Corrosion Behaviour of $[(\text{Fe}_{0.6}\text{Co}_{0.4})_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$ Bulk Glassy Alloy in Sulphuric Acid Solutions

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The influence of structural changes such as structural relaxation and crystallization on the corrosion behavior of the $[(\text{Fe}_{0.6}\text{Co}_{0.4})_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$ bulk glassy alloy has been investigated in aerated 0.1 and 0.5 kmol/m³ sulphuric acid solutions. All tests were carried out with the same materials in different states: as-cast and relaxed glassy and crystalline states. It was found that the multicomponent $[(\text{Fe}_{0.6}\text{Co}_{0.4})_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$ glassy alloy had an ability to passivation in aerated sulphuric acid solutions irrespective of microstructure. The subsequent complete crystallization of the bulk glassy alloy leads to a significant decrease in corrosion resistance, while appropriate structural relaxation results in an increase in corrosion resistance. The corrosion results were discussed and correlated with the evolution of crystallization processes by means of XRD and DSC. The effect of temperature of the corrosive medium on the corrosion behavior of the as-cast $[(\text{Fe}_{0.6}\text{Co}_{0.4})_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$ glassy alloy has also been analyzed. [doi:10.2320/matertrans.47.2566]

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1. Introduction

Since the first syntheses of bulk glassy alloys (BGAs) in lanthanide (Ln)- and Mg-based systems by copper mold casting in 1989,^{1,2)} a large number of BGAs have been developed and some of them have been used as practical materials.^{3–5)} Although the formation of BGAs before 1995 was limited to nonferrous alloy systems,^{3–5)} a Fe-based BGA was synthesized for the first time in the Fe–(Al,Ga)–metal-loid system in 1995.⁶⁾ Subsequently, a variety of Fe-based BGA systems have been synthesized because of their potential magnetic applications.^{7–12)} Recently, considering that mechanical properties of Fe-based BGAs are also important for their applications as structural materials, we have investigated mechanical properties of Fe-based bulk ferromagnetic glassy alloys, and found that the $(\text{Fe}_{0.75}\text{B}_{0.15}\text{Si}_{0.1})_{96}\text{Nb}_4$ and $\text{Fe}_{77}\text{Ga}_3\text{P}_{9.5}\text{C}_4\text{B}_4\text{Si}_{2.5}$ BGAs exhibit high strength of about 3000 MPa.¹³⁾ Subsequently, Ponnambalam *et al.* also have synthesized a class of Fe-based BGAs with nonferromagnetism that is assumed to exhibit fracture strengths of 3000–4000 MPa when there are no casting-induced defects.¹⁴⁾ However, there had been no data on the synthesis of a Fe-based BGA system exhibiting high glass forming ability (GFA), super-high fracture strength (σ_f) over 4000 MPa, as well as good soft magnetic properties and high saturation magnetization (I_s) above 1 T. Recently, a cast $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ BGA has been designed containing large amounts of Co and B which exhibits excellent soft magnetic properties, as well as ultrahigh σ_f over 5000 MPa resulting from the strong bonding nature of Co–Ta, Ta–B, and Fe–B atomic pairs.^{15,16)} Consequently, with the aim of searching for a Fe-based BGA system with high GFA and σ_f in addition to good soft magnetic properties and high I_s , we examined the effect of the replacement of Fe by Co and the effect of increasing the B to Si concentration ratio in the $(\text{Fe}_{0.75}\text{B}_{0.15}\text{Si}_{0.1})_{96}\text{Nb}_4$ glassy alloy. $[(\text{Fe}_{1-x}\text{Co}_x)_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$ ($x = 0–0.5$) BGAs with diameters up to 5 mm were success-

fully synthesized.^{17,18)} This BGA system simultaneously exhibits ultrahigh σ_f of 3900–4250 MPa, high I_s of 0.8–1.1 T, low coercive force (H_c) of 1.5–2.7 A/m, high permeability (μ_e) exceeding 1.2×10^4 and lower saturation magnetostriction (λ_s) of $9–12 \times 10^{-6}$, which are promising for future applications as new structural and functional materials.

