Oxidation Behavior of Amorphous and Crystallized Fe$_{78}$Si$_{12}$B$_{13}$ Alloys

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Amorphous and crystallized Fe$_{78}$Si$_{12}$B$_{13}$ alloys were oxidized in a 20%O$_2$-Ar gas stream at the temperatures of 623 to 973 K for 70 to 80 ks. The mass change of the sample was continuously measured during the oxidation. The oxidation products formed on the sample surface were examined with using XRD, SEM, EPMA, ESCA and SIMS. The mass gain of the amorphous sample during the oxidation at 673 K for 72 ks was higher than that of the crystallized alloy. The thin oxide film formed on the amorphous and crystallized samples were about 13 and 8 nm, respectively.

SIMS profile revealed that the thin oxide was mainly composed of Fe-oxides and SiO$_2$ in the outer and inner portions, respectively. Nodular oxides which were composed of Fe$_2$O$_3$, Fe$_3$O$_4$, SiO$_2$ and B$_2$O$_3$ were also formed on the amorphous sample. As the temperature was raised, the number and size of the nodular oxides increased, and the oxide formed at 973 K was composed of Fe-oxides, SiO$_2$ and B$_2$O$_3$. The oxidation rate of the alloy was much lower than the pure Fe due to the formation of the thin oxide film containing SiO$_2$.

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I. Introduction

Amorphous materials have recently received considerable attention in various fields, since it has been proved that they possess several properties superior to crystallized materials such as high mechanical strength, high toughness, anti-abrasion, soft-magnetism, high resistance to corrosion, etc.\(^{(1),(2)}\). It is expected, therefore, that amorphous materials might be used widely even under corrosive environments in the future, and it is important to clarify chemical behavior under various kinds of atmosphere.

A great deal of work on the corrosion chemistry of amorphous alloys in various aqueous solutions at lower temperatures has so far been reported\(^{(3)-(5)}\). On the other hand, only a few investigations have been reported on the oxidation behavior of the alloys under gaseous atmosphere at higher temperatures. Hunderi and Bergersen\(^{(6)}\) studied oxidation of amorphous Fe–Ni–P–B alloy (Metglas 2826) in dry and wet air at the temperatures below 473 K. They measured the oxidation rate by ellipsometry and reported that the oxidation rate in moist air was slower than that in dry air, and that an addition of Cr to the amorphous Fe–Ni–P–B alloy resulted in a significant decrease in the oxidation rate.

The oxidation behavior of amorphous Cu$_{78}$Zr$_{12}$ alloy reported by Bigot et al.\(^{(5)}\) is very interesting; the oxidation proceeded faster in Ar gas containing O$_2$ of partial pressure of 6.6 Pa than in air or pure O$_2$ gas, and the oxidation rate of the amorphous alloy was higher than the crystallized alloy of the same composition.

Taniguchi et al.\(^{(6)}\) studied thermo-gravimetrically oxidation of amorphous Fe–Si–B and Fe–Cr–Si–B alloys in a gas mixture of 2.3 kPa (17 torr) O$_2$ and 0.4 kPa (3 torr) Ar at the temperatures up to 923 K and examined the effect of Cr content on the oxidation rate. They found that the oxidation rate became minimum when the Cr content in the alloy was 12 to 16 at%, at which the Cr concentration in the oxide film reached maximum. However, the surface of the samples prepared by them
was rough and this irregularity made it difficult to clarify the oxidation mechanism.

It is intended in this work to examine the roles of Si and B in the oxidation of amorphous and crystallized Fe–Si–B alloys and to compare the oxidation rate of the amorphous alloy with the crystallized alloy.

II. Experimental

The amorphous Fe₇₅Si₃B₁₃ alloy used in this work was produced by a single-roller method in a ribbon shape of about 20 μm thick (Metglas 2605 S2, Allied Chemical Corporation). This ribbon was cut into rectangular sheets of 15 mm in width and 25 mm in length. Iron sheets of 0.1 mm in thickness and 99.9% purity were also used in some experimental runs to compare the oxidation rate with that of amorphous alloy. The iron sample was polished to make its surface smooth as a mirror with Al₂O₃ particles of 0.05 μm size after abrading by SiC paper.

