Abridged version

KAWASAKI STEEL TECHNICAL REPORT
No.23 (October 1990)
R&D of High-Technology Research Laboratories,
Commemorating the 20th Anniversary
of the Technical Research Division

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Magnetic Properties of Amorphous Fe-B-Si Alloy with Surface Films*

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Synopsis:

Surface coatings on $Fe_{79.5}B_{12}Si_{8.5}$ (mol %) amorphous alloy ribbons have been studied to obtain high insulating resistance and high corrosion resistance. (1) A surface coating of lithium silicate with a molecular ratio $SiO_2/Li_2O = 3.5$ has been found to induce compressive stress in the ribbons. It achieves constant permeability to an extent of approximately 2 000 A/m and an increase in the iron loss of the amorphous alloy. (2) A surface coating of lithium silicate with $SiO_2/Li_2O = 7.5$ has no mechanical interactions with the ribbons and does not deteriorate magnetic properties. This surface coating is available for Fe-based amorphous alloy ribbons to be used for transformer core materials. (3) Although alumina sol surface coating has no mechanical interaction with the ribbons, water vapor evaporated from alumina sol during annealing in N_2 atmosphere causes surface crystallization and an increase in the iron loss of the ribbons. The surface crystallization and deterioration of magnetic properties have not been observed when the ribbons are annealed either in vacuum or in air.

1 Introduction

Amorphous Fe-B-Si alloy ribbons made by rapid quenching from the melt have a high saturation magnetic flux density, an excellent ultra-low core loss and a practical heat stability. Consequently active research and development programs are being promoted both in Japan and the United States to apply the amorphous Fe-B-Si alloy ribbons to iron cores of electric power transformers, for which grain-oriented silicon steel sheets were widely employed. Particularly in the U.S., where the core loss evaluation system of transformers has been established and sufficient economic evaluation is given to the design techniques for improving magnetic characteristics of transformers, pole transformers which use amorphous Fe-B-Si alloy as iron core material have come to be in wide commercial use since around 1988.[1)]

The amorphous alloy has a high specific resistance compared with the silicon steel sheets. Therefore the amorphous alloy ribbon has been used bare without applying an insulation film, as in the case of silicon steel sheets. However, as the sheet width of the amorphous alloy ribbon increases, the voltage generated between the wound ribbons becomes higher, while interlayer resistance decreases as the surface becomes smoother. This makes it impossible to ignore the eddy current loss.[2,3)] Further, considering a poor corrosion resistance of amorphous Fe-B-Si alloy ribbons, the existence of a surface film is desirable because of an enhancement of its resistance to the environment.

In view of the above, several types of surface films were tried in the past which would be used for the amorphous Fe-B-Si alloy.[3-8)] When partial sticking occurs during annealing between wound ribbons in the toroidal coil, it has been found that the existence of a surface film shows a particularly important improving effect.[1-8)] On the other hand, it is reported that the magnetic properties of the amorphous alloy ribbons with a surface film are significantly dependent upon the annealing temperature and annealing atmosphere.[3)] However, to date, mainly the AC magnetic property has been measured, and there were few reports studying in detail the magnetic property of the amorphous alloy ribbons with surface films.

The present study was started with a wide search into surface films to be applied to the amorphous Fe-B-Si alloy ribbons.

The amorphous Fe-B-Si alloy ribbons are worked into

* Originally published in *Kawasaki Steel Giho*, **21**(1989)4, pp. 316–322

an iron core shape, given annealing in the magnetic field ordinarily at a temperature of 623 to 673 K and then used as a transformer iron core. Therefore, a surface film of the organic resin type cannot be used because it will lose electric insulation by a chemical reaction during annealing at high temperatures. Thus the present study has been carried out aiming at an inorganic type surface film, and it has been found that surface films can be divided into the following two kinds in respect of effects on the magnetic properties of the amorphous alloy:

(1) A surface film which applies large compressive stress to the amorphous alloy ribbons and lowers permeability, but realizes constant permeability up to a considerably high magnetic field.
(2) A surface film which scarcely has a mechanical interaction with the amorphous alloy ribbon and thus has nothing to do with magnetic properties.

This report describes typical examples of the respective kinds. Further, it has been found that annealing atmosphere has a remarkable effect on the crystallization behaviors of the amorphous alloy ribbon coated with a certain kind of film, thus effecting the magnetic properties of the amorphous alloy ribbon. Therefore, the report also touches upon the effect of the annealing atmosphere.

2 Experimental Procedures

2.1 Preparation and Surface Coating of Amorphous Alloy Ribbon

The specimen of amorphous alloy ribbon was made by injecting molten metal with a composition of $Fe_{79.5}B_{12}Si_{8.5}$ (mol %) through a slit nozzle on the copper-alloy-made cooling roll surface. The ribbon was 50 mm in width and 23 μm in thickness.

The as-cast surface of the amorphous ribbon was lightly rubbed with a sponge in flowing water, then coated with an aqueous-solution-based coating solution, dried and baked in air at 473 to 573 K and finally annealed in a magnetic field. The surface-treated amorphous $Fe_{79.5}B_{12}Si_{8.5}$ alloy ribbons were sandwiched and bundled between two stainless steel plates and then annealed at a temperature of 673 K in the DC magnetic field of 1 600 A/m for 3.6 ks. The annealing method in this experiment was to simulate the annealing method to be given to the amorphous Fe-B-Si alloy ribbon after the iron core assembling process for the transformer. The gas flow rate in the annealing furnace was set to 16.7×10^{-6} m^3/s (1 l/min).