It is known that normal atmospheric corrosion is unavoidable in many applications where soft magnetic materials are used and the soft magnetic properties of glassy alloys are sensitively affected by corrosion.¹⁹⁾ The structure, mechanical strength and magnetic properties of $[(\text{Fe}_{1-x}\text{Co}_x)_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$ ($x = 0–0.5$) BGAs have been investigated in details. However, there have been no experimental data on corrosion properties of the BAG series produced by the copper mold casting method. Due to their promising application potential, it is of fundamental interest to understand their corrosion behavior for lifetime prediction and further alloy development. Moreover, to our knowledge, there has been no report on the effect of microstructure on the corrosion resistance of Fe-based bulk glassy alloys. In this paper, following our previous work, we report an evaluation of the corrosion resistance of $[(\text{Fe}_{0.6}\text{Co}_{0.4})_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$ bulk glassy alloy including the effects of structural relaxation, crystallization and temperature of the corrosive medium. This bulk glassy alloy possesses the highest strength for all Fe-based bulk glassy alloys reported up to date (*i.e.* 4250 MPa).

2. Experimental Procedure

Multi-component Fe-based alloy ingots with composition of $[(\text{Fe}_{0.6}\text{Co}_{0.4})_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$ were prepared by arc melting the mixtures of pure Fe, Co and Nb metals, pure Si and B crystal in an argon atmosphere. The alloy compositions represent the nominal atomic percentages. From the alloy ingots, rod shaped bulk samples with a diameter of 2 mm and a length of about 50 mm were produced by copper mould casting. Samples were studied in the as-cast and annealed states. The as-cast samples were sealed in Pyrex tubes in a

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vacuum of $\leq 2.67 \times 10^{-3}$ Pa and then isothermally annealed for 3.6 ks at 573, 773 and 973 K, respectively.

Thermal stability associated with glass transition temperature (T_g), crystallization temperature (T_x) and supercooled liquid region ($\Delta T_x = T_x - T_g$) was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. The above-mentioned annealing temperatures of samples were determined on the basis of the DSC data of the cast glassy alloy rod. Structural changes were characterized by means of DSC and X-ray diffraction (XRD). Corrosion resistance was examined by both mass loss and potentiodynamic polarization measurements. The mass loss testing at 298 K was carried out in aerated 0.1 M sulphuric acid (H_2SO_4) solutions for different times and was repeated three times for each condition. Before the experiment, the sample area was measured and weighed on a scale with 10^{-4} g accuracy. Once the experiment was over, the sample was extracted, cleaned with acetone and distilled water, dried with compressed air, and then weighed again. Consequently, the mass loss per unit surface area during the different times of the test was calculated. The corroded surface of the as-cast and annealed samples exposed to 0.1 kmol/m^3 H_2SO_4 during 168 h was examined by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). A three-electrode cell was used for potentiodynamic polarization measurements. The working electrode corresponded to the tested alloy. The counter electrode was a platinum mesh and the reference electrode was an Ag/AgCl electrode. A Luggin capillary was placed near the working electrode to minimize the solution resistance. For electrochemical corrosion tests a wire was soldered on the backside of the sample and it was then embedded in a non-conducting resin. The exposed face with an area of approximately 0.0314 cm^2 was prepared by grinding with silicon carbide paper to 1500 grit. The grinding was followed by diamond polishing with 6-micron grit diamond paste. The samples were degreased with acetone, rinsed with distilled water and dried with compressed air, before they were immersed in the solutions. During the potentiodynamic sweep experiments, the samples were first immersed into aerated 0.5 kmol/m^3 H_2SO_4 solutions for 20 min to stabilize the open-circuit potential. Subsequently, potentiodynamic curves were recorded by sweeping the potential from the open-circuit potential to anodic and cathodic directions at a scan rate of $50 \text{ mV} \cdot \text{min}^{-1}$. For all corrosion experiments in the present study, test solutions were prepared from analytical grade reagents and distilled water. Temperature of test solutions was controlled by thermostat water tank. The working temperatures were kept constant during the whole tests at 298, 313, 333 and 353 K.

