times in a furnace with purified argon atmosphere to ensure their homogeneity. In the last melting, the liquid melt was then suction-cast into the water-cooling Cu mold to form plates (with the dimension of 20 mm in width, 50 mm in length and 3 mm in thickness) and rods (2–6 mm in diameter). The amorphous state of the BAS plates and rods was ascertained by X-ray diffraction analysis (XRD, Bruker D8 X-ray diffractometer) with monochromatic Cu Kα radiation. The XRD patterns were obtained from the central area of the BAS rods. Thermal analyses of the as-cast samples were carried out by differential scanning calorimeter (DSC, NETZSCH STA 449C) and high temperature differential scanning calorimeter (HTDSC, NETZSCH STA 449F3), respectively. The samples for DSC and HTDSC analyses were cut from the top end of the BAS rods near the pouring gate. The tests of hardness and fracture toughness for all Fe-BAS alloys were carried out by the indentation method by a micro-hardness tester (Mitutoyo, HM-221) with a load of 1–2 kgf. The Fe-based BAS plates, 3 mm in thickness, were machined into a shape of scalpel blade by the wire electrical discharge cutting process. The blade was then reduced in thickness, sharpened at its edge-tip and finally fine-polished. The edge-tip has an angle of 30°, identical to the commercial blade. The surface morphology of blades was examined by low vacuum SEM (Hitachi S-3500N) with energy dispersive spectrometry (EDS). For the blade sharpness evaluation, a self-made rig was established based on the report of McCarthy et al. [15,16] and the experiment reported by our previous work [12].

3. Results and discussion

The XRD patterns of the Fe-based BAS rods (4 mm in diameter) demonstrate the amorphous nature with a broadened and diffused hump in the 2θ range of 30–50° for all of these Fe41Cr15-Co-Mo-C-B, (x = 5–10) alloys, no resolvable crystalline peak is detected, as shown in Fig. 1(a). This indicates that a fully amorphous state of these alloys has been achieved by the Cu-mold suction casting method. In addition, the typical appearance of the amorphous rods (even up to 6 mm in diameter) for the Fe41Cr15-Co-Mo-C-B (Fe-B9) BAS alloy (Fig. 1(b)) shows the characteristic shining surface.

The DSC curves of the Fe41Cr15-Co-Mo-C-B (x = 5–10) BAS rods with a diameter of 4 mm are shown in Fig. 2. All of the samples exhibit a clear glass transition followed by a supercooled liquid region and then exothermic reaction due to crystallization. The glass transition temperature (Tg), crystallization temperature (Tx), and supercooled liquid region (∆Tg = Tx - Tg), changed with increasing boron content, as listed in Table 1. It can be seen from Table 1 that the liquidus temperature (measured by HTDSC) decreases with increasing boron content. According to the analyses of Turnbull [17], the best metallic glass forming alloys are at or

![Fig. 1. XRD patterns of the Fe41Cr15Co-Mo-C-B (x = 5–10) alloy rod samples of 4 mm in diameter, and (b) appearance of the as-quenched Fe41Cr15Co-Mo-C-B, Y2Co7 BAS rod of 6 mm diameter.](image)

![Fig. 2. (a) DSC plots of the Fe41Cr15Co-Mo-C-B (x = 5–10) BASs with a heating rate of 20 K/min, and (b) the activation energy estimated by the Kissinger plots as a function of boron content for the Fe41Cr15Co-Mo-C-B (x = 5–10) BASs.](image)
near the deep eutectic composition and would correspond to the highest glass forming ability (GFA). As a result, the values of typical GFA index (γ and γm, where γ = Tp/(Tc + Tl) [18] and γm = (2Tx − Tp)/Tl [19]) all exhibit an increasing trend with the boron additions and reach to the optimum value of 0.400 and 0.687, respectively, at the Fe-B9 alloy. In parallel, this alloy also presents very large supercooled liquid region up to 81 K. Therefore, it is suggested that the GFA of the Fe41Cr15Co7Mo14C21-B8Y2 alloy system can be increased by adjusting the carbon/boron ratio appropriately.

The activation energies of crystallization for the Fe41Cr15Co7Mo14C21-B8Y2 (x = 5–10) alloys were determined by means of the Kissinger plot [20]:

$$\ln\left(\frac{b}{T^2}\right) = -\frac{E_a}{R}T + \text{constant},$$

where b is the heating rate, Tp is the peak temperature of crystallization, R is the gas constant, and Ea is the activation energy. The activation energy of crystallization can be determined from the slope of a plot of the ln(b/Tp²) against 1/Tp. Fig. 2(b) shows the activation energy of crystallization calculated by the Kissinger plot as a function of boron content for the Fe41Cr15Co7Mo14C21-B8Y2 (x = 5–10) BASs. It indicates that all of the compositions have relatively high activation energies (>290 kJ/mol).

