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Surface crystallization of amorphous Fe–B–Si alloy annealed in a gas atmosphere containing organic vapour

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The relationship between the annealing atmosphere and the magnetic properties of $Fe_{78.5}B_{13}Si_{8.5}$ amorphous alloy has been studied, showing that annealing in an inert gas atmosphere containing a borosiloxane resin significantly improves the core loss of the amorphous ribbon, and that annealing in an inert gas without any organic resins, gives much better results than annealing in an inert gas atmosphere containing cellulose and vinyl acetate resins. A boron-depletion zone was detected by Auger electron spectroscopy under the oxide film formed during annealing in the inert gas atmosphere containing cellulose and vinyl acetate resins. Annealing of the amorphous ribbon in the cellulose and vinyl acetate resins selectively oxidizes boron in the alloy to form a B_2O_3 film and a boron depletion zone; the alloy in this zone is then crystallized into α-Fe. This surface crystalline layer induces out-of-plane magnetic anisotropy in the amorphous ribbon and thus deterioration of the core loss. On the other hand, annealing in the borosiloxane resin results in neither selective oxidation of boron nor surface crystallization of the amorphous ribbon

1. Introduction

The development of superior soft magnetic properties in iron-based amorphous alloy ribbons requires annealing below the crystallization temperature and cooling in a magnetic field. To obtain low core losses and low excitation, annealing must be performed at a temperature high enough to relieve the residual stresses resulting from the casting operation, but not so high as to cause crystallization of the amorphous alloy [1].

Partial surface crystallization of amorphous ribbon surfaces has been reported to take place during casting, due to segregation of the alloy composition or to a slow cooling rate [2–4], and also during annealing, even at temperatures well below the normal crystallization temperature [5–7]. Further, some amorphous ribbon surfaces exposed to an annealing atmosphere have been reported to crystallize easily because of the change in alloy composition resulting from reactions with components of the annealing atmosphere, and because of the oxidation reaction upon annealing [7–10].

We have reported [11] the effect of annealing atmospheres on the magnetic properties of amorphous $Fe_{78.5}B_{13}Si_{8.5}$ alloy ribbon, when the core loss of the amorphous alloy was improved significantly upon annealing in nitrogen, hydrogen, oxygen and argon atmospheres, but increased on annealing in H_2–H_2O. It was found that annealing in an H_2–H_2O atmosphere selectively oxidizes boron in the amorphous alloy to form a B_2O_3 film and a boron depletion zone immediately below the surface oxide layer; the alloy in this zone then crystallizes into α-Fe, even at temperatures below the normal crystallization temperature. Because the density of this α-Fe is higher than that of the amorphous alloy, the surface crystalline layer generates a compressive stress in the amorphous alloy ribbon bulk and thus induces out-of-plane anisotropy through high magnetostriction of the amorphous Fe–B–Si alloy, causing deterioration of the core loss.

Because amorphous Fe–B–Si alloys annealed in a magnetic field have an excellent ultra-low core loss, a high saturation magnetic flux density and a practical heat stability, much active research and many development programmes are being promoted to apply the amorphous Fe–B–Si alloy ribbons to iron cores of electric power transformers [12], for which grain-oriented silicon steel sheets are widely used. The thickness of amorphous alloy ribbons is usually 20–30 μm, so the process of winding these ribbons into an iron core shape requires a lot of machine time. In order to alleviate this problem, many new manufacturing techniques for thick amorphous alloy sheets have been reported, including an improved casting process [13], a technique which allows more than one amorphous alloy ribbon to be joined by rolling [14], and a technique which allows the piling of several amorphous alloy ribbons with adhesives. These techniques, however, have not been widely accepted because of some difficulties in applying them to industrial production. Amorphous alloy ribbons sometimes come into contact with organic adhesives in piling up and impregnating treatments, and also with organic compounds such as insulation oil for transformer cooling. Some kinds of transformer oil have been reported to deteriorate the magnetic properties of amorphous al-

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loy ribbons [15], but this mechanism is not so clear. The purpose of this work was to clarify both surface oxidation and surface crystallization, and their influence on the magnetic properties of amorphous Fe–B–Si alloy annealed in an argon gas atmosphere containing organic vapour.

2. Experimental procedure

An amorphous alloy with a nominal composition of $Fe_{78.5}B_{13}Si_{8.5}$ was prepared by rapid quenching from the melt. The resulting ribbon was 50 mm wide and approximately 21×10^{-3} mm thick.

