Effect of Difference in Ion Plating Method on the Magnetic Properties of TiN-coated Grain Oriented Silicon Steel Sheet[†]

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The hollow cathode discharge (HCD) and electron beam (EB)+radio frequency (RF) ion plating methods were, respectively, applied to investigate the influence on the magnetic properties of TiN-coated silicon steel sheet, and to clarify the difference in the properties of the TiN film and ionization resulting from the HCD and EB+RF methods. The TiN ceramic coating and measurement of the ionization by using these two kinds of ion plating methods were both performed inside an ion plating apparatus.

The experimental results obtained are summarized as following items.

(1) The magnetic flux density [B_8 (T)] and the iron loss [$W_{17/50}$ (W/kg)] of the silicon steel sheets TiN-coated by the two ion plating methods were both dramatically improved, in good agreement with our previous experimental results, but the degree of improvement by the HCD method was about twice that by the EB+RF method. This improvement in magnetic properties by both methods was most marked in the silicon steel sheets with the magnetic flux density of $B_8=1.93$ T.

(2) The surface appearance of the silicon steel sheet TiN-coated by the HCD method showed a gold color, whereas that by the EB+RF method showed a brown color. A thin-film X-ray diffraction inspection after HCD indicated a strong (111) peak of TiN, while that after EB+RF indicated comparatively strong (200), (111) and (220) peaks, and weak (311) and (222) peaks. Scanning electron microscopic observation of the TiN film deposited by the HCD method showed a fine and smooth surface, whereas that by the EB+RF method showed a rougher surface.

(3) The ionization level by the HCD method was 43%, whereas that by EB+RF was 6%.

(4) The silicon steel sheet TiN-coated by HCD method had a stronger compressive stress dependence than that coated by the EB+RF method.

(5) The adhesion of the TiN film deposited by the HCD method was stronger than that deposited by the EB+RF method.

(6) It is considered that, due to the higher ionization by the HCD method than that by EB+RF, it was possible to apply a strong surface tension to the near-surface of the TiN-coated silicon steel sheet, resulting in a fine and smooth TiN film with good adhesion, thereby endowing the TiN-coated silicon steel sheet with a reduced iron loss.

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I. Introduction

Grain oriented silicon steel sheet, in which secondary recrystallized grains are highly aligned in the (110) [001] orientation, namely, the Goss orientation, is mainly used as a core material in transformers and other electrical machinery and equipment. The development of grain oriented silicon steel sheet with lower core loss has become increasingly important since the oil crises as one of the methods of saving energy. In a recent innovation⁽¹⁾⁽²⁾, an ultra-low iron loss was obtained by applying a ceramic coating such as TiN, CrN or TiC by the physical vapor deposition (PVD) or chemical vapor deposition (CVD) method to polished silicon steel sheets. These ceramic film-coated silicon steel sheets which showed no deterioration in magnetic properties after strain-relief annealing, had superior compressive stress sensitivity on magnetostriction and good lamination performance. The attain-

ment of the ultra-low iron loss was due to an improvement in the hysteresis loss obtained by using a polished steel surface that was clean and free from impurities and to the reduced eddy current loss arising from the strong surface tension of the ceramic film.

It is possible to obtain a higher evaporation rate at lower temperature for ceramic coating by PVD than by CVD, so that the coating by PVD can prevent the deformation of a thin steel sheet during the coating process, and can be deposited within a short time. Therefore, for application to a manufacturing process, ceramic coating by PVD is considered better than that by CVD. It is important to investigate in detail the influence of the PVD process on the magnetic and related properties of a silicon steel sheet, and to evaluate whether these magnetic properties are strongly influenced by different plasma coating methods.

This report presents experimental results describing the influence of different PVD coating methods on magnetic properties. The PVD methods studied here were the HCD and EB+RF methods used for applying a TiN coating with a PVD apparatus. This report also clarifies the

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different properties of the TiN film and ionization level obtained with the HCD and EB+RF methods.

