Texture Formation of TiN Films Deposited on (011)[100] Single Crystal of Silicon Steel

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In order to clarify the texture of TiN deposited onto (011) [100] single crystals of silicon steel, TiN ceramic coating by the HCD method was done on the surface of polished silicon steel samples. Pole figures of the TiN films and related silicon steel samples were measured simultaneously using an SSD auto pole figure apparatus.

(111)_{TiN} pole figure of the TiN film showed the dominant texture of (1 $\bar{1}$ 1) [110] orientation, and (100)_{Si-steel} pole figure of the (011) [100] single crystal of silicon steel showed the dominant texture of (011) [100] orientation. The orientation relationship between the TiN films and a single crystal of silicon steel is considered to be (1 $\bar{1}$ 1)_{TiN}//(011)_{Si-steel}, [110]_{TiN}//[100]_{Si-steel}.

It should be noted that the dominant texture of TiN with (1 $\bar{1}$ 1) [110] orientation was formed preferentially on the surface of (011) [100] single crystal of silicon steel, and the orientation relationship between the TiN films and a single crystal of silicon steel was very good misfit within several percent.

KEY WORDS: TiN film; grain oriented silicon steel sheet; (011) [100] single crystal; HCD method; ion plating; orientation relationship; pole figure; texture of TiN film.

1. Introduction

In recent years, ceramic coating has been widely used to improve properties such as wear resistance, corrosion resistance, and decorative characteristics. Various plasma coating techniques, including the HCD (Hollow Cathode Discharge), EB (Electron Beam)+RF (Radio Frequency), plasma CVD (Chemical Vapor Deposition), Magnetron Sputtering, Multi Arc, and Arc Discharge methods, have been studied extensively. Among these methods, plasma coating by the HCD method has a high ionization rate of 20–40% and comparatively high evaporation rate of 0.05–0.5 $\mu\text{m}/\text{min}$,¹⁾ so it is known to be better in producing ceramic coatings²⁾ such as TiN, TiC, CrN, etc., than ion plating by the EB method, which cannot give a fine and smooth TiN film with good adhesion. The HCD method, due to its high rate of ionization, also has the particular merit of producing good ceramic coating films, even if such coating conditions as the bias voltage, coating temperature, amount of reactive N₂ gas, and degree of vacuum vary slightly during TiN coating.

On the other hand, recent studies^{3,4)} have shown that ultra-low iron loss can be achieved by using a ceramic coating such as TiN, CrN, or TiC applied by the PVD or CVD method to polished silicon steel sheets. It has been also considered that a ceramic coating applied to the polished silicon steel sheets by such techniques is the best way to improve iron loss, and that the attainment of ultra-low iron loss is closely related to the properties of the

ceramic films coated on the polished silicon steel sheets.

The structure of ceramic films deposited onto the surface of steel sheets has been investigated by thin-film X-ray diffraction analysis. It is well known that the texture of these ceramic films or the orientation relationship between the ceramic film and steel matrix greatly influences the properties of the coated products. However, no investigation has been carried out to date because of the complexities associated with the dual structure of the thin ceramic film and steel matrix.

This paper presents experimental results on the texture of TiN-coated thin films by the HCD method on the surface of the polished (011)[100] single crystals of silicon steel sheets. In particular, pole figures of the TiN films and their related (011)[100] single crystal in the silicon steel sheet were measured simultaneously by the SSD auto pole figure method. The orientation relationship between the TiN films and (011)[100] single crystal of the silicon steel sheet was determined with the intention of clarifying the mechanism by which ultra-low iron loss is obtained in TiN-coated grain oriented silicon steel sheet.

2. Experimental Procedure

The starting materials were grain oriented silicon steel sheets 0.23 mm in thickness, the chemical compositions (mass%) of the raw material being C: 0.043, Si: 3.31, Mn: 0.072, Se: 0.019, Sb: 0.023, and Mo: 0.012. This silicon steel product was cut down to a sample size

Fig. 1. Schematic diagram of (a) HCD (Hollow Cathode Discharge) ion plating apparatus and (b) tensile holder used in TiN coating.

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 is usually applied for magnetic measurements. Since the magnetic flux density of the silicon steel products used in this experiment was closely related to the degree of the alignment of the (011)[100] orientation, an initial measurement of the magnetic flux density was made to assess the suitability of samples for use in this experiment. Samples with high magnetic flux densities of above 1.93 T was selected.

The insulating coating of the silicon steel samples so far obtained was removed by dipping in an NaOH solution, and the forsterite films was then removed by dipping in 10% HCl solution at 353 K. The orientation of samples with large secondary recrystallized grains of about $25\text{--}30\text{ mm}\phi$ was measured using a fully automatic apparatus⁵⁾ which is capable of measuring the orientation of single crystals. A further selection was next made to obtain samples with an ideal orientation of (011) crystallographic plane with [100] axis, in which α , β , and γ ⁶⁾ were less than 1 degree. The surface of these silicon steel samples was finally chemically polished by dipping in a 3% HF + 97% H₂O₂ solution. The method of selection of single crystal has been done by the same method,⁷⁾ where the magnetic domain in the TiN-coated silicon steel sheet has already been observed.