3. Results

Figure 1 shows the DSC curves of the as-cast and annealed samples. The Curie temperature (T_c), the glass transition temperature (T_g), the onset temperature of crystallization (T_x) and the temperature span of the supercooled liquid region are also marked with arrows in this figure. The supercooled liquid region was defined as the difference between T_g and T_x , $\Delta T_x (= T_x - T_g)$. The T_g was determined by the intersection of the extrapolation from the base line of DSC curve

Fig. 1 DSC curves of the as-cast sample (a), 573 K annealed sample (b), 773 K annealed sample (c) and 973 K annealed sample (d).

and the endothermic reaction curve due to glass temperature. From Fig. 1(a), it is clearly seen that the as-cast sample exhibited the Curie magnetic transition at 680 K, followed by distinct glass transition at 827 K, a large supercooled region of 51 K and then crystallization at 875 K as expected for glassy alloys. Besides, crystallization occurs through a mostly single exothermic peak, and its peak temperature of the first crystalline reaction is 896 K. Based on DSC analysis, the as-cast samples were annealed at 573 K, below the Curie temperature (T_c , 680 K), at 773 K, about 50 K below T_g , and at 973 K, above the temperature of the first crystalline peak. Similar to the as-cast sample, the samples annealed at both 573 and 773 K also show a glass transition and a supercooled liquid region prior to crystallization, suggesting that structural relaxation takes place corresponding to these two annealing temperatures, as shown in Figs. 1(b)–(c). On the other hand, there also exist some differences between the DSC data of the as-cast and the annealed (573 and 773 K) samples. For example, the changes in the Curie temperature and the enthalpy (ΔH_{endo}) due to structural relaxation caused by annealing are reflected on the curves, as shown in Fig. 1. In comparison with the as-cast sample, the Curie temperature increases and ΔH_{endo} value decreases for the samples annealed at 573 and 773 K, implying that the glassy structure of the annealed samples tends to evolve towards to more stable glassy structure.^{20,21} The thermal stability parameters of the as-cast and relaxed samples are tabulated in Table 1. The annealing at 973 K caused full crystallization, as evidenced from the DSC curve without exothermic peaks (Fig. 1(d)). The DSC data on the structure of the as-cast and annealed samples will further be confirmed by the following XRD examination.

Table 1 The thermal stability parameters of the as-cast and relaxed $[(\text{Fe}_{0.6}\text{Co}_{0.4})_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$ bulk amorphous alloy rods with a diameter of 2 mm.

Sample	T_c (K)	T_g (K)	T_x (K)	ΔT (K)	ΔH_{endo} (mJ/mg)
As-cast	680	827	878	51	9.02
Annealed at 573 K	697	835	883	48	7.52
Annealed at 773 K	700	834	883	49	7.34

Fig. 2 X-ray diffraction patterns of the as-cast sample (a), 573 K annealed sample (b), 773 K annealed sample (c) and 973 K annealed sample (d).

Figure 2 shows the X-ray diffraction patterns of the as-cast and annealed samples. It is seen that the diffraction intensity increases gradually with approaching $2\theta = 20$ degrees. However, this increase is due to the cellophane adhesive tape, which was used for the fixing of the sample. The as-cast sample has a glassy structure, and its structure remains almost unchanged even after annealing at 573 and 773 K, respectively. The XRD pattern of the sample annealed at 973 K exhibits many well-defined diffraction peaks. Combined with the DSC results already mentioned, it can be concluded that the 973 K annealed sample has fully crystallized. The structure of this sample is identified as a mixed structure of $(\text{Fe,Co})_{23}\text{B}_6$, α -(Fe,Co), $(\text{Fe,Co})_3\text{B}$ and $(\text{Fe,Co})_2\text{B}$. It has been reported that the primary precipitation phase of $(\text{Fe,Co})_{23}\text{B}_6$ is in a metastable state resulting from the construction of a network-like structure, which leads to the high stability of the supercooled liquid against crystallization, and enables the formation of a bulk glassy alloy by the copper-mold casting process.²²⁾

Figure 3 shows the mass loss measurements in an aerated $0.1 \text{ kmol/m}^3 \text{ H}_2\text{SO}_4$ solution for the as-cast and annealed samples at 298 K. It is obvious from Fig. 3 that the mass loss of either the as-cast or annealed sample is not linear function of immersion time, and initially increases rapidly and then more slowly increase with immersion time. By comparing the annealed samples with the as-cast sample, one notices that the corrosion resistance of the $[(\text{Fe}_{0.6}\text{Co}_{0.4})_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$ glassy alloy is strongly dependent on its micro-structure. The sample in a full crystalline state caused by annealing at 973 K exhibits the lowest corrosion resistance (largest mass loss) and its mass loss is one order of magnitude higher than that of the other samples studied. The mass loss of both as-cast and annealed samples decreased in the following order of 973 K annealed sample > the as-cast sample > 573 K annealed sample > 773 K annealed sample.