II. Experimental Procedure

The starting materials were grain oriented silicon steel sheets of 0.23 mm in thickness, the chemical compositions of the two raw materials being, in mass% (1) C: 0.043, Si: 3.31, Mn: 0.072, Se: 0.019, Sb: 0.023, and Mo: 0.012, and (2) C: 0.040, Si: 3.28, Mn: 0.070, and S: 0.017. These silicon steel products were cut down to a sample size of $0.23 \times 30 \times 300$ mm, and strain-relief annealing was carried out for 7.2 ks at 1073 K. This specimen size was determined by the frame size of the single sheet tester (SST) that usually applied for magnetic measurements. Since the magnetic flux density of the silicon steel products used in these experiments had an influence on the iron loss, three kinds of specimens with different magnetic flux densities at 800 A/m, B_8 of (A) 1.93 T, (B) 1.90 T and (C) 1.87 T were selected from the silicon steel products. The iron loss at 1.7 T, 50 Hz, $W_{17/50}$ of (A), (B) and (C) were, respectively, 0.88–0.91, 0.89–0.90 and 0.94–0.98 W/kg.

The insulating coating of the silicon steel products was removed by dipping to an NaOH solution, and the forsterite film was then removed by dipping in 10% HCl solution at 353 K. The surface of each silicon steel sheet sample was finally chemically polished by dipping in 3% HF + 97% H_2O_2 solution.

The TiN ceramic coating was applied to the polished silicon steel samples by using the ion plating apparatus shown in Fig. 1. This PVD apparatus can be used for either of the two coating methods of HCD or EB+RF in its operation.

Figure 2 shows the sample holders used in the PVD apparatus, which enable the tension of 0.5–20 MPa to be applied to the specimen while rotating the specimen holder in one direction to simultaneously deposit a uniform coating on both surfaces. By using these specimen holders in the ion plating apparatus, it was possible to investigate in detail the influence on the magnetic properties by the two PVD coating methods. These specimen holders also prevented the thin silicon steel samples from deformation during coating. The magnetic properties of the

Fig. 1 Schematic diagram of the ion plating apparatus employing the HCD and EB+RF methods.

Fig. 2 Schematic diagram of the tensile holders for (a) small and (b) large specimens.

coated silicon steel under the optimum tension⁽³⁾ were investigated by changing the applied weight, the ordinarily tension being 3.5 MPa.

Ion plating by the HCD method was done with 20 kW power, 0.093 Pa vacuum, -100 V bias at 673 K substrate temperature in 150 SCCM reactive N_2 gas. The conditions for the EB+RF method were 15 kW power, 0.040 Pa vacuum, -500 V bias, 673 K substrate temperature, 500 W RF power, and 150 SCCM reactive N_2 gas. As can be seen from Fig. 2, it was possible to simultaneously deposit the ceramic coating on five small specimens of 30×300 mm or two large specimens of 150×300 mm.

The ionization rate can be determined by measuring the ion current⁽⁴⁾ applied to the substrate. Figure 3 shows a schematic diagram of the method used for measuring the ionization rate by the HCD method. The ionization rate can be determined by using eqs. (2-1) and (2-2). The incident frequency of a Ti atom to the ion collector per unit area and unit time in Fig. 3 is

$$\nu_{Ti} = \frac{1}{60} \times (R \times 10^{-4}) \times \rho_{Ti} \frac{N_A}{M_{Ti}} [\text{molecules} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}] \quad (2-1)$$

Fig. 3 Schematic diagram of the method for measuring ionization.

where the symbols have the following meanings:

- $R \times 10^{-4}$: evaporation velocity of Ti (cm/min)
 ρ_{Ti} : density of Ti (g/cm³)
 N_A : Avogadro's number
 M_{Ti} : atomic weight of Ti