A quartz tube 50 mm in diameter was used as a reaction tube and was heated by a silicon carbide furnace. Five sheets of amorphous alloy were hooked on a platinum wire and hung from an automatic microbalance in a hot zone of the reaction tube by quartz fibers 0.3 mm in diameter. The amount of mass increase during the oxidation was very small and five sheets of amorphous alloy were used in every experimental run to obtain measurable amount of mass increase. The sample was heated in an Ar gas stream which was deoxygenated in advance by passing through a layer of spongy titanium heated at about 1070 K. After the sample was heated up to a predetermined temperature, the oxidation was started by switching the Ar gas to an O₂–Ar gas mixture. The mass change of sample during the oxidation was continuously measured by a Shimadzu automatic microbalance, RMB-50V. The oxidation was conducted at the temperatures between 623 and 973 K. The oxygen partial pressure and flow rate of the O₂–Ar gas mixture were maintained at 20 kPa and 5 × 10⁻⁶ m³·s⁻¹, respectively.

The samples oxidized for 70 to 80 ks were examined under SEM. Identification of the oxidation products was carried out by X-ray diffraction (XRD) using Co Kα radiation and the concentration profiles of elements in the oxidized layer on the sample surface was determined by EPMA. The surface layer of the oxidized samples was also examined with ESCA and SIMS.

III. Experimental Results and Discussion

1. Crystallization of amorphous Fe–Si–B alloy

Figure 1 shows a DSC pattern of the as-received sample used in this work at a heating rate of 0.33 K·s⁻¹ (20 K·min⁻¹); two distinct exothermic peaks due to the crystallization are observed at 783 and 828 K. Chang and Marti(7) obtained the activation energies of 358 and 347 kJ·mol⁻¹ for first and second crystallization of the amorphous Fe₇₅B₁₂Si₈ alloy by using the following relationship between the heating rate φ and the crystallization temperature \( T_p \):

\[
\ln \left( \frac{\phi}{T_p} \right) = \frac{E_c}{RT_p} + c
\]

where \( E_c \), \( R \) and \( c \) are the effective activation energy, the gas constant and a constant, respectively. Their results are shown in Fig. 2 by solid
diffraction peaks of α-Fe and Fe₃B are clearly seen, indicating that the crystallization proceeded during the annealing for 3.6 ks. On the other hand, the sample annealed at 673 K for 3.6 ks showed the same pattern as that of the as-received sample. When the heating duration increased to 36 ks, however, the most intensive peak of α-Fe, which is assigned to (110) spacing, was faintly observed on the diffused peak due to the amorphous structure.

2. Mass gain during oxidation

The change of mass gain per unit surface area of the samples during the oxidation at 673 K is shown in Fig. 4. The notations of α-(Fe, Si, B) and c-(Fe, Si, B) designate the amorphous Fe–Si–B alloy heated in the Ar gas up to 673 K followed by the oxidation and the alloy precrystallized by heating in the Ar gas at 873 K for 3.6 ks followed by the oxidation at 673 K, respectively. The experimental runs were repeated three and two times for the α- and c-(Fe, Si, B) alloys, respectively. It is seen in this figure that the mass gain of the alloys is very small in comparison with the pure Fe. This means that the alloying elements of Si or B play an important role in the resistance to oxidation.

Moreover, the oxidation of the amorphous Fe–Si–B alloy proceeded faster than the crystallized alloy; in the case of the crystallized sample, no appreciable mass gain was observed even after the oxidation for 72 ks. The similar results were also reported in the oxida-

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Fig. 2 Plot of $\ln(\phi \cdot T_p^{-1})$ against $T_p^{-1}$.

Fig. 3 X-ray diffraction patterns of samples annealed in Ar gas.

Fig. 4 Mass change of samples during oxidation at 673 K.
tion of the amorphous Cu-Zr alloy. This will be discussed later.

The crystallized samples were oxidized in the temperature range of 723 to 973 K and measured mass gain is shown in Fig. 5. The rate of mass gain of samples increased with temperature, and a remarkable mass gain was observed at 973 K. However, the rate of mass gain of the alloy was much lower than that of iron.

3. Oxidation product

(1) Observation under SEM

SEM photographs shown in Fig. 6 are the free-side surfaces of samples produced by the single-roll method. It can be seen that small nodular crystals of sub-micron size are formed at random on the surface of the sample oxidized at 673 K which is in contrast to smooth surfaces of the samples of the as-received and precrystallized at 873 K. When the oxidation temperature was raised, the number of nodular crystals considerably increased and they also grew up in size.

On the other hand, though the oxidation product on the wheel-side surface also showed a similar temperature dependence, the nodular

![Figure 5: Mass change of crystallized samples.](image5.png)

![Figure 6: SEM photographs of free-side surface of the samples; (a): as-received, (b), (c) and (d): oxidized at 673, 773 and 873 K, respectively, and (e): precrystallized and oxidized at 673 K.](image6.png)
products were concentrated around irregular portions of the surface which might arise from inert gas entrainment or irregular surface of the roll for quenching.