The alloy's magnetic properties were measured using a single sheet of the ribbon, 150 mm long and 50 mm wide, which had previously been sandwiched, bundled between two stainless steel plates and wrapped together with stainless steel sheets with an organic adhesive in aluminium foil, as shown in Fig. 1, and then annealed in a flowing argon gas atmosphere. The adhesives used here were vinyl acetate, cellulose and borosiloxane resins.

Thin-film X-ray diffraction with CuK_α radiation at a fixed incidence angle of 2° (Seemann-Bohlin geometry) was employed to identify the thin surface crystalline phases formed during annealing. Fourier transform infrared reflection spectroscopy at an incidence angle of 80° was used to identify the oxide films formed on the ribbon surfaces during annealing. Auger electron spectroscopy with an argon-ion sputtering system was used to study the composition profiles in the surface layer of the annealed ribbons. The sputtering rate of an iron plate by argon ions was approximately 0.04 nm s^{-1} under the conditions used here.

γ-ray absorption Mössbauer spectroscopy with ^{57}Co(Rh) of about 27 mCi was used to study the magnetic anisotropy in the amorphous alloy ribbon bulk. The measurements were made at room temperature and α-Fe was used for the correction of speed.

Gas chromatography with a thermal decomposition apparatus was used to identify the thermal decomposition gases generated from organic resins during heating.

3. Results

3.1. Magnetic properties

The core loss, $W_{1.3/50}$, at 1.3 T and 50 Hz, and the magnetic flux density, B_1, at 100 A m^{-1}, of amorphous $Fe_{78.5}B_{13}Si_{8.5}$ alloys annealed in argon gas atmospheres, containing various organic resins at various temperatures, for 3.6 ks are shown in Fig. 2. By annealing in an argon atmosphere containing borosiloxane resin at 673 K, the core loss improves to approximately 0.18 W kg^{-1}, which is equal to the core loss of the amorphous alloy ribbons annealed in nitrogen and dry hydrogen [10]. However, annealing in vinyl acetate and cellulose resins at temperatures higher than 648 K results in increased core loss compared with the borosiloxane resin. The magnetic flux density, B_1, increases sharply on annealing at temperatures higher than 648 K, but this improvement is independent of the annealing atmospheres used.

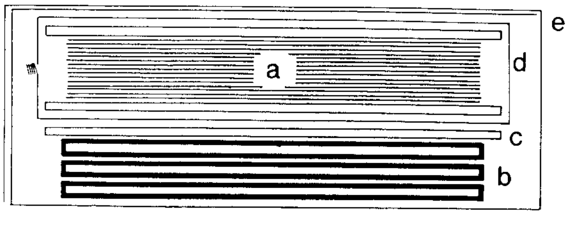

Figure 1 Sample preparation for annealing. a, Amorphous alloy ribbons; b, stainless steel sheets with an adhesive; c, stainless steel sheet; d, stainless steel wire; e, aluminium foil.