The incident frequency of a Ti⁺ ion to the ion collector per unit area and unit time is

$$v_{\text{Ti}} = \frac{1}{50} \times \frac{I_c(\text{Ar} + \text{Ti}) - I_c(\text{Ar})}{1.60206 \times 10^{-19}} \quad (2-2)$$

where $I_c(\text{Ar} + \text{Ti})$ is the total current for the collector of Ar⁺ and Ti⁺ ions, and $I_c(\text{Ar})$ is the current for the collector of only the Ar⁺ ion. In eq. (2-2) when the HCD method is applied, it is necessary to deduct the Ar⁺ ion due to the presence of both Ar⁺ and Ti⁺ ions. Finally, the ionization rate for the Ti⁺ ion can be calculated by the following equation:

$$\frac{v_{\text{Ti}}}{v_{\text{Ti}}} \times 100(\%). \quad (2-3)$$

The magnetic properties of each silicon steel sample after applying the TiN ceramic coating were measured, and for some specimens, examinations of the TiN coating by thin-film X-ray diffraction and by color monitoring were made. An observation of the magnetic domain was also made by an electron microscope (H-700). Thin-film X-ray diffraction measurements were done with RU-300 X-ray apparatus (Rigaku) and color monitoring was done with a SM-3 color computer (Suga Experimental Instruments Corp.) data from the color measurements being plotted by using the Z8701 method of JIS. The TiN film on the silicon steel sheet was also observed under the conditions of an accelerating voltage of 15 kV and beam current of 0.05 nA by a scanning electron microscope (JSM-KCVSEM). The surface roughness of the TiN films was observed under the conditions of an accelerating voltage of 5 kV and beam current of 0.5 nA by a three dimensional analyzing apparatus (Type: RD-500) of a scanning electron microscope (Hitachi S-4100).

III. Experimental Results

Figure 4 shows the variation in magnetic flux density B_8 (T) and iron loss $W_{17/50}$ (W/kg) plotted for each process from the original silicon steel product to the TiN-coated sample, using the products with three different values of magnetic flux density as the starting specimens. Each point plotted in Fig. 4 shows the average magnetic properties of five samples TiN-coated by use of specimen holder (a) in Fig. 2. It is evident from Fig. 4 that B_8 (T) resulting from chemical polishing, after the insulating coating and forsterite film had been removed, increased moderately by 0.004–0.011 T, and that $W_{17/50}$ (W/kg) was greatly improved by 0.05–0.11 W/kg. After the subsequent TiN coating, it can be seen that the degree of improvement in both B_8 (T) and $W_{17/50}$ (W/kg) by the HCD method was about twice that by the EB+RF method; namely, the

Fig. 4 Variations in magnetic flux density B_8 (T) and iron loss $W_{17/50}$ (W/kg) with each process from the original silicon steel product to the TiN-coated sample with the HCD and EB+RF methods.

HCD method gave a B_8 (T) improvement of 0.003–0.007 T, while for EB+RF, B_8 (T) was improved by 0.001–0.003 T. In contrast, the HCD method gave a significant $W_{17/50}$ (W/kg) improvement of 0.09–0.15 W/kg, while for EB+RF, $W_{17/50}$ (W/kg) was improved by about half (0.04–0.08 W/kg) the figure achieved with HCD. This improvement in magnetic properties of the silicon steel sheet TiN-coated by the HCD method is in good agreement with the previous results⁽¹⁾, within an experimental error of 5%. The improvement in magnetic properties of the silicon steel sheet TiN-coated by both the HCD and EB+RF methods was the greatest for the silicon steel material with $B_8=1.93$ T; namely, for the silicon steel sheet with $B_8=1.93$ T, the changes in B_8 and $W_{17/50}$, ΔB_8 and ΔW , after TiN ceramic coating by the HCD method were 0.007 T and 0.15 W/kg, respectively, while the figures by the EB+RF method were 0.003 T and 0.08 W/kg.

Figure 5 shows an example of the surface appearance of the silicon steel sheet TiN-coated by the HCD and EB+RF methods. The sample TiN-coated by the HCD method manifests the gold color characteristic of TiN film, while the sample TiN-coated by the EB+RF method manifests a brown color.

Figure 6 shows a comparison of the X-ray diffraction charts for the TiN film deposited by the HCD and EB+RF methods. It is evident that the sample TiN-coated by the HCD method produced a strong (111) peak of TiN, while the sample TiN-coated by the EB+RF

Fig. 5 Surface appearance of grain oriented silicon steel with a TiN ceramic film deposited by the HCD and EB+RF methods.

