Effects of Yttrium addition on glass-forming ability of Fe-based bulk metallic glasses: Structural and mechanical properties by Nanoindentation Technic

Accepted 20th May, 2017

ABSTRACT

Effect of yttrium on glass-forming ability (GFA), thermal stability and mechanical properties of glassy Fe-Cr-Mo-C-B-Y alloy were studied. Amorphous alloys with composition (%) Fe_{40}Cr_{13}Mo_{14}Cu_{3}B_{5}Y_{2} were prepared using a commercial AISI430 steel as the base material. Bulk Metallic Glass (BMG) was prepared by using commercial grade raw materials and rods of 2 mm diameter obtained by copper mold casting. Ribbons of width 5 mm and thickness of about 30 µm were prepared from the arc-melted ingots using a single roller melt spinner at a wheel speed of 40 m/s. The thermal and structural properties of the samples were measured by a combination of differential scanning calorimetric (DSC), x-ray diffraction and scanning electron microscopy. Chemical compositions were checked by energy dispersive spectroscopy analysis. X-ray diffraction and scanning electron microscopy observations confirmed that an amorphous structure is obtained in all the samples. A minor fraction of crystalline phases (oxides) was detected on the cast surface. Values of hardness and Young modulus were measured by Nanoindentation for both alloys. The effects of adverse casting conditions (such as air atmosphere, non-conventional injection copper mold casting and partial replacement of pure elements with commercial grade raw materials) on the glass formation and properties of the alloy are discussed.

Keywords: metallic glass, iron-based alloy, yttrium, mechanical properties, Nanoindentation Technic

INTRODUCTION

Metallic glasses (MGs) or amorphous metallic alloys are non-crystalline metals which lack long-range atomic periodicities because they are generally formed with fast quench rates for the retention of the glassy state from the melt. Metallic glasses have attracted much attention due to their fascinating properties such as high strength and hardness, ultra-soft magnetic properties and good corrosion resistance (Sheng et al., 2005; Takeuchi and Inoue, 2004). The first Fe-based metallic glasses of Fe–P–C alloy were synthesized by Duwez and Lin (1967). At first, Fe-based BMGs were developed with the purpose of obtaining very good soft ferromagnetic properties due to the structural isotropy of the material (high Fe content alloys in Fe–B–Si system) (Inoue and Takeuchi, 2002; Inoue and Shen, 2004).

However, during the last decade, these materials were prepared with lower Fe content showing a paramagnetic behavior at room temperature. These amorphous Fe-based alloys are known as amorphous steels (Lu et al., 2004). Therefore, these arch for Fe-based bulk metallic glasses prepared from low cost raw materials is important for practical applications. Recently, it was found that the addition of minor amount of rare-earth elements dramatically enhanced the glass forming ability (GFA) of Fe-based glassy alloys. It was suggested that the rare-earth elements with larger atomic sizes may either act as oxygen scavenger or stabilize the supercooled liquid alloy, consequently improving the GFA. Inoue and Shen (2004)
succeeded in preparing a Fe-based bulk metallic glass of Fe_{48}Cr_{12}Mo_{14}C_{15}B_{6}Y_{2} with great glass-forming ability by copper mould casting and a ribbon with same alloy by melt-spinning using raw materials and quenched in air atmosphere.

**MATERIALS AND METHODS**

In order to evaluate the possibility of an industrial scale production of the structural amorphous steels, a yttrium containing system was also prepared using an AISI430 steel (55.7 wt%) and a commercial grade FeB alloy (7.3 wt%) as base materials; the desired stoichiometry was obtained by adding Mo (25.7 wt%), C (3.4 wt%), Cr (5.4 wt %) and Y (3.4 wt%) in the form of pure elements. Master alloys were produced by arc-melting under Argon atmosphere.