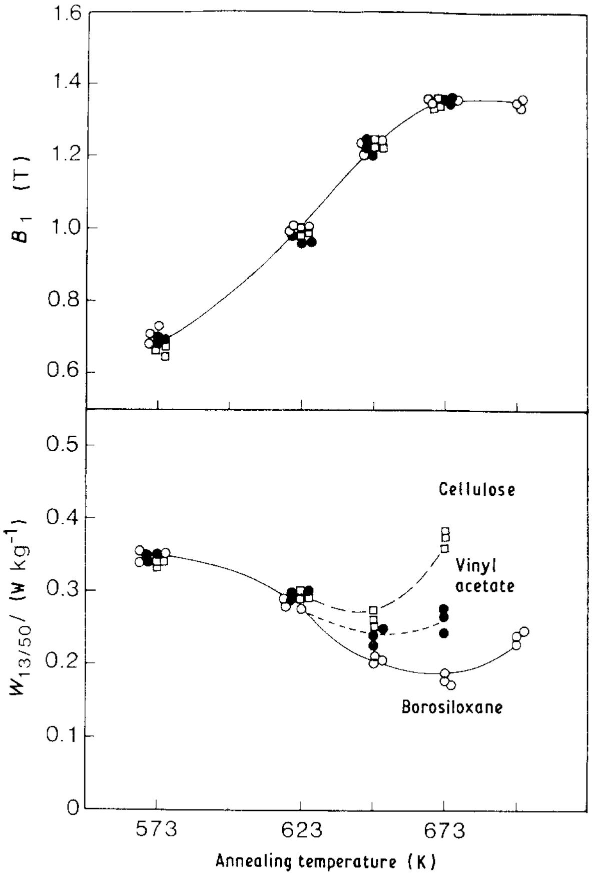

Figure 2 Annealing temperature dependence of magnetic properties of $Fe_{78.5}B_{13}Si_{8.5}$ amorphous alloys annealed for 3.6 ks in argon gas atmospheres containing various resins.

When the amorphous Fe–B–Si alloy ribbons, annealed in an inert gas atmosphere containing cellulose resin at 673 K, were chemically polished to remove about 0.3 μm of the ribbon surface, the core loss recovered to the level obtained by annealing in a dry hydrogen atmosphere.

The magnetic properties induced by annealing in the argon atmosphere containing a borosiloxane resin are similar to those of amorphous $Fe_{78.5}B_{13}Si_{8.5}$ alloy ribbon annealed in argon, nitrogen and dry hydrogen [10]. The annealing temperature dependence of magnetic properties, after annealing in vinyl acetate and cellulose resins, is analogous to the behaviour in wet hydrogen. The deterioration of the core loss, due to annealing in a wet hydrogen atmosphere, results from the generation of biaxial compressive stress in the amorphous bulk, due to the surface α-Fe crystalline layer, as previously described in detail [10,11]. Therefore, the deterioration of the core loss, which resulted from annealing in the argon atmosphere containing vinyl acetate and cellulose resins at around 673 K, also seems to be due to the formation of the surface crystalline layer.

3.2. Surface crystallization

According to X-ray diffraction, no crystalline phases were observed on the amorphous $Fe_{78.5}B_{13}Si_{8.5}$ alloy ribbons annealed for 3.6 ks in the argon atmosphere containing a borosiloxane resin at 673 K. This result agrees with that from the amorphous alloy annealed in nitrogen and dry hydrogen atmospheres [10].

On the other hand, the X-ray diffraction pattern from the amorphous alloy annealed in the argon atmosphere containing a vinyl acetate resin at temperatures higher than 623 K, indicates the formation of an α-Fe crystalline phase in addition to the halo pattern based on an amorphous structure, as shown in Fig. 3. The intensity of the α-Fe (1 1 0) peak increased with higher annealing temperatures. These results indicate that the crystallization temperature in the surface layer of the amorphous alloy ribbon, annealed in the argon atmosphere containing vinyl acetate resin, is more than 50 K lower than that in dry hydrogen and in the argon atmosphere containing borosiloxane resin. This crystallization, shown in Figs 3 and 4, is considered to take place at the surface of the amorphous Fe–B–Si alloy ribbon, because the α-Fe diffraction peak disappears after chemical polishing which removes about 0.5 μm of the ribbon surface.

Fig. 4 shows the influence of the annealing temperature on X-ray diffraction patterns from amorphous $Fe_{78.5}B_{13}Si_{8.5}$ alloy ribbon annealed in an argon atmosphere, containing cellulose resin, for 3.6 ks. In this case, no diffraction peaks of crystalline phase were detected from the amorphous ribbon annealed at 623 K, but, obviously, annealing at 673 K resulted in diffraction peaks of α-Fe. These results mean that the crystallization temperature in the surface layer of amorphous $Fe_{78.5}B_{13}Si_{8.5}$ alloy ribbon, annealed in the argon atmosphere containing cellulose resin, is between that of vinyl acetate resin and that of borosiloxane resin.

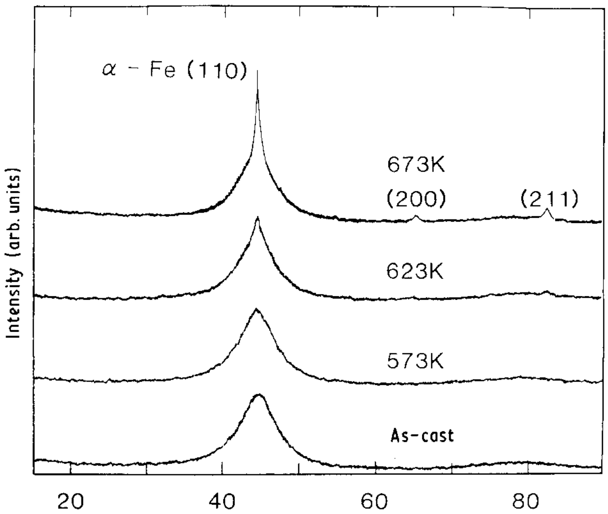

Figure 3 Change in X-ray diffraction patterns from $Fe_{78.5}B_{13}Si_{8.5}$ amorphous alloys annealed for 3.6 ks in an argon gas atmosphere containing a vinyl acetate resin upon annealing at various temperatures.