Fig. 6 X-ray diffraction charts for the TiN films deposited by the HCD and EB+RF methods.

method produced comparatively strong (200), (111) and (220) peaks, and weak (311) and (222) peaks.

Figures 7, 8 and 9 show, respectively, the variation in color, scanning electron micrographs of the TiN films and the surface roughness by three dimensional analyzing after the TiN coating had been applied by the HCD and EB+RF methods. From the color measurements in Fig. 7, it is evident that the sample TiN-coated by the HCD method manifests a gold color of 0.385 (x) and

Fig. 7 Color difference in the TiN films deposited by the HCD and EB+RF methods.

HCD method

EB+RF method

Fig. 8 Scanning electron micrographs of the TiN films deposited by the HCD and EB+RF methods.

0.382 (y), where x and y show the two classes in a XYZ system under the JIS standard (Z8701). Also, the sample TiN-coated by the EB+RF method manifests a brown

Fig. 9 Surface roughness measured by three dimensional analyzing apparatus of scanning electron microscope after TiN coating by the HCD and EB+RF methods.

color of 0.367 (x) and 0.354 (y). This result is also consistent with the surface appearance shown in Fig. 5. These color measurements for the sample TiN-coated by the HCD method are in good agreement with the previous HCD experimental results⁽¹⁾ and with the results of Matsumura and Ou⁽⁵⁾. The scanning electron microscopic observations of the TiN films shown in Fig. 8 indicate that a fine and smooth TiN film could be deposited by the HCD method. In contrast, a rougher appearance is evident after EB+RF deposition. Also, from the observation of the surface roughness shown in Fig. 9, it is apparent that the surface by the HCD method is much smoother than that by EB+RF.

Figure 10 shows the magnetic domains of the TiN-coated silicon steel sheets of (B) samples due to the HCD and EB+RF methods. Also, Table 1 shows the comparison of the domain wall spacings due to the HCD and EB+RF methods observed in Fig. 10. The observations shown in Fig. 10 and Table 1 indicate that the magnetic domains were greatly refined by the TiN coating, the degree of refinement by the HCD method being about 1.5 times as large as that by the EB+RF method.

Figure 11 shows a comparison between the compressive stress sensitivity of magnetostriction in the original grain oriented silicon steel and TiN-coated materials of (B) samples by the HCD and EB+RF methods. It is apparent that the TiN-coated silicon steels improved markedly compressive stress sensitivity within the measured range, and that due to the HCD method was more

Fig. 10 Magnetic domains of the silicon steel samples TiN-coated by the HCD and EB+RF methods.

Table 1 Domain spacings observed in Fig. 10.

	HCD method	EB+RF method
Domain wall spacing	0.15 ~ 0.25 mm	0.25 ~ 0.40 mm

Fig. 11 Comparison of the compressive stress sensitivity of magnetostriction for normal grain oriented silicon steel sheet and TiN-coated silicon steels by the HCD and EB+RF methods.

marked than that due to the EB+RF method. From the results of the compressive stress sensitivity against magnetostriction, it is considered that the strong surface tension added to the silicon steel sheet by the TiN ceramic coating was about 1.5–2 times as large as that added by forsterite and glass films on grain oriented silicon steel sheets. Moreover, this result obtained with the HCD method was in good agreement with the results reported in a previous paper⁽¹⁾.

Table 2 shows the results of adhesion test⁽⁶⁾ between TiN films and silicon steel sheet performed after TiN coating by the HCD and EB+RF methods. Table 2 shows that the adhesion of TiN film to the samples produced by the HCD method was better than that by the EB+RF method. The TiN film by the EB+RF method showed no peeling off at 20 mm ϕ and showed slight peeling off at 10 mm ϕ and almost complete peeling off at 5 mm ϕ . The ceramic coating of TiN on the silicon steel sheets manifested good adhesion, because the grain oriented silicon steel sheet with forsterite and glass films has generally been accepted to be good with no peeling at up to 30 mm ϕ .