At the temperature of 973 K, as shown in Fig. 7, the sample surface was covered with the nodular products of oxidation and the photograph of cross section of the sample revealed that a thin film of oxide was formed on the surface. An oxide film like this was not observed even under SEM in the oxidation at the temperature below 973 K. This coincides with the fact that the mass gain of the sample at 973 K was remarkably higher than that observed at the lower temperatures.

(2) XRD pattern
Figure 8 shows the XRD patterns for the samples oxidized for 72 ks at different temperatures. It is seen in these patterns that the highest peak due to the crystallization of $\alpha$-Fe appeared when the sample was oxidized at 673 K and that Fe$_3$B was also formed at the temperatures above 773 K. When the sample was oxidized at 973 K, the peak of B$_2$O$_3$ is clearly seen and small amounts of Fe$_2$O$_3$, Fe$_3$O$_4$ and SiO$_2$ are also formed. At 873 K, however, the peak of B$_2$O$_3$ can scarcely be observed, though there is a faint indication of the formation of Fe-oxides. The formation of oxides was not confirmed for the samples oxidized at the lower temperatures below 873 K.

(3) EPMA analysis of elements
The oxygen profile on the sample surface was obtained with WDX line analysis and an example of the results was demonstrated in Fig. 9 for the sample oxidized at 873 K. This result indicates that the nodular products shown in Fig. 6 are an oxide.

The WDX line analysis of Fe, Si, B and O was made on the surface of the sample oxidiz-
Fig. 9  WDX line analysis of oxygen along the surface of the sample oxidized at 873 K.

ed at 973 K, where both of the size of nodular oxides and the thickness of oxide film sufficiently grew for analysing with EPMA. The concentration profiles of Fe, Si, B and O along a white line drawn in Fig. 10(a) are demonstrated in Fig. 10(b). At the cracks of the oxide layer observed in Fig. 10(a), the oxygen intensity decreased and iron intensity conversely increased; this might be an information obtained from the alloy under the oxide film. It is also seen that Fe, Si and B are observed in the positions where the oxygen intensity is high. Taking into account of the results of XRD shown in Fig. 8, it can, therefore, be concluded that the nodular oxide is composed of FeO, Fe₂O₃, SiO₂ and B₂O₃.

(4) Chemical analysis of surface with ESCA

It is thought that a very thin oxide film which neither XRD nor EPMA can detect is formed on the sample surface in addition to the nodular oxide. Then, the sample surface was examined with ESCA and SIMS.

Figure 11 demonstrates the X-ray photoelectron spectra of O 1s, Si 2p, Fe 3p and B 1s on the surfaces of the as-received and oxidized samples. It is seen from the spectra for oxygen that an oxide layer has already formed even on the surface of as-received sample which is named “native oxide”. The peak at 532 eV is assigned to oxygen of OH group. The position of this peak did not shift even when the as-received sample was oxidized at 623 K, but the peak disappeared at 973 K. The peak around 530.5 eV is assigned to oxygen of oxide of which binding energy became higher from 531 to 533.5 eV as the oxidation temperature was elevated from 623 to 973 K; this means that an effect of the native oxide still remained even when the sample was oxidized at 623 K and that the stable oxide film was formed at 973 K, without remaining any trace of the native oxide.

The spectra of Si exhibit that the peak at 102 eV of the as-received sample shifted to
102.8 and 104.0 eV when the sample was oxidized at 623 and 973 K, respectively. This corresponds clearly to the pattern of spectrum shift of oxygen\(^{10}\).

It is very interesting to compare the spectra of Fe and B. Iron existed on the surface of the sample oxidized at 623 K, but it disappeared at 973 K. On the contrary, boron was not detected in the lower temperature while it appeared at higher temperature. As described before, the oxide film formed at 973 K consisted of SiO\(_2\), B\(_2\)O\(_3\), Fe\(_2\)O\(_3\) and Fe\(_3\)O\(_4\), and the examination with ESCA revealed that these Fe-oxides existed slightly below the sample surface and that SiO\(_2\) and B\(_2\)O\(_3\) covered the Fe-oxides.
(5) Depth profile of concentration of elements measured with SIMS

The concentration profiles of elements were measured with SIMS in the vicinity of the surface of amorphous (a-(Fe, Si, B)) and crystallized (c-(Fe, Si, B)) samples which were oxidized at 673 K, and they are demonstrated in Fig. 12. The atomic percent on the ordinate of this figure is based on total amount of Fe, Si and B. The O concentration was determined just qualitatively. The SIMS profiles show that the oxide layer formed on the sample a-(Fe, Si, B) is thicker than that of c-(Fe, Si, B).