2.2 Magnetic Measurement

Magnetic properties were measured using a ribbon 50 mm in width and 150 mm in length by a Single Sheet Tester (Toei Industries Co., Ltd.). In order to investigate changes in magnetic properties caused by external forces, magnetic measurement was carried out while the weight was added through thin sheets, which were fixed to both ends of the sample in the lengthwise direction on the outside of the magnetic circuit using adhesive tape.

2.3 Thin-Film X-Ray Diffraction

To identify the surface crystalline phase, thin film X-ray diffraction with a high sensitivity near the surface was used. For the X-ray generator, RU-300 with Cu rotating target (Rigaku Co., Ltd.) was used at 55 kV and 250 mA. The specimen was stuck to a glass plate of 35 mm in diameter, and was rotated around the normal line of the specimen surface during measuring taking crystalline polarization into consideration. Seemann-Bohlin geometry, at an incident angle of 2°, was used in this study, and the penetration depth of the Cu Kα-ray to the specimen was estimated at about 0.7 μm.

2.4 Mösbauer Spectroscopy

The Mösbauer spectroscop measurement apparantus used in this experiment was MS-900 (Ranger Scientific Inc). A γ-ray of 14.4 keV was detected by the proportional counter tube, and the γ-ray source was ^{57}Co of about 26 mCi. Measurement was made at room temperature, and α-Fe was used for correction of velocity.

The polarization of the magnetic moment was evaluated using the following formula:[9)]

$$\langle\theta\rangle = \frac{\pi}{2} - \sin^{-1}\left(\frac{\frac{3}{2}\times\frac{A_{2,5}}{A_{1,6}}}{1+\frac{3}{4}\times\frac{A_{2,5}}{A_{1,6}}}\right)^{1/2}$$

where $\langle\theta\rangle$ is a mean value of angles formed by the specimen surface and the magnetic moment, $A_{2,5}$ is a mean area of peacks 2 and 5, and $A_{1,6}$ is a mean area of peaks 1 and 6. Namely, when $A_{2,5}/A_{1,6} = 0$, the magnetic moment is vertical to the specimen surface; when $A_{2,5}/A_{1,6} = 1.33$, the magnetic moment was parallel to the specimen surface.

2.5 Fourier Transformation Infrared Absorption Spectroscopy (FTIR)

In order to identify the thin film on the metallic surface, a high sensitivity reflection method by FTIR JIR-100 (JEOL Ltd.) was used. Incident light in the high sensitivity reflection optical system provided inside its specimen chamber was in a parallel polarization state. The incident angle was 80°, the resolution 4 cm^{-1} and the summing number of times 200. The detector was MCT type. The reference spectrum was obtained by measuring as-cast material under the same conditions.

3 Results and Discussion

3.1 Surface Film That Gives Compressive Stress

As a typical example of a surface film that can give compressive stress to the amorphous Fe-B-Si alloy ribon, Lithium Silicate 35 (LSS 35) with its SiO_2/LiO_2 molecular ratio of 3.5, made by Nissan Chemical Industries, Ltd., was used. The thickness of the surface film was controlled by changing the specific gravity of the lithium silicate aqueous solution, rotating speed and pressing quantity of the coating rubber roll.

3.1.1 Changes in magnetic properties by LSS 35 surface film

Figure 1 shows the effect of the film amount of LSS 35 on the the B–H curve of amorphous $Fe_{79.5}B_{12}Si_{8.5}$ alloy. It is found that the coating of an LSS 35 surface film significantly decreases the slope of B–H curve of amorphous $Fe_{79.5}B_{12}Si_{8.5}$ alloy, indicating that a decrease in permeability stabilizes the B–H curve up to a fairly high magnetic field, meaning an attainment of a constant permeability.

Flux density at 100 A/m, B_1, after annealing in the magnetic field of the amorphous $Fe_{79.5}B_{12}Si_{8.5}$ alloy ribbon without a surface film is 1.52 T and the core loss at 1.3 T and 50 Hz, $W_{13/50}$ is about 0.1 W/kg, but when LSS 35 surface film is coated with a film amount of about 1 g/m^2, B_1 drops to 0.35 T, and the core loss increases to about 0.4 W/kg. Therefore, the LSS 35 surface film on amorphous Fe-B-Si alloy ribbons is not suitable for iron cores of power transformers, but since such ribbons can obtain constant permeability up to a high magnetic field of about 2 000 A/m, new applications such as filters for communication equipment and thyrister protective circuits can be expected of them.