Table 3 shows the ionization rates for the Ti⁺ ion measured with the HCD and EB+RF methods. It should be noted from Table 3 that ion plating by the HCD method produced a high ionization rate of 43%, but that by the EB+RF method produced a much lower rate of 6%. These results are consistent with those by Okada⁽⁷⁾.

IV. Discussion

1. Difference in the magnetic properties of TiN-coated silicon steel sheet samples after applying the HCD and EB+RF methods

The experimental results shown in Fig. 4 clarify that the degree of improvement in iron loss of the silicon steel sheet TiN-coated by the HCD method was about twice

that by the EB+RF method. Table 4 shows a comparison of the improvement of magnetic flux density and iron loss. It should be noted that, in all the samples, silicon steel TiN-coated by the HCD method manifested better magnetic properties than that coated by the EB+RF method.

It can be clearly seen in the magnetostriction data of Fig. 11 that the TiN coating by the HCD method added a strong surface tension of more than 8 MPa, while that by the EB+RF method was 6.5 MPa. Although this improvement in iron loss of the TiN-coated silicon steel sheet was due to the reduced eddy current loss arising from the strong surface tension induced in the near-surface of the sheet by the TiN ceramic coating, it should be noted that the degree of this improvement in magnetic properties was greatly influenced by the coating methods.

On the other hand, from measurements of the ionization rate, it should be noted that ion plating by the HCD method had a high ionization of 43%, and is known to give a fine and smooth TiN film, whereas ion plating by the EB+RF method had a lower ionization of 6%. Therefore, the fine and smooth TiN film with superior adhesion (see Table 2) to the silicon steel substrate by the HCD method was possible to induce an effective surface tension on the near-surface of the silicon steel sheet. From a comparison of the magnetic domains by the HCD and EB+RF methods shown in Fig. 10 and Table 1, magnetic domain refinement by the HCD method was about 1.5 times compared with the EB+RF method. These observations indicate that ion plating by the HCD method makes it possible to obtain the lowest iron loss in the TiN-coated silicon steel sheet.

2. Difference in properties of the TiN film deposited by the HCD and EB+RF methods

A comparison of the surface appearances, thin-film X-ray measurements, color monitoring, scanning electron microscopic observations and the magnetic domain appearance of the TiN films deposited by the HCD and EB+RF methods in Figs. 5–10 show that the TiN film deposited by the HCD method was finer and smoother than that by EB+RF. Thin-film X-ray measurements of the TiN films also show that the film deposited by the HCD method produced a strong (111) peak of TiN, whereas that by EB+RF produced comparatively strong (200), (111) and (220) peaks, and weak (311) and (222) peaks. This marked difference in the structure of the TiN film would have been due to the method of ion plating;

Table 2 Adhesion between TiN films and silicon steel sheet after TiN coating by the HCD and EB+RF methods.

	HCD method	EB+RF method
5 mm ϕ	Δ	$\times$
10 mm ϕ	$\circ$	Δ
20 mm ϕ	$\circ$	$\circ$
30 mm ϕ	$\circ$	$\circ$

$\circ$: No peeling off.

Δ : Slight peeling off.

$\times$: Peeling off.

Table 3 Ionization rates measured with the HCD and EB+RF methods.

	HCD method	EB+RF method
Ti ions	43%	6%
Ti atoms		

Table 4 Magnetic properties after TiN coating by the HCD and EB+RF methods for various original levels of magnetic flux density.