The samples were re-melted in an induction furnace and quenched in air atmosphere into a water-cooled copper mould in order to obtain a glassy structure. BMG alloy was cast in a rod shape using a cylindrical copper mould of 2 mm diameter. Ribbons of width 5 mm and thickness of about 30 µm were prepared from the arc-melted ingots using a single roller melt spinner at a wheel speed of 40 m/s. The amorphous character was identified by X-ray diffraction (XRD) using the Philips PW1830 (Co Kα, λ=1.7897 Å) diffractometer. All the XRD patterns were reported as a function of the wave vector \( S=4\pi\sin(\theta)/\lambda \), where \( \theta \) corresponds to the scattering angle.

Scanning electron microscopy (SEM) investigations were performed using a Leica Stereoscan 420 microscope instrument and chemical compositions checked by Energy Dispersive Spectroscopy (EDS) analysis. Thermal analysis was performed in a Perkin Elmer Diamond differential scanning calorimeter (DSC) and in a Setaram high-temperature differential scanning calorimeter (HTDSC) at a heating rate of 10 K/min. Nanoindentation tests were carried out with a Fischerscope HM2000 employing a Vickers indenter. Several indents were performed to make sure that the maximum penetration displacement was significantly lower than 1/10 of the sample thickness. Values of indentation hardness (\( H_{TV} \)) and elastic indentation modulus (\( E_{TV} \)) were obtained from the loading and unloading curves, respectively, according to the procedure proposed by Oliver and Pharr (1992).

**RESULTS AND DISCUSSION**

Figure 1 shows the X-ray diffraction (XRD) patterns of the cast glassy Fe_{48}Cr_{12}Mo_{14}C_{15}B_{6}Y_{2}. X-ray diffraction pattern as-cast ribbon (Figure 1a) show only a broad halo without crystalline peaks indicating the presence of a fully amorphous structure. In the case of the cross section of the rod (Figure 1b), it is clearly seen that there is no crystalline phase existing in the amorphous matrix in the rod sample.

Figure 2 shows the back scattered SEM images of the as-cast samples. Chemical analysis was obtained by EDS only for metals because light elements cannot be detected with accuracy. Figure 2a shows the SEM back scattering micrograph of the cross-section taken from the top-middle part of the rod. It is possible to distinguish some micrometric sized precipitates that are homogeneously distributed across the section. EDS chemical analysis reveals that the precipitates present very high fraction of Y and O, while the surrounding amorphous matrix has less Y content than expected. The same phenomenon was found for ribbon (Figures 2b and 3).

Additionally, Y_{2}O_{3} found is certainly formed due to the high reactivity of yttrium with the oxygen. It is known that minor addition of rare earth elements (REs) is a powerful mean for modifying the properties and the glass forming
ability of metallic glasses and this was employed in Fe-based BMGs (Wang, 2007). The oxygen scavenging effects of REs is to retard the nucleation and growth of carbides, stabilizing the undercooled melt and, consequently, favoring the amorphization (Lu et al., 2004).

The crystallization and melting curves behavior of all amorphous samples was studied by High Temperature Differential Scanning Calorimeter (HTDSC) at a heating rate of 10 K/min (Figure 4). In order to identify glass transition temperature ($T_g$) and crystallization temperature ($T_c$), the experiment was repeated with the conventional DSC for the same as-cast sample (Figure 5). Table 1 shows the main characteristic temperatures and the thermal parameters describing the glass forming ability. The thermograms sample of the bulk and ribbon melts in a single endothermic peak. The melting temperature appears in high temperature events that might be due to the melting of impurities present in the commercial grade raw materials. The apparent liquidus temperature of samples BMG is significantly higher than the one observed for samples ribbon leading to a decrease of the parameter $\gamma = T_x/(T_g + T_l)$ used for assessing the glass forming ability. The maximum amorphous thickness achievable (critical casting thickness) is at least 2 mm in the case of B2 (BMG) alloy. However, it is expected that the use of raw
Figure 4: HTDSC curves of as-cast bulk and ribbon.