However, similar concentration profiles of elements were obtained for both samples, as seen in Fig. 12. The concentrations of Si and Fe at the surface are nearly the same as the bulk composition of the alloy, respectively, while the B concentration is rather lower near the surface: This coincides with the X-ray photoelectron spectra demonstrated in Fig. 11 which revealed that Fe and Si existed on the surface but B was not detected at the lower temperature of 623 K. In the inner part of the oxide layer, the concentration of Si increases and that of Fe decreases. Boron seems to be slightly concentrated around the oxide/alloy interface.

4. Comparison of oxidation rates between amorphous and crystallized alloys

The nodular-type oxidation products were not observed on the surface of the sample c-(Fe, Si, B) oxidized at 673 K, which is quite contrary to the sample a-(Fe, Si, B), as shown in Fig. 6.

Therefore, the mass gain can be calculated from the thickness of the oxide film on the sample c-(Fe, Si, B). The thickness of the oxide layers estimated from the depth profile of SIMS shown in Fig. 12 are about 13 and 8 nm for the samples a- and c-(Fe, Si, B), respectively. The density of the oxide was estimated as $3.7 \text{ g cm}^{-3}$ from mass-average value of densities of SiO$_2$, Fe$_3$O$_7$, and B$_2$O$_3$. With using this value of density, mass gain corresponding to the thickness of 8 nm is calculated at about 0.01 g m$^{-2}$. This value of mass gain is too small to measure by the microbalance used in this work, and this is why the mass gain was scarcely detected in the oxidation of the sample c-(Fe, Si, B) for 72 ks. Then, it can be said that the mass gain observed in the oxidation of sample a-(Fe, Si, B) is due to the formation of the nodular oxide.

As described in Introduction, Bigot et al.(5) reported that the oxidation rate of the amorphous Cu–Zr alloy was higher than the crystallized alloy in the oxidation at oxygen partial pressure of 6.6 Pa. This is on the same line with the results obtained in the present work though the $O_2$ partial pressure was different. They indicated that the amorphous alloy had “high reactivity”, but did not mention the details of the reactivity.

In the present work, as mentioned above, the higher oxidation rate of the amorphous alloy is owing mainly to the formation of nodular-type oxide. However, it has not yet been clarified why the nodular oxide was easy

![FIG. 12 SIMS profiles of Fe, Si, B and O in the oxide films formed at 673 K; (a) amorphous and (b) crystallized Fe–Si–B alloy.](image-url)
to form on the amorphous sample.
Moreover, the thin oxide film formed on the amorphous sample was thicker than that on the crystallized sample as shown in Fig. 12. Similar concentration profile of elements was observed in the outer part of the oxide films of both samples corresponding to sputtering time of 0 to about 60 seconds in the amorphous sample, while it decreased to the bulk concentration in the crystallized sample. Thus the following can be deduced from this observation: After the initial formation of a thin oxide film, the average composition of which is nearly the same as the bulk alloy, the rate of further growth of the oxide layer is affected by the diffusion in the alloy and the bulk diffusion of elements in the amorphous alloy is faster than in the crystallized alloy.

IV. Summary

Ribbon samples of amorphous and crystallized Fe$_{78}$Si$_{8}$B$_{13}$ alloys were oxidized in the 20% O$_2$–Ar gas stream at the temperatures ranging from 623 to 973 K. The results are summarized as follows.

1. Two exothermic peaks due to the crystallization were observed at 783 and 828 K in a DSC analysis at the heating rate of 0.33 K·s$^{-1}$.

2. In the oxidation at 673 K for 72 ks, the very thin oxide film of about 13 nm thick was formed on the sample surface; the film was composed of primarily outer Fe oxides and inner SiO$_2$. Nodular oxides of about 0.5 $\mu$m size which were composed of Fe$_2$O$_3$, Fe$_3$O$_4$, SiO$_2$ and B$_2$O$_3$ were also formed over the thin oxide film.

3. The alloy has much higher resistance to oxidation in comparison with pure Fe. This is due to the formation of the thin oxide film containing Si-oxide.

4. The oxidation rate was much reduced when the amorphous sample was preliminarily crystallized at 873 K. No nodular oxide was observed and the thickness of the oxide film was about 8 nm which was also thinner than that formed on the amorphous sample.

5. As the reaction temperature was raised, both the number and size of the nodular oxides increased. At 973 K, the nodular oxides coalesced with each other to form a thick film and the rate of mass gain became much higher.

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