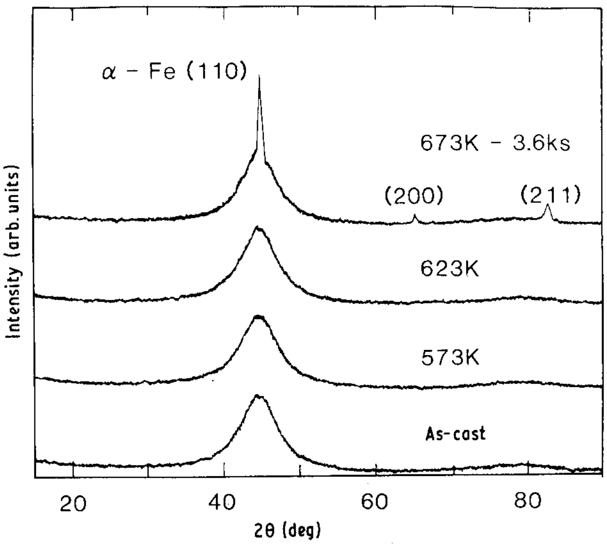

Figure 4 Change in X-ray diffraction patterns from $Fe_{78.5}B_{13}Si_{8.5}$ amorphous alloys annealed for 3.6 ks in an argon gas atmosphere containing a cellulose resin upon annealing at various temperatures.

3.3. Surface oxidation

Infrared reflection spectra (Fig. 5) from amorphous $Fe_{78.5}B_{13}Si_{8.5}$ alloy ribbons, annealed at 673 K for 3.6 ks, show that annealing in the argon atmosphere containing organic resins causes the formation of B_2O_3 in the main. The intensity of the absorption peak of B_2O_3, i.e. the thickness of the oxide film, depends heavily on the kind of organic resins coexisting in the annealing atmosphere. The oxide film of B_2O_3 on the amorphous alloy ribbon, annealed in argon atmospheres containing vinyl acetate and cellulose resins, is much thicker than that of borosiloxane. As shown in Fig. 6, the film thickness of B_2O_3 decreases with decreased annealing temperatures, and the annealing atmosphere dependence of the film thickness formed at 573 K is insignificant.

3.4. Depth profiles in the surface layer

As described above, thick B_2O_3 films are formed on the surface of amorphous Fe–B–Si alloy ribbons annealed in argon atmospheres containing vinyl acetate and cellulose resins. Fig. 7 shows the depth profiles of iron, boron and silicon in the surface layer of amorphous Fe–B–Si alloy ribbons annealed at 673 K for 3.6 ks in borosiloxane resin. The depth profiles of iron, boron and silicon in the alloy beneath the thin oxide film were almost flat and their concentration were the same as the nominal alloy composition. These tendencies were also observed in the ribbons annealed in nitrogen and dry hydrogen atmospheres [10].