Figure 5: DSC curves of as-cast bulk and ribbon.

materials reduced the amorphous thickness of the alloy with respect to the use of pure elements. The reduction on the GFA can be inferred from differences in \( \gamma \) parameter which was suggested to be correlated with the critical
thickness (Lu and Liu, 2002). In the case of samples, the HTDSC traces of crystallization appear to be very similar for ribbons and BMG.

DSC curves of the two samples of alloys exhibit the sequential transition of amorphous solid, glass transition, supercooled liquid and crystallization (Figure 4). The DSC scan of sample BMG exhibits the characteristic wide supercooled liquid region

$$\Delta T_x = T_{x(onset)} - T_{g(onset)} = 45^\circ C.$$  

The sample crystallizes through a sharp single exothermic crystallization peak.

Nanoindentation tests were performed on the BMG and ribbon. The sample thicknesses are 30 µm for ribbon and 2 mm for BMG. The hardness and elastic modulus were found to be 16.73 ± 3.83 and 192.49 ± 3.3 GPa, respectively, for BMG and 16.29 ± 2.7 and 166.34 ± 1.69 GPa, respectively, for ribbon (Table 1). Such values are higher compared to the results previously reported for the same alloy prepared with pure elements and conventional injection casting technique (H=13 GPa, E=180 to 200 GPa) (Ponnambalam et al., 2004) as well as for alloys with similar composition (H=13.8 GPa) (Lu et al., 2004). In addition, nanoindentation hardness values and minor addition of Y in the base alloy Fe_{68}Cr_{15}Mo_{14}C_{15}B_{6}Y_{2} is beneficial to the mechanical properties.

For this alloy, the increase in the hardness value can be explained by the presence of an amount of the micrometric crystals Y_{2}O_{3} incorporated in the amorphous matrix. There are two supposed views to explain the role of Y element on GFA and thermal stability of glassy alloys. One is concerning with the intrinsic role of minor alloying elements, that is, Y element has strong effect to destabilize the competing crystalline phase and stabilize the liquid phase (Ponnambalam et al., 2004; Lu et al., 2004; Lu and Liu, 2004). Another is that Y element improved the manufacturability of these alloys by scavenging the oxygen impurity from it through the formation of innocuous yttrium oxides.

**Conclusion**

Glass-forming ability of the glassy Fe_{68}Cr_{15}Mo_{14}C_{15}B_{6}Y_{2} alloy is enhanced by addition of (2) at% Y element. As-cast bulk amorphous alloys showed large thermal stability with glass transition temperatures above 850 K and supercooled liquid regions above 40 K and high strength with Vickers hardness larger than HV 1600. Cylindrical glassy rods with a diameter of 2 mm can be easily obtained by copper mold casting.

**REFERENCES**


Inoue A, Shen BL, Chang CT (2004). Super-high strength of over 4000 MPa for Fe-based bulk glassy alloys in [(Fe_{1-x}Co)_{0.75}B_{1-x}]Si_{2}C_{0.56}N_{0.44} system. Acta. Mater. 52(14): 4903-4909.


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**Table 1: Thermal and mechanical properties of samples.**

<table>
<thead>
<tr>
<th>Variable</th>
<th>T_{g}(^\circ C)</th>
<th>T_{x}(^\circ C)</th>
<th>T_{m}(^\circ C)</th>
<th>T_{l}(^\circ C)</th>
<th>Y</th>
<th>H (GPa)</th>
<th>E (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMG</td>
<td>590</td>
<td>635</td>
<td>1122</td>
<td>1255</td>
<td>0.344</td>
<td>16.73 ± 3.8</td>
<td>192.49 ± 3.3</td>
</tr>
<tr>
<td>Ribbon</td>
<td>595</td>
<td>632</td>
<td>1114</td>
<td>1344</td>
<td>0.325</td>
<td>16.29 ± 2.7</td>
<td>166.34 ± 1.69</td>
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