In order to understand changes in magnetic properties caused by the above-mentioned LSS 35 film, B_1 and $W_{13/50}$ were measured, while applying single-axis tensile stress to an as-bared amorphous $Fe_{79.5}B_{12}Si_{8.5}$ alloy ribbon after ananealing in a magnetic field and to another ribbon with an LSS 35 surface film of 2.6 g/m^2. The result is shown in **Fig. 2**. The amorphous alloy ribbon without a surface film after annealing in a magnetic field shows hardly any changes in flux density and core loss. This is considered attributable to the fact that in material having positive magnetostriction as in the amorphous Fe-B-Si alloy ribbon, application of tensile stress will align axes of easy magnetizing in the lengthwise direction,[10] but the annealed material, which has already reached such a state, shows no similar effect of the tension. On the other hand, in the case of the amorphous alloy ribbon with an LSS 35 surface film, tension of about 45 MPa restores B_1 to 1.45 T and also improves $W_{13/50}$ to 0.17 W/kg. Namely, the bad influence of LSS 35 on the magnetic properties of amorphous Fe-B-Si alloy is considerably relieved by tension. In the low tension range, even an increase in the core loss is observed. The reason for this is presumed to be that the uneven stress field which has been formed in the alloy ribbon by the surface film has been further disturbed by external stress.

Another example of developing constant permeability in the amorphous Fe-B-Si ribbon by surface treatment techniques is a method in which 0.4% Al, which is an impurity in the alloy, is surface-oxidized by the casting process in air to form an oxide film on the ribbon sur-

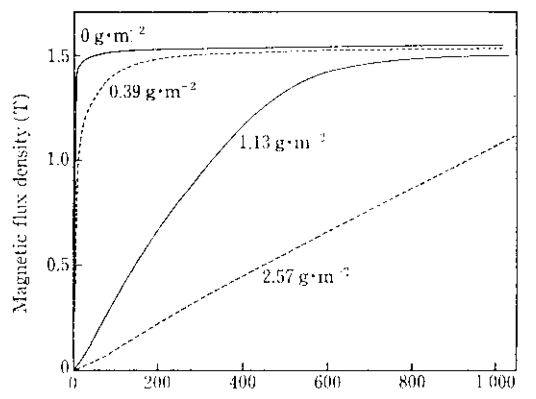

Fig. 1 Changes in B–H curves of amorphous $Fe_{79.5}B_{12}S_{8.5}$ alloys with LSS 35 surface films of various film amounts annealed at 673 K for 3.6 ks in vacuum under a magnetic field

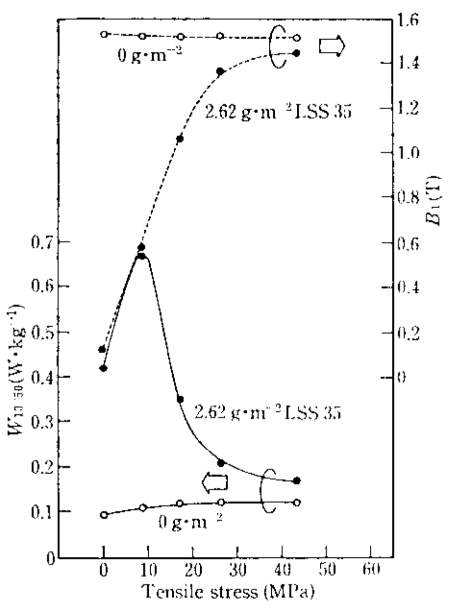

Fig. 2 Tensile stress dependence of magnetic properties of amorphous $Fe_{79.5}B_{12}S_{8.5}$ alloys without and with LSS 35 surface films annealed at 673 K for 3.6 ks in vacuum under a magnetic field

face.[11,12] This development of constant permeability may also have been caused by a compressive stress field which was generated inside the amorphous alloy ribbon by the surface oxide film.

3.1.2 Changes in Mösbauer spectra due to LSS 35 surface film

As shown in Fig. 1, an LSS 35 surface film markedly increased the magnetic anisotropy of the amorphous $Fe_{79.5}B_{12}Si_{8.5}$ alloy. In the present section, the polarization of the magnetic moment in the specimen is examined by Mösbauer spectrocopy.

Figure 3 shows influences of the film amount of LSS 35 on the Mösbauer spectra measured by the transmission method, indicating that as the film amount increases, the strength at peaks 2 and 5 decreases significantly. The numerical values shown in the figure indicate the $A_{2,5}/A_{1,6}$ ratio. The ratio of $A_{2,5}/A_{1,6} = 1.25$ in the as-bared amorphous $Fe_{79.5}B_{12}Si_{8.5}$ alloy after annealing in a magnetic field means that the magnetic moment is almost in parallel with the ribbon surface. On the other hand, $A_{2,5}/A_{1,6} = 0.18$ at a film amount of 2.3 g/m^2 of the LSS 35 film shows that the magnetic moment is polarized almost perpendicularly to the ribbon surface. This has caused a development of magnetic anisotropy and an increase in the core loss due to LSS 35 surface film shown above.