Figure 4 shows SEM micrographs of the corroded surface of the as-cast and annealed samples after immersion for 168 h in an aerated $0.1 \text{ kmol/m}^3 \text{ H}_2\text{SO}_4$ solution. Figs. 4(a)–(d) correspond to SEM images of the corroded surface of the as-cast, as well as 573 and 773 and 973 K annealed samples,

Fig. 3 Mass loss of the as-cast and annealed samples as a function of immersion time obtained in aerated $0.1 \text{ kmol/m}^3 \text{ H}_2\text{SO}_4$ solutions at 298 K.

Fig. 4 SEM images of the corroded surface of the as-cast sample (a), 573 K annealed sample (b), 773 K annealed sample (c) and 973 K annealed sample (d).

respectively. It can be seen that during immersing tests, a thick corrosion products is formed on the surfaces of both as-cast and annealed samples and exhibits a similar surface morphology, *i.e.*, a characteristic 'dried riverbed' cracked structure, although the size of the crack in the film is distinctly different from each other. The existence of crack implies the poor protectiveness of the surface film formed on these samples. Furthermore, a comparison of Figs. 3 and 4 shows that the wider the crack, the larger is the mass loss. It means that the width of crack reflects the degree of corrosion resistance of the samples. The EDS analysis indicates that silicon, niobium and iron are main components of the film (not shown here).

Fig. 5 Potentiodynamic polarization curves of the as-cast sample (a), 573 K annealed sample (b), 773 K annealed sample (c) and 973 K annealed sample (d) obtained in aerated 0.5 kmol/m³ H₂SO₄ solutions at 298 K. The inset enlarges the anodic polarization curves around the marked position.

In order to obtain a better understanding of the corrosion behavior of the $[(\text{Fe}_{0.6}\text{Co}_{0.4})_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$ alloy in the as-cast glassy, relaxed glassy and crystalline states, potentiodynamic polarization measurements were carried out in an aerated 0.5 kmol/m³ H₂SO₄ solution at 298 K. Figure 5 shows potentiodynamic polarization curves of the as-cast and annealed samples. Variations in the anodic current densities in the vicinity of the corrosion potential are presented in details in inset. It is clear that both as-cast and annealed samples exhibit similar polarization behavior. The corrosion potential is around -0.36 V vs. Ag/AgCl. Upon increasing the potential above the corrosion potential, the current density increases monotonically with the electrode potential. Subsequently, an apparent active-passive transition and a passive region are observed. With a further increase in the potential, the current density increases once again due to the trans-passive dissolution. After polarization, a grayish film was observed on the surface of the samples, indicating the formation of a protective passive film. Here, it is important to point out that the 'passivation' in this text means a marked decrease in anodic activity, and not conventional passivation whereby anodic activity becomes close to zero. On the other hand, some differences can be observed between the anodic behaviour of the as-cast and annealed samples (Fig. 5). For instance, at a given potential, the sample annealed at 973 K exhibits the highest corrosion current, followed by the as-cast sample, and then the 573 K annealed sample. The 773 K annealed sample has the lowest corrosion current. Potentiodynamic polarization measurements clearly demonstrate that the as-cast and annealed samples exhibit different corrosion resistance in aerated 0.5 kmol/m³ H₂SO₄ solutions, which is in agreement with the results of mass loss analysis discussed earlier.

Figure 6 shows potentiodynamic polarization curves of the as-cast sample in an aerated 0.5 kmol/m³ H₂SO₄ solution at different test temperatures (indicated in the plot). Corrosion potentials do not present any clear trend with temperature, while corrosion current values increase for the as-cast sample as the temperature increases from 298 to 353 K. The corrosion potential of the as-cast sample remains very constant,

Fig. 6 Potentiodynamic polarization curves of the as-cast sample in an aerated 0.5 kmol/m³ H₂SO₄ solution at different test temperatures: (a) 298 K, (b) 313 K, (c) 333 K and (d) 353 K.