The TiN ceramic coating was applied to the polished silicon steel single crystals by an ion plating apparatus of the type shown in (a) of Fig. 1. Figure 1(b) shows the sample holder used in the PVD apparatus, which enables a 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. This specimen holder also prevents deformation of the thin silicon steel samples during coating. The magnetic properties of the TiN-coated silicon steel under the optimum tension⁸⁾ were investigated by changing the applied weight, the ordinarily tension being 3.5 MPa.

Ion plating by the HCD method was performed at 20 kW power, 0.093 Pa vacuum, -100 V bias, 1.5 kW focusing coil power, 673 K substrate temperature, 150

SCCM reactive N₂ gas, coating rate $0.1\text{ }\mu\text{m}/\text{min}$, and coating thickness $1\text{ }\mu\text{m}$.

The textures of the TiN films and silicon steel single crystal after applying the TiN ceramic coating were measured under the an accelerating voltage of 60 kV and beam current of 250 mA using an SSD auto pole figure apparatus (Rigaku Corp.).

To examine the texture of the thin film of TiN, the variation of the intensity of the TiN was measured using the random X-ray intensity of α -iron according to the Schulz method. This method was adopted for the following reasons:

① It was not possible to correct for the intensity of the TiN film. (The thin film of TiN, being $1\text{ }\mu\text{m}$ in thickness, made it impossible to measure the total intensity of TiN.)

② From the crystallographic planes and lattice spacings of TiN (NaCl structure) and α -Fe (BCC structure), as can be seen in Table 1, it was possible to simultaneously measure the $(111)_{\text{TiN}}$ and $(100)_{\text{Si-steel}}$ or $(110)_{\text{TiN}}$ and $(110)_{\text{Si-steel}}$ pole figures of the TiN films and silicon steel matrix, respectively, with the same sample. However, in the measurement of pole figures, it was impossible to use this method with samples having similar lattice spacings. To make the pole figure of α -Fe, I/I_0 was corrected for the total areal intensity to the value of 1.

Furthermore, to directly check the difference of textures between the single crystal itself (chemically polished area) and TiN-coated area, a single giant secondary recrystallized Goss grain of about $60\text{ mm}\phi$ was selected and polished, and finally TiN-coated by making distinct areas of chemical polishing (the bare surface was protected by stainless foil wrapping) and TiN coating, as shown in the schematic diagram at the top of Fig. 4.

3. Experimental Results

Figure 2 shows a typical example of a $(111)_{\text{TiN}}$ pole figure (a) of the TiN films and $(100)_{\text{Si-steel}}$ pole figure (b) of a (011)[100] single crystal of silicon steel that were measured simultaneously using the SSD auto pole figure apparatus. The left-hand diagram in this figure shows

Fig. 2.
(a) $(111)_{\text{TiN}}$ pole figure of TiN films and
(b) $(100)_{\text{Si-steel}}$ pole figure of $(011)[100]$
single crystal of silicon steel TiN-coated on
the polished silicon steel sample. The
left-hand schematic diagram shows a
cross-sectional sheet of the dual structure
of the TiN films and single crystal, and
the method of measuring the X-ray pole figure.

Fig. 3.
(a) $(110)_{\text{TiN}}$ pole figure of TiN films and
(b) $(110)_{\text{Si-steel}}$ pole figure of $(011)[100]$
single crystal of silicon steel TiN-coated on
the polished silicon steel sample. The
left-hand schematic diagram shows a
cross-sectional sheet of the dual structure
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As can be clearly seen in Fig. 2, the crystallographic orientation of the dominant texture of the TiN films in the $(111)_{\text{TiN}}$ pole figure (a) is $(1\bar{1}1)[110]$, whereas that of the $(011)[100]$ single crystal of the silicon steel sample in the $(100)_{\text{Si-steel}}$ pole figure (b) is $(011)[100]$. In the pole figure shown in Fig. 2(b), it should also be noted that six (220) pole peaks of the TiN films, the crystallographic orientation of which was $(1\bar{1}1)[110]$, were detected

simultaneously. Among them, the conjugated peaks of two (200) poles of silicon steel and two (220) poles of TiN films on TD axis manifested elliptical shape.

Figure 3 shows a typical example of the $(110)_{\text{TiN}}$ pole figure (a) of the TiN films and $(110)_{\text{Si-steel}}$ pole figure (b) of $(011)[100]$ single crystal of silicon steel. In the $(110)_{\text{TiN}}$ pole figure (a) of the TiN film, (200) pole peaks of silicon steel were also detected simultaneously. On the other hand, in the $(110)_{\text{Si-steel}}$ pole figure (b) of silicon steel, (200) pole peaks of the TiN films were detected simultaneously.

Fig. 4. Schematic diagram of distinct areas of chemical polishing and TiN-coating inside a single giant secondary Goss grain and related pole figures. (b') shows the (100)_{Si-steel} pole figure of the chemically polished area, and (a) and (b) show respectively (110)_{TiN} pole figure of the TiN films and (110)_{Si-steel} pole figure of the (011)[100] single crystal of silicon steel inside the TiN-coated area.

Figure 3 shows that the crystallographic orientation of the dominant texture of the TiN films in the (110)_{TiN} pole figure (a) is (111)[110], whereas that of the (011)[100] single crystal of the silicon steel sample in the (110)_{Si-steel} pole figure (b) is (011)[100]. Also, in (a) of Fig. 3, (200) poles of silicon steel, the crystallographic orientation of which is (011)[100], and in (b) (200) poles of the TiN films