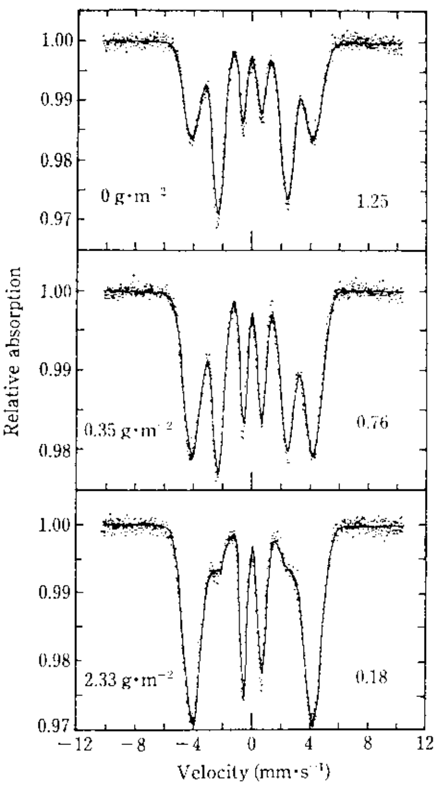

Fig. 3 Changes in Mössbauer spectra of amorphous $Fe_{79.5}B_{12}S_{8.5}$ alloys with LSS 35 surface films of various film amounts annealed at 673 K for 3.6 ks in vacuum under a magnetic field (see text for the meaning of the numerical values)

Such an effect of the LSS 35 film on the polarization of the magnetic moment can be understood by the formation of a compressive stress field inside the ribbon. Namely, since the amorphous Fe-B-Si alloy ribbon has significant positive magnetostriction, application of compressive stress causes the magnetic moment to polarize out of plane,[13] and as a result, B_1 also dropped. This is the same as the effect on magnetic properties of the surface crystalline layer formed during annealing at a temperature higher than the optimum annealing temperature.[14] Further, the effect of external tension shown in Fig. 2 can be well understood as the result of compensating compressive stress due to the LSS 35 film.

3.1.3 Changes in thin film X-ray diffraction due to LSS 35 surface film

From the point of view of surface crystallization, to be mentioned later, the thin film X-ray diffraction of the amorphous alloy ribbon with the LSS 35 surface film was measured, but no crystalline phase was detected in the ribbon surface layer.

3.2 Surface Film Which Gives No Compressive Stress

In the preceding section, it was found that since the amorphous Fe-B-Si alloy ribbon has a significant positive magnetostriction, the existence of a surface film, that will cause a mechanical interaction with the ribbon, exercises an undesirable effect on the magnetic characteristics of the iron core of the power transformer. As surface films, which do not apply compressive stress to the amorphous alloy ribbon, the authors used AS 200 (Nissan Chemical Industries, Ltd.) which has alumina sol as a main component, and Lithium Silicate 75 (LSS 75) with SiO_2/Li_2O molecular ratio of 7.5.

3.2.1 Changes in magnetic properties due to LSS 75 surface film

When the amorphous $Fe_{79.5}B_{12}Si_{8.5}$ alloy is coated with an LSS 75 surface film at a film amount of 0.3 g/m^2 and then annealed in the magnetic field of 1 600 A/m at 673 K in vacuum for 3.6 ks, B_1 and $W_{13/50}$ are practically the same as those for the amorphous alloy without a surface film, as shown in **Fig. 4**. Namely, the LSS 75 surface film, different from the case of LSS 35, does not deteriorate magnetic properties of the amorphous Fe-B-Si alloy ribbon, as shown in Fig. 4. In other words, it is considered that the LSS 75 surface film has given no compressive stress to the amorphous alloy.

Further, it was found that in the case of the LSS 75 surface film annealing in nitrogen results in only a slight deterioration in core loss, but no core loss was seen in

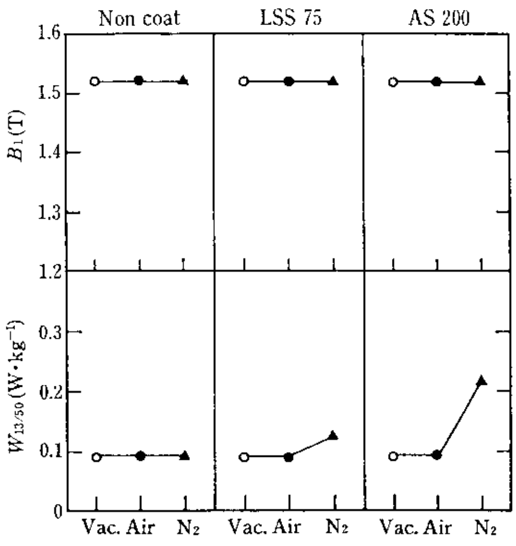

Fig. 4 Magnetic properties of amorphous $Fe_{79.5}B_{12}S_{8.5}$ alloys without surface film and with LSS 75 or AS 200 surface films of about 0.3 g/m^2 annealed at 673 K for 3.6 ks in varia-ous annealing atmospheres under a magnetic field