about -0.36 V vs. Ag/AgCl, over the whole temperature range studied. It is well known that the rise of temperature accelerates corrosion, in general, the rise of temperature favors the kinetics of corrosion reactions; however, it also promotes the fast growth of passive films on metallic surfaces.²³⁾ For the as-cast sample studied, the former effect predominates. Interestingly, as shown in Fig. 6, the passivation region of the as-cast sample becomes narrow with an increase of the test temperature. This trend can be easily understood in terms of the effect of temperature on active/passive transition and transpassivation potential. When the temperature increases, the active/passive transition potential shifts towards more positive, on the contrary, the transpassivation potential shifts to less noble potential. Thus, the passivation range of the as-cast sample becomes narrower as the temperature is raised. In addition, as can be seen in Fig. 6, the current spikes (or current oscillations) are observed along the passive region, and their number and intensities tend to increase with increasing test temperature. Similar results have been reported by Garfias-Mesias *et al.*²³⁾ for 25Cr duplex stainless steel in 1 kmol/m³ HCl+0.6 kmol/m³ NaCl electrolytes at a temperature of 333 K. Although the reason for these current spikes is not clear at this point, it could be due to the decrease in the protective properties of the passive film with test temperature, as is evidenced from the changes in the passivation current and pitting potential evolution with temperature shown in Fig. 6.

4. Discussion

From the above results, we can see that the microstructural states of the $[(\text{Fe}_{0.6}\text{Co}_{0.4})_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$ bulk alloy have a noticeable effect on its corrosion behavior. As shown in Figs. 3 and 5, the sample annealed at 973 K exhibits larger mass loss and higher corrosion current when compared to the other samples, implying that the fully crystallized sample exhibits a marked deterioration of corrosion resistance. This may be mainly attributed to galvanic effects between adjacent phases with different compositions.²⁴⁾ Comparing the samples annealed at 573 and 773 K with the as-cast

sample, these two annealed samples exhibit lower mass loss and corrosion current density, indicating a higher corrosion resistance in these samples. This may be attributed to the structural relaxation and stress relief caused by annealing.²⁵⁾ It is known that during structural relaxation the metallic glass tends to a more stable structure, thereby causing a decrease in the reactivity of its elements and increasing the alloy's chemical stability. The lower mass loss and corrosion current density of the sample annealed at 773 K, compared to the sample annealed at 573 K, mean that the higher temperature annealing results in greater structural relaxation, thereby increasing the corrosion resistance. The increase in corrosion resistance of the alloy analyzed in this study is in agreement with results published in the literature for other soft magnetic amorphous and glassy alloys, such as Fe₇₈B₁₃Si₉,²⁶⁾ Fe₈₄Nb₇B₉,²⁷⁾ and Fe_{65.5}Cr₄Mo₄Ga₄P₁₂C₅B_{5.5},²⁸⁾ alloys. It was reported that the increase in corrosion resistance of these alloys by annealing was achieved below the crystallization temperature, although no structural characterization of the samples was done.

A comparison of our mass loss data with those of Fe₇₈-Si₉B₁₃,²⁶⁾ Fe₈₃Zr_{3.5}Nb_{3.5}B₉Cu₁,²⁷⁾ and Fe₇₄Cu₁Nb₃Si_{13.5}-B_{8.5},²⁹⁾ amorphous and/or nanocrystalline soft magnetic alloys shows that the corrosion resistance of [(Fe_{0.6}Co_{0.4})_{0.75}-B_{0.2}Si_{0.05}]₉₆Nb₄ bulk glassy alloy is superior to that of the former two alloys and not inferior to that of the latter alloy in an aerated 0.1 kmol/m³ H₂SO₄ solution. Therefore, this alloy is promising as a new soft-magnetic material with superhigh strength and enhanced corrosion resistance.

5. Summary

The influence of structural changes such as structural relaxation and crystallization on the corrosion behaviour of the [(Fe_{0.6}Co_{0.4})_{0.75}B_{0.2}Si_{0.05}]₉₆Nb₄ bulk glassy alloy has been investigated in aerated 0.1 and 0.5 kmol/m³ sulphuric acid solutions. The following conclusions can be drawn from this study:

- (1) The structural relaxation increases the Curie temperature, indicating an increase in chemical short range ordering.
- (2) The corrosion resistance is improved due to structural relaxation and depends sensitively on the extent of annealing below crystallization temperature.
- (3) A full crystallization decreases significantly the corrosion resistance.
- (4) The corrosion resistance decreases with an increase of the test temperature of the corrosive medium.

- (5) The glassy alloy has an ability to passivation in aerated sulphuric acid solutions irrespective of structure.

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