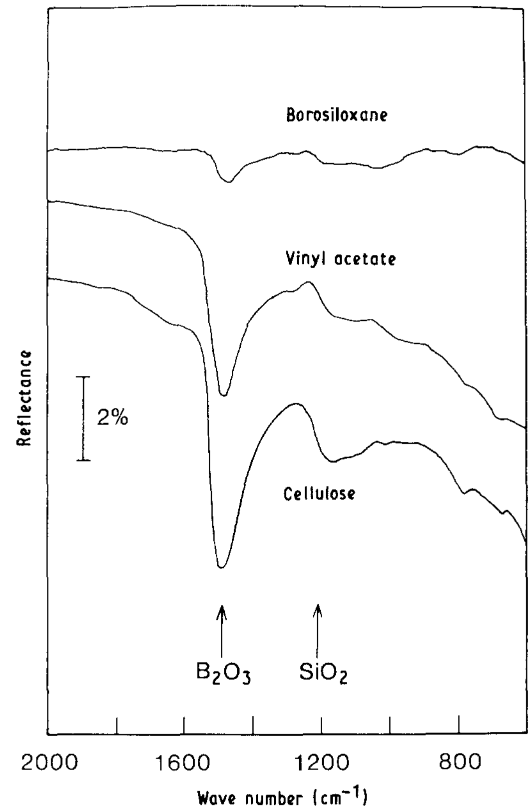

Figure 5 Infrared reflection spectra from $Fe_{78.5}B_{13}Si_{8.5}$ amorphous alloys annealed at 673 K for 3.6 ks in argon gas atmospheres containing various resins.

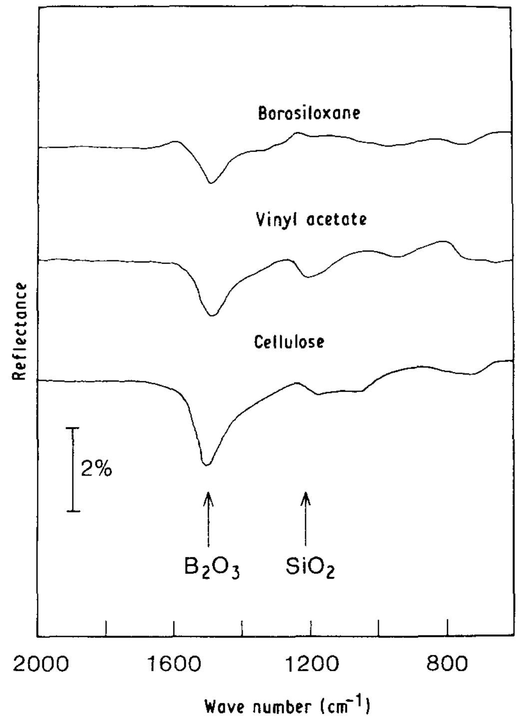

Figure 6 Infrared reflection spectra from $Fe_{78.5}B_{13}Si_{8.5}$ amorphous alloys annealed at 573 K for 3.6 ks in argon gas atmospheres containing various resins.

On the other hand, the amorphous alloy ribbons annealed in argon atmospheres containing vinyl acetate and cellulose resins had thick oxide films with a remarkably high concentration of silicon. Further, below the oxide layer a boron depletion zone with an extremely low concentration of boron was observed over a thickness of several tens of nanometres, as shown in Figs 8 and 9. The boron depletion zone, formed on the amorphous ribbon annealed in the argon atmosphere containing a cellulose resin, was thicker than that in a vinyl acetate resin. The alloy in the boron depletion zone, formed by annealing in the argon atmosphere containing a vinyl acetate resin, contained 6–9 mol % Si and 2–4 mol % B, while the boron depletion zone, with an alloy composition of 4–8 mol % Si and 1–4 mol % B, was formed with a cellulose resin.

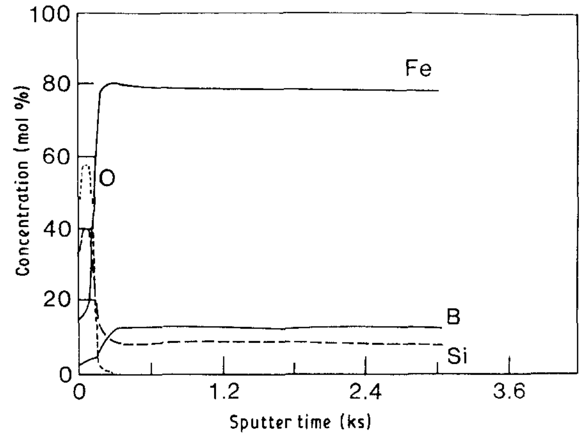

Figure 7 Depth profiles of iron, boron, silicon and oxygen at the surface of $Fe_{78.5}B_{13}Si_{8.5}$ amorphous alloy annealed at 673 K for 3.6 ks in an argon gas atmosphere containing a borosiloxane resin.