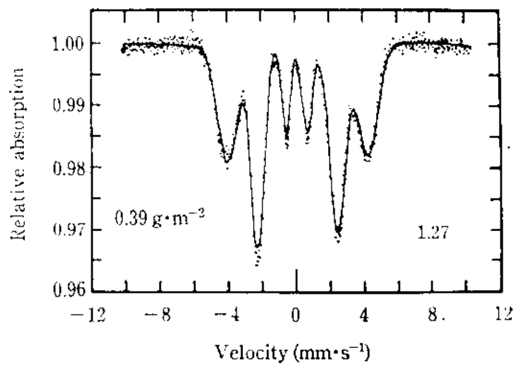

Fig. 5 Mössbauer spectrum of amorphous $Fe_{79.5}B_{12}S_{8.5}$ alloys with LSS 75 surface film annealed at 673 K for 3.6 ks in vacuum under a magnetic field (see text for the meaning of the numerical value)

annealing in the air, as shown in Fig. 4. Now, when the amorphous alloy ribbon is used for iron core of the power transformer, the role to be played by the surface film is to increase the interlayer insulation resistance between the wound amorphous alloy ribbons, in order to lower the eddy current loss. However, since the experimental data of magnetic properties in the present report are limited to the results measured by a single sheet tester, it is difficult to confirm this effect. Namely, if the surface film does not deteriorate the magnetic properties in the measurement using a single sheet tester, the surface film is judged to be satisfactory. Therefore it can be understood that LSS 75 has satisfied the necessary conditions as a surface film, when the amorphous Fe-B-Si alloy ribbons are used for iron core of the power transformer.

3.2.2 Changes in Mösbauer spectra due to LSS 75 surface film

Figure 5 shows Mösbauer spectra of the amorphous Fe-B-Si alloy ribbon annealed in a magnetic field after coating with an LSS 75 surface film. The $A_{2,5}/A_{1,6}$ ratio is 1.27, which is practically the same as that of the mor-phous alloy without a surface film. Namely, it can be seen that the magnetic moment is almost parallel to the surface of the ribbons and, in addition, the existence of the LSS 75 surface film has exercised no effect on the polarization of the magnetic moment inside the amor-phous Fe-B-Si alloy ribbons. As mentioned in the pre-ceding section, this corresponds to the fact that the LSS 75 surface film gave no compressive stress to the amor-phous alloy.

3.2.3 Changes in thin film X-ray diffraction due to LSS 75 surface film

X-ray diffraction from the amorphous alloy surface with the LSS 75 surface film annealed in a magnetic field in vacuum or in nitrogen atmosphere at 573 K is shown in **Fig. 6**. In both case, no diffraction peak occurred which suggests the existence of the crystalline phase. The weak hallo at about 22° is caused by the LSS 75 surface film, and its strength is proportional to the film amount.

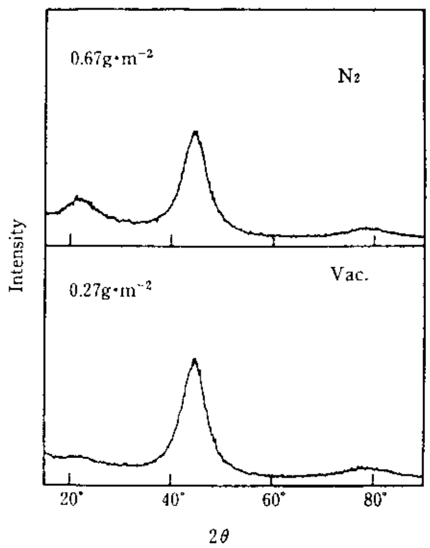

Fig. 6 X-ray diffraction patterns from amorphous $Fe_{79.5}B_{12}S_{8.5}$ alloys with LSS 75 surface film annealed at 673 K for 3.6 ks in N_2 and vacuum atmospheres

3.2.4 Changes in magnetic properties due to AS 200 surface film

When the amorphous $Fe_{79.5}B_{12}Si_{8.5}$ alloy is coated with the AS 200 surface film at a film amount of 0.3 g/m^2 and annealed in a magnetic field of 1 600 A/m in vacuum at 673 K for 3.6 ks, B_1 and $W_{13/50}$ were practically the same as those of the amorphous alloy without a surface film, as shown in Fig. 4. When the amorphous Fe-B-Si alloy with the AS 200 surface film is annealed in a magnetic field in vacuum, the deterioration in the magnetic properties of the amorphous Fe-B-Si alloy ribbon is not observed, contrary to the case of LSS 35. In other words, it is considered that the AS 200 surface film gives no compressive stress to the amorphous alloy.

3.2.5 Effect of annealing atmosphere on AS 200 surface film

However, when the amorphous $Fe_{79.5}B_{12}Si_{8.5}$,alloy with an AS 200 surface film is annealed in a magnetic field in nitrogen atmosphere as shown in Fig. 4, B_1 hardly changes, but $W_{13/50}$ shows extraordinary deterioration, increasing to 0.2 W/kg or above. On the other hand, when it is annealed in a magnetic field in vacuum or in air, no deterioration of magnetic properties was found. This significant difference in annealing atmosphere dependence of magnetic properties of the amorphous ribbon is the feature of the AS 200 surface film. The advantage of vacuum or oxygen-containing atmosphere is also reported in the case of the phosphoric and chromic acid-based surface films coated on the amorphous Fe-B-Si alloy ribbon.[3)]

Incidentally, when the deterioration of the magnetic properties due to annealing in a nitrogen atmosphere was examined, it was found that even if AS 200 was not directly coated on the ribbon surface, the same degree of deterioration in core loss occurred, when an amorphous Fe-B-Si alloy ribbon was arranged adjacent to the AS 200 surface film during annealing in the nitrogen atmosphere. In other words, it can be seen that the effect of the annealing atmosphere on the magnetic properties of the amorphous Fe-B-Si alloy with the AS 200 surface film has not been caused by the direct mechanical interaction between the alloy ribbon and the surface film.