Fig. 3 shows potentiodynamic polarization curves of the Fe-B9 BAS, 304 SS and 316 SS in the Hank’s salt solution. The corrosion potential (Ecorr), the pitting potential (Epit) and the corrosion current density (Icorr) can be measured from the polarization curves and are listed in Table 2. Values of the corrosion current density (Icorr) for the Fe-B9 BAS, 304 SS and 316 SS estimated by the Tafel slope method are about 9.82 × 10⁻⁸, 7.83 × 10⁻⁸, and 5.96 × 10⁻⁸ A/cm², respectively, in the Hank’s solutions. The comparison of the polarization curves indicates that the Fe41Cr15Co7Mo14C21-B8Y2 BAS exhibits a wider passive region than the 304 SS and 316 SS, the passive region (Epit − Ecorr) of Fe-B9 BAS can be up to about 1.356 V. This implies that with a small corrosion current density (Icorr) and a higher pitting potential (Epit) in simulated body fluids, the Fe-B9 BAS exhibits better corrosion resistance than 304 SS and 316 SS. Without defects such as grain boundaries on the surface, the amorphous structure of the BAS leads to a more...
homogeneous passive film after anodic polarization. Moreover, the increase of the molybdenum content will increase the stability of passive layer, thus preventing from the over-pitting phenomenon on the surface.

The representative surface micrographs of the Fe-B9 BAS alloy, 304 SS and 316 SS after polarization in the Hank’s solution are shown in Fig. 4. It can be clearly seen that massive pits appeared on the surface of 304 SS and 316 SS, the hole sizes were about 50–100 \( \mu \)m and 150–300 \( \mu \)m, respectively. Conversely, the surface micrograph of the Fe-B9 BAS sample still presents a flat surface without any pit after polarization, indicating that the Fe-B9 BAS has better corrosion resistance than 304 and 316 SS.

The results of hardness tests reveal that the ratio of carbon/boron does not affect the hardness of these \( \text{Fe}_{41}\text{Cr}_{15}\text{Co}_{7}\text{Mo}_{14}\text{C}_{x}\text{B}_{x}\text{Y}_{2} \) \((x = 5–10)\) BASs. All of these BASs present similar high hardness readings about 1200 ± 30 Hv. Furthermore, the fracture toughness measured by the indentation method [21] could be improved significantly from the \( \text{Fe}_{41}\text{Cr}_{15}\text{Co}_{7}\text{Mo}_{14}\text{C}_{16}\text{B}_{5}\text{Y}_{2} \) BAS (Fe-5B BAS,
The SEM observation on the surface of the blade edge-tip before cutting test shows that the Fe-B9 blade has much smoother edge-tip surface than the commercial blade (2.78 ± 0.67 μm), as shown in Fig. 7. The highly smooth surface of the Fe-B9 blade would impose benefit in reducing its friction forces during cutting and would result in increasing sharpness. Fig. 8 shows the SEM image of the blade edge-tip after different cutting lengths. The edge-tip of the commercial blade was curled and blunt after cutting testing for 25 cm length (Fig. 8(b)) and presents only slightly damaged morphology after cutting testing for 50 cm length (Fig. 8(f)). This demonstrates that the Fe-B9 BAS blade possesses much better cutting durability than the commercial one.

The SEM observation on the surface of the blade edge-tip after different cutting lengths. The edge-tip of the commercial blade was curled and blunt after cutting testing for 25 cm length (Fig. 8(b)) and presents much worse damaged morphology after cutting testing for 50 cm length (Fig. 8(c)). On the contrary, the Fe-B9 BAS blade exhibits the almost same shape of edge-tip as the original after cutting testing for 25 cm length (Fig. 8(e)) and presents only slightly damaged morphology after cutting testing for 50 cm length (Fig. 8(f)). This demonstrates that the Fe-B9 BAS blade possesses the higher sharpness as well as cutting durability than the commercial one, it has high potential for the application of medical tools.

4. Conclusions

Based on the results of XRD and DSC analyses, the Fe-based BAS can be successfully fabricated by using the raw materials of cast iron and industrial ferrous alloys in this study. This demonstrates that the production cost can be much lower than that of other based BMGs. The optimum GFA (γ = 0.4, γm = 0.69) can be obtained by adjusting the composition ratio of carbon/boron and the optimum alloy composition locates at Fe41Cr15Mo14C12B8Y2Co7.

Meanwhile, this alloy also presents very large supercooled liquid region up to 81 K. Due to the amorphous structure nature, the Fe-based BAS shows lower corrosion current density values and displays higher pitting potential values (Epit - Ecorr = 1.356 V) than 304 and 316 SS in the Hank’s solution. In addition, the Fe-based BAS blade presents a higher cutting sharpness with a lower BSI value (0.264) than the commercial one (0.312). In addition, the Fe-based BAS blade exhibits much better wear durability than the commercial blade during the cutting test because of its extremely high hardness about 1200 Hv. The Fe-based blade still remains a relatively lower BSI value of 0.376 in comparison with the value of 0.596 for the commercial blade after cutting testing for 50 cm length.

Acknowledgement

It is gratefully to acknowledge the sponsorship by National Science Council of Taiwan, ROC, under the Project Nos. NSC101-2221-E-008-043- MY3 and NSC101-2120-M-110-007.

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