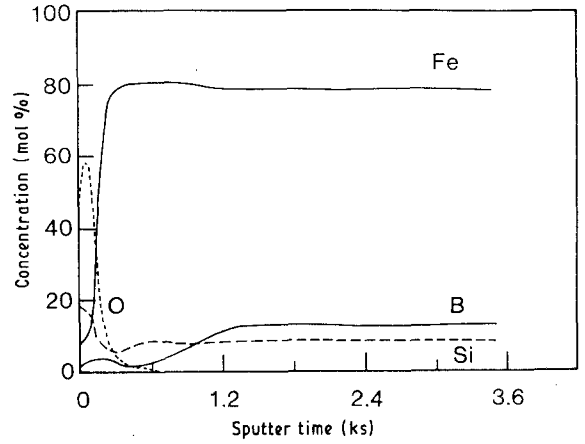

Figure 8 Depth profiles of iron, boron, silicon and oxygen at the surface of $Fe_{78.5}B_{13}Si_{8.5}$ amorphous alloy annealed at 673 K for 3.6 ks in an argon gas atmosphere containing a vinyl acetate resin.

3.5. Thermal decomposition gas

As described above, the oxidation reaction, the boron depletion behaviour and the surface crystallization behaviour in the amorphous Fe–B–Si alloy ribbon change remarkably with the kind of organic resins which are contained in the annealing atmosphere. These differences are considered to be due to the kinds and the amount of gases generated from organic resins by the thermal decomposition during annealing.

Fig. 10 shows a gas chromatograph of gases generated from a borosiloxane resin held for 60 s at 673 K.

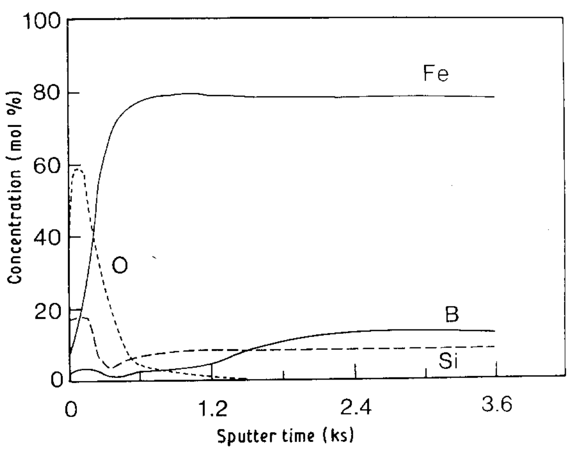

Figure 9 Depth profiles of iron, boron, silicon and oxygen at the surface of $Fe_{78.5}B_{13}Si_{8.5}$ amorphous alloy annealed at 673 K for 3.6 ks in an argon gas atmosphere containing a cellulose resin.

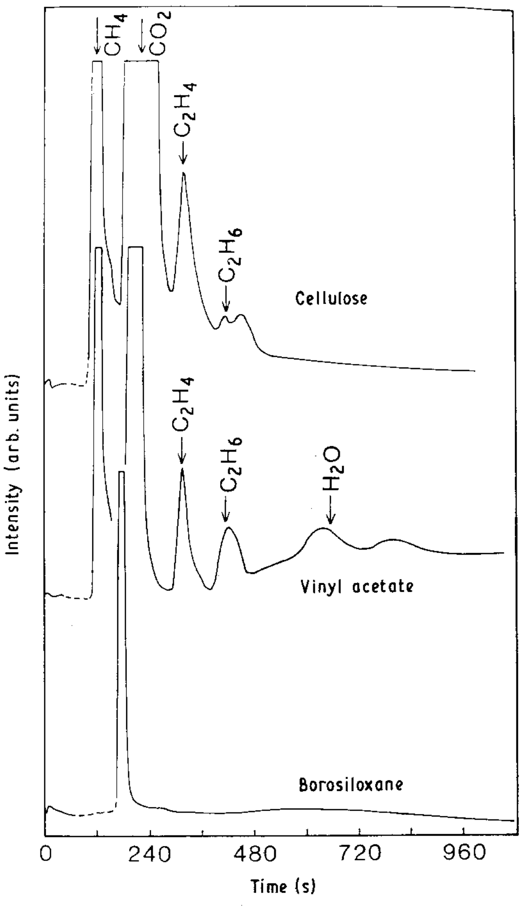

Figure 10 Gas chromatograph of gases generated from various resins held for 60 s at 673 K.

Only a small quantity of CO_2 gas was observed. The small amount of gas generated by the thermal decomposition of borosiloxane resin at around 673 K was also recognized by the thermal gravimetric analysis (TGA).