3.2.6 Effect of AS 200 surface film on surface crystallization Phenomenon

The authors previously reported the effect of the annealing atmosphere on the magnetic properties and surface crystallization of the amorphous Fe-B-Si alloy.[15)] When moisture is contained in the annealing atmosphere, boron in the surface layer of the amorphous alloy is selectively oxidized to form a region with a low concentration of boron just below the oxide film. Since the crystallization temperature of this boron-depletion zone is very low, the surface layer of the amorphous ribbon

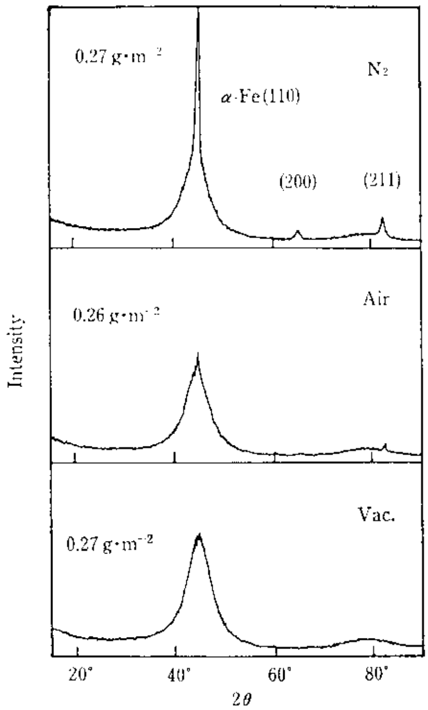

Fig. 7 Changes in X-ray diffraction patterns from amorphous $Fe_{79.5}B_{12}S_{8.5}$ alloys with AS 200 surface films annealed at 673 K for 3.6 ks in various annealing atmospheres

is easily crystallized during annealing to form α-Fe. Since the density of the surface crystalline phase is greater than that of the amorphous alloy, the ribbon surface layer is contracted as a result of crystallization, a compressive stress field is formed inside the amorphous alloy ribbon to cause core loss deterioration.

As shown in Fig. 4, the annealing atmosphere dependence of magnetic properties is significant in the case of the amorphous alloy ribbon with the AS 200 surface film. To study this phenomena using the above-mentioned mechanism, thin film X-ray diffraction was measured, as shown in **Fig.** 7. On the surface of the amorphous alloy annealed in a magnetic field in vacuum, no diffraction peak due to a crystalline substance is observed, but on the surface of the amorphous $Fe_{79.5}B_{12}Si_{8.5}$ alloy ribbon annealed in nitrogen, a diffraction peak due to α-Fe is clearly detected. Such a difference due to annealing atmosphere can be understood from the thermal decomposition behavior of alumina sol which is the main component of AS 200. **Figure 8** shows the thermogravimetric curve of AS 200 dried at room temperature, and indicates a weight loss due to moisture discharge of about 10% in the heating process from 500 K (baking) to 673 K (annealing). Consequently, when the amorphous alloy was annealed in a nitrogen atmosphere, the surface of the amorphous alloy with the AS 200 film comes to be exposed to a high dew-point atmosphere. As mentioned in detail in

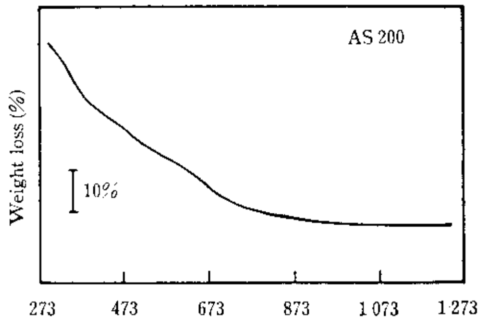

Fig. 8 Thermogravimetric analysis curve of AS 200 dried at room temperature

the previous report, this is one of the environments in which the surface of the amorphous Fe-B-Si alloy ribbon is easily crystallized. In the case of the vacuum atmosphere, on the other hand, it is considered that moisture discharged from AS 200 during heating is evacuated out of the system, thereby preventing surface crystallization.

According to this viewpoint, moisture discharged during annealing in air will also stay in the surrounding atmosphere, and ought to have caused surface crystallization of the same degree as during annealing in nitrogen atmosphere. This, however, would contravene the experimental results shown in Fig. 7. As shown in **Fig. 9**, surface crystallization rate in an annealing in air depends on the film amount of AS 200. In other words, with film amount at or below 0.3 g/m^2, diffraction peak of the crystalline substance is hardly detected, but some degree of surface crystallization advances along with an increase in film amount. These experimental results suggest that an inhibition of surface crystallization by the air atmosphere is caused, because the oxide film formed by oxygen in the atmosphere obstructs the selective oxidation of boron in the alloy to inhibit the formation of a low boron concentration zone which would have caused the surface crystallization.