Original levels of magnetic flux density	HCD method		EB+RF method	
	ΔB_8	$\Delta W_{17/50}$	ΔB_8	$\Delta W_{17/50}$
(A) $B_8=1.93$ T	0.007 (T)	0.15 (W/kg)	0.003 (T)	0.08 (W/kg)
(B) $B_8=1.90$ T	0.005	0.12	0.002	0.06
(C) $B_8=1.87$ T	0.003	0.09	0.001	0.04

namely, the HCD method⁽⁸⁾ used in this experiment could create a high ionization of 43% from a low voltage (40 V) and large current (500 A) whereas the EB+RF method needed the addition of RF radiation to enhance the ionization⁽⁹⁾ by way of vaporization. To inhibit abnormal spattering during plasma coating, the EB+RF method needs to deposit the TiN film under a higher vacuum than that by HCD. In order to obtain a fine and smooth TiN film with good adhesion to the silicon steel sheet, it proved essential to use the HCD method, with which it was possible to simultaneously dissolve and ionize titanium without enhancing the ionization by directly using a plasma beam with a large diameter of about 20 mm ϕ in conjunction with a low voltage and a large current. The HCD method also has the particular advantage of being able to provide a fine and smooth TiN film with good adhesion to the silicon steel sheet due to its high ionization potential, even if such coating conditions⁽⁸⁾ as the bias voltage, coating temperature, amount of reactive N₂ gas, and degree of vacuum vary slightly during the coating process. Therefore, it is considered that plasma coating by this HCD method⁽¹⁰⁾⁽¹¹⁾ can give a strong tension in the near-surface of the silicon steel sheet, enabling a fine and smooth TiN film with good adhesion to the silicon steel sheet, for obtaining ultra-low loss silicon steel sheet.

Finally, it can be pointed out that TiN coating by the HCD method showed the gold color characteristic of a TiN film that was free from oxygen. This is quite different from that by the EB+RF method, which showed a brown color due to about 2%⁽¹²⁾ of oxygen in the TiN film. It cannot be clarified from this experiment whether the existence of oxygen in a TiN film has a deteriorating effect on the magnetic properties of the TiN-coated silicon steel sheet. This needs to be investigated further.

V. Conclusion

The influence on the magnetic properties of TiN-coated silicon steel sheet was investigated by applying the different HCD and EB+RF plasma coating methods with the PVD apparatus. The experimental results obtained are summarized as follows:

(1) The magnetic flux density and iron loss of the silicon steel sheets TiN-coated by the PVD method were both significantly improved. These results are in good agreement with the previous experimental results for the TiN-coated silicon steel sheet.

(2) The degree of improvement in the magnetic flux density and iron loss of the silicon steel sheet TiN-coated by the HCD method was about twice that by the EB+RF method.

(3) This improvement in magnetic properties of the silicon steel sheet TiN-coated by both the HCD and EB+RF methods was most marked in the silicon steel product with $B_8=1.93$ T, and the changes in the mag-

netic flux density and iron loss after TiN ceramic coating by the HCD method were 0.007 T and 0.15 W/kg, respectively, while the values by the EB+RF method were 0.003 T and 0.08 W/kg.

(4) The surface appearance of the TiN film deposited by the HCD method showed a gold color, whereas that by the EB+RF method showed a brown color.

(5) Thin-film X-ray diffraction inspection after coating by the HCD method indicated a strong (111) peak of TiN, while that by the EB+RF method indicated comparatively strong (200), (111) and (220) peaks, and weak (311) and (222) peaks.

(6) Observations by scanning electron microscopy of the TiN film deposited by the HCD method indicated a fine and smooth film, whereas that by the EB+RF method was rougher.

(7) Ion plating by the HCD method manifested a high ionization of 43%, whereas that by the EB+RF manifested a lower ionization of 6%.

(8) The silicon steel sheet TiN-coated by the HCD method had stronger compressive stress sensitivity than that coated by the EB+RF method. It is estimated that a tension of greater than 8 MPa with the HCD method and a tension of about 6.5 MPa with the EB+RF method were added to the TiN-coated silicon steel sheet, which was about 1.5–2 times as large as that added by the forsterite and glass films on the grain oriented silicon steel sheet.

(9) In a test of adhesion between the TiN film and silicon steel sheet, the adhesion of the TiN film deposited by the HCD method was stronger than that deposited by the EB+RF method.

(10) It is considered that the higher ionization potential of the HCD method than that possible with EB+RF induced a strong surface tension in the near-surface of the TiN-coated silicon steel sheet, enabling a fine and smooth TiN film with good adhesion to be deposited and thereby markedly reducing the iron loss.

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