A vinyl acetate resin, decomposed thermally at 673 K, generated CO_2 and H_2O (Fig. 10), which are oxidizing gases. TGA showed a weight loss of about 75 % during the heating of a vinyl acetate resin up to 673 K.

A cellulose resin, decomposed thermally at 673 K, generated a large amount of CO_2, but not H_2O. TGA showed a weight loss of about 90 % during the heating of a cellulose resin up to 673 K. This implies that a cellulose resin generates large quantities of oxidizing gases in the heating process as well as a vinyl acetate resin.

4. Disscussion

4.1. Annealing atmosphere dependence of oxidation behaviour

As shown in the infrared reflection spectra of Fig. 5, the oxidation products and the thickness of oxide films formed on the amorphous Fe–B–Si alloy ribbon surface, during annealing at 673 K in the argon atmosphere containing a borosiloxane resin, are almost the same as those of oxide films formed in inert gases, reducing gases and the $N_2 + 20\%\ O_2$ atmospheres reported previously [10]. In other words, small quantities of hydrocarbon and CO_2 gases evacuated through thermal decomposition of a borosiloxane resin are considered to be insignificant in promoting oxidation reactions in amorphous Fe–B–Si alloys.

On the other hand, when vinyl acetate and cellulose resins were heated in an inert gas atmosphere, oxidizing gases such as H_2O and CO_2 were generated in addition to CO and hydrocarbon gases such as propylene and butane. As shown in the infrared reflection spectra of Fig. 5, B_2O_3 is mainly formed to grow into a fairly thick film on the amorphous Fe–B–Si alloy ribbon surface, when it is annealed at 673 K in the argon atmosphere containing vinyl acetate and cellulose resins. These features are similar to that of the previously described [10] oxide film formed on amorphous $Fe_{78.5}B_{13}Si_{8.5}$ alloy ribbon annealed in a wet hydrogen gas atmosphere. This implies that the oxidizing force of the argon atmosphere, containing vinyl acetate and cellulose resins, on amorphous Fe–B–Si alloy at 673 K, is almost the same as that of a wet hydrogen gas atmosphere with a dew point of 323 K.

4.2. Formation of a boron depletion zone and surface crystallization

When amorphous $Fe_{78.5}B_{13}Si_{8.5}$ alloy ribbons are annealed in an argon atmosphere containing vinyl acetate or cellulose resins, below the oxide layer, a boron depletion zone with an extremely low boron concentration was observed over a thickness of several tens of nanometres. The thickness of the boron depletion zone in the ribbons annealed in the argon atmosphere containing a cellulose resin is larger than that in a vinyl acetate resin. The decrease of boron concentration in the boron depletion zone is also larger in the amorphous ribbon annealed in the cellulose resin. The alloy composition in the boron depletion zone formed during annealing in the vinyl acetate resin is approximately 6–9 mol % Si and 2–4 mol % B, while that in the cellulose resin is 4–8 mol% Si and 1–4 mol% B.

The composition dependence of the crystallization temperature of the amorphous Fe–B–Si alloy system has been reported by Luborsky *et al.* [16], who indicated that the crystallization temperature of the alloy composition in the boron depletion zone, formed by annealing in the argon atmosphere containing the cellulose resin, is lower than that in the vinyl acetate resin. On the other hand, it is considered that the crystallization temperature upon annealing in the borosiloxane resin is the same as the nominal composition. These findings correspond well with the results of X-ray diffraction patterns shown in Figs 3 and 4. Surface crystallization was not detected on the amorphous ribbon annealed at 673 K in the argon atmosphere containing the borosiloxane resin. On the other hand, surface crystallization was observed clearly in the vinyl acetate and cellulose resins.

4.3. Magnetic properties

The effect of the annealing temperature on the magnetic properties of amorphous $Fe_{78.5}B_{13}Si_{8.5}$ alloy ribbon, annealed in an argon atmosphere containing a borosiloxane resin, can be understood in the same way as annealing in an inert gas atmosphere. Namely, the improvement of the magnetic properties by annealing at temperatures lower than 673 K is due to the relaxation of the stress introduced during casting, and the deterioration at temperatures higher than 673 K is due to a decrease of the in-plane magnetic anisotropy by annealing in a paramagnetic state and by compressive stress from the crystalline α-Fe surface layer formed during annealing [1].