In the case of the LSS 75 surface film, neither vacuum nor nitrogen atmosphere caused surface crystallization of the amorphous Fe-B-Si alloy ribbon, as shown in Fig. 6. This may be due to the very small quantity of moisture in LSS 75 and consequently also due to the scanty quantity of discharged moisture in the annealing process, as can be clearly seen in the intensity of the absorption peak based on H_2O of 3 400 cm^{-1} and 1 600 cm^{-1} in the infrared reflection spectra of the surface film after baking, as shown in **Fig. 10**.

As described above, deterioration of magnetic properties occurred simply by annealing the amorphous Fe-B-Si alloy ribbon adjoining the AS 200 film, instead of directly coating the AS 200 surface film on the ribbon surface. From this result, it has been concluded that the effect of the annealing atmosphere on the magnetic

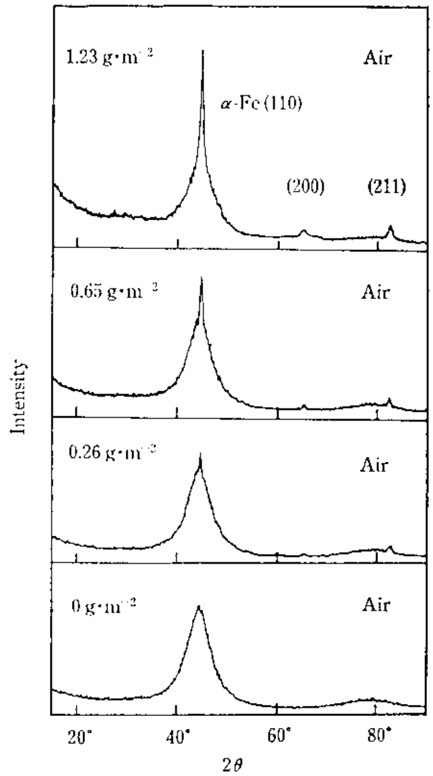

Fig. 9 Changes in X-ray diffraction patterns from amorphous $Fe_{79.5}B_{12}S_{8.5}$ alloys with AS 200 surface films of varioaus film amounts annealed at 673 K for 3.6 ks in air

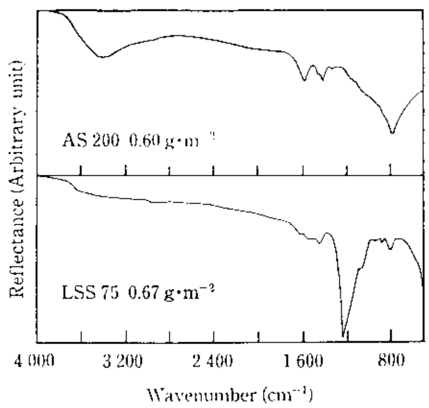

Fig. 10 Infrared reflection spectra from LSS 75 and AS 200 surface films on amorphous $Fe_{79.5}B_{12}S_{8.5}$ amorphous alloys baked at 473 K for 300 s in air

properties of the amorphous Fe-B-Si alloy with the AS 200 surface film was not caused by the mechanical interaction between the surface film and the alloy ribbon. This conclusion is considered reasonable from the result of the X-ray diffraction shown in **Fig. 11**. Namely,

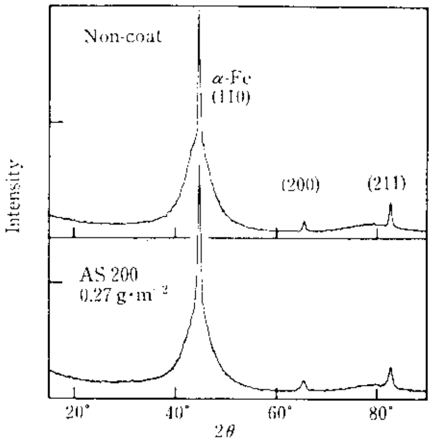

Fig. 11 X-ray diffraction patterns from amorphous $Fe_{79.5}B_{12}S_{8.5}$ alloys without surface film and with AS 200 annealed side by side at 673 K for 3.6 ks in N_2 atmosphere

even if AS 200 is not directly coated on the surface of the amorphous alloy ribbon, a crystalline layer is formed on the surface of the adjoining ribbon during annealing in a nitrogen atmosphere. This can be understood by the mechanism in which moisture discharged from AS 200 mentioned earlier causes the surface crystallization.

As discussed above, the effect of annealing atmosphere on the surface crystallization of the amorphous $Fe_{79.5}B_{12}Si_{8.5}$ alloy with an AS 200 or LSS 75 surface film can be clearly understood by the mechanism mentioned in the previous report.[15]

3.3 Difference between Surface Films

As mentioned above, the effects of surface films on the magnetic properties of the amorphous alloy ribbon depend significantly upon the properties of films. Since the amorphous Fe-B-Si alloy has significant positive magnetostriction, experiments show that changes in magnetic properties occur, in many cases, as a result of the mechanical interaction. Influences of the surface film on the magnetic properties can be summarized as follows:

(1) The surface film gives compressive stress to the amorphous alloy ribbon and changes magnetic properties through magnetostriction of the amorphous alloy (LSS 35).

(2) The surface film promotes crystallization near the surface of the amorphous alloy ribbon to generate a stress field inside the ribbon from the difference in density and the thermal expansion coefficient between the surface crystalline phase and the amorphous alloy, and changes magnetic properties through the magnetostriction (AS 200 annealed in nitrogen atmosphere).