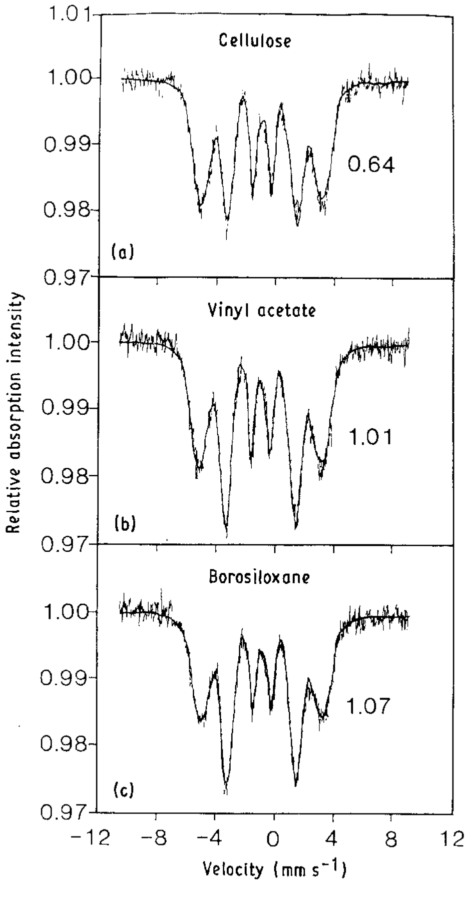

Figure 11 Mössbauer spectra from $Fe_{78.5}B_{13}Si_{8.5}$ amorphous alloys annealed at 673 K for 3.6 ks in argon gas atmospheres containing (a) cellulose, (b) vinyl acetate and (c) borosiloxane.

As shown in Fig. 2, when the amorphous alloy ribbons are annealed in argon atmospheres containing cellulose and vinyl acetate resins, a remarkable deterioration in core loss has been observed at temperatures higher than 648 K. According to X-ray diffraction, it corresponds with the temperature range in which the surface crystallization takes place. Therefore, the deterioration in core loss is considered to result from an out-of-plane anisotropy of magnetic moment due to the generation of biaxial compressive stress introduced by the formation of the higher density crystalline surface layer.

Fig. 11 shows transmission Mössbauer spectra of amorphous $Fe_{78.5}B_{13}Si_{8.5}$ alloy ribbon annealed at 673 K. The numerical values in Fig. 11 represent the ratio $A_{2,5}/A_{1,6}$ which is closely related to the direction of the magnetic moment [17], where $A_{n,m}$ is the average area of the nth and the mth peaks of Mössbauer spectra. When the amorphous alloy ribbon was annealed in an argon atmosphere containing the cellulose resin, the $A_{2,5}/A_{1,6}$ ratio decreased to 0.64. This means that the magnetic moment is fairly randomized in comparison to that of the ribbons annealed in borosiloxane and vinyl acetate resins. This is the reason why annealing in the argon atmosphere containing the cellulose resin results in a remarkable deterioration in core loss.

5. Conclusions

Annealing of an amorphous Fe–B–Si alloy ribbon in an inert gas atmosphere containing a borosiloxane resin results in a core loss similar to that of the amorphous ribbon annealed in an inert gas without any organic resins. On the other hand, annealing in an inert gas atmosphere, containing cellulose and vinyl acetate resins, results in a deteriorated core loss.

1. Annealing at 673 K in the argon atmosphere containing cellulose and vinyl acetate resins resulted in the selective oxidation of boron, and a B_2O_3 oxide film was formed preferentially on the amorphous alloy ribbon.
2. A boron depletion zone was formed at the surface of the amorphous alloy ribbon through the selective oxidation of boron. The thickness of the boron depletion zone is larger in the argon atmosphere containing the cellulose resin than that containing the vinyl acetate.
3. Annealing at 673 K in the argon atmosphere containing the borosiloxane resin resulted in no surface crystallization. On the other hand, annealing in the argon atmosphere containing the cellulose and the vinyl acetate resins resulted in surface crystallization.
4. The orientation of the magnetic moment in amorphous alloy ribbon bulk is remarkably randomized mostly by annealing in the argon atmosphere containing the cellulose resin. The extent of the deterioration in core loss due to organic resins coexisting in the annealing atmospheres, depends on the degree of the randomness in the orientation of the magnetic moment in the amorphous alloy ribbon.

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