(3) The surface film has no mechanical interaction with the ribbon, and thus has no direct effect on the magnetic properties of the amorphous alloy ribbon (LSS 75 and AS 200 annealed in vacuum).

An examination was also undertaken into the difference between surface films themselves which have different effects on the magnetic properties of the amorphous alloy ribbon.

3.3.1 Lithium silicate

Solid materials dried from lithium silicate aqueous solution change their properties conspicuously depending upon the SiO_2/Li_2O molecular ratio. Namely, in the range where the SiO_2/Li_2O molecular ratio is larger (LSS 75), lithium silicate has similar properties to colloidal silica, and the waterproofing property of its film improves, although film adhesion is poor. It is known that as the quantity of Li_2O increases, the dried solids obtain similar properties to lithia glass, their mechanical strength is enhanced and their adhesion to the substrate increases.[16]

The above agrees well with the experiemental results of this study. The LSS 75 surface film peels when quantities of 1.5 g/m^2 or above are coated on the amorphous Fe-B-Si alloy ribbon, and should be decreased to 1 g/m^2 or less. The reason why LSS 75 has no mechanical interaction with the amorphous alloy ribbon may be that the film itself is soft and adhesion is not so strong. On the other hand, LSS 35 has significant film strength, and its adhesion is high; hence it will not peel even with film of 10 g/m^2. Further, the silicate of water-soluble alkaline metal like lithium silicate discharges a large quantity of water during the film-forming process, and results in significant contraction to generate a compressive stress field inside the alloy ribbon.

3.3.2 Alumina sol

AS 200 is alumina sol stabilized by CH_3COO^-,[17] and contains large quantities of structural water and adsorption water as can be seen in the infrared reflection spectra in Fig. 10. Adhesion of the surface film to the amorphous alloy ribbon is excellent, but its structure is soft, and dried solids are porous and their mechanical strength is not so high. Consequently, it has no mechanical interaction with the ribbon in the same way as LSS 75, unless a secondary surface crystallization phenomenon occurs due to moisture discharged during annealing. As shown in the thermogravimetric analysis curve of Fig. 8, discharge of moisture from alumina sol occurs in a wide temperature range, and the bonding energy distribution of water is very wide. This is the reason why selective oxidation of boron occurs on the surface of the amorphous Fe-B-Si alloy, resulting in surface crystallization during annealing in nitrogen in which the atmosphere stagnates at the surroundings of the ribbon.

3.4 Surface Film Suitable for Amorphous Alloy Ribbon for Transformers

The basic composition of the amorphous alloy used for iron cores of power transformers will be limited to the Fe-B-Si system due to factors such as saturation magnetic flux density, core loss, thermal stability and cost, even though there will be some improvements made in the future. The magnetostriction of the amorphous Fe-B-Si alloy is proportional to the Fe quantity, and its value is extremely large.[18] As repeatedly described in this report, the magnetic properties of the amorphous Fe-B-Si alloy will deteriorate, if the alloy ribbon has mechanical interaction with its surface film. Therefore, the characteristics which are required of the surface film from the viewpoint of magnetic properties are summarized as follows:

(1) The thermal expansion coefficient of the surface film is nearly the same as that of the amorphous alloy ribbon, and thus no compressive stress field will be formed inside the amorphous alloy ribbon.

(2) The moisture quantity in the surface film is small, or at least, the discharged quantity of water during the annealing process is small. Thus surface crystallization of the amorphous alloy ribbon is not promoted. Incidentally, this surface crystallization can be suppressed to a certain extent by an improvement of the annealing atmosphere.

(3) The interlayer resistance should be increased, provided that the film thickness will not be so large as to decrease the space factor.

4 Conclusions

The effect of the surface film on the magnetic properties of the amorphous $Fe_{79.5}B_{12}Si_{8.5}$ alloy ribbon was investigated, and the following conclusions were obtained:

(1) Surface films, such as Lithium Silicate 35 ($SiO_2/Li_2O = 3.5$), which generate a compressive stress field in the amorphous Fe-B-Si alloy ribbon can, by polarizing the magnetic moment vertically to the ribbon surface, lower the flux density at 100 A/m, B_1, realize constant permeability to a higher magnetic field and increase the core loss at 1.3 T and 150 Hz, $W_{13/50}$.

(2) The surface film of Lithium Silicate 75 ($SiO_2/Li_2O = 7.5$) has no mechanical interaction with the amorphous Fe-B-Si alloy ribbon and induces no surface crystallization, regardless of annealing atmosphere, and therefore, will have hardly any effects on the magnetic properties of the amorphous alloy. Thus Lithium Silicate 75 is a surface film suitable as a amorphous alloy for transformer use.

(3) The surface film of Alumina Sol 200 has no mechanical interaction with the amorphous Fe-B-Si alloy ribbon but discharges moisture during annealing and promotes surface crystallization in a nitrogen atmosphere to deteriorate the core loss $W_{13/50}$. During annealing in vacuum or air atmosphere, however, the surface crystallization is suppressed, thereby having no effect on the magnetic properties of the amorphous alloy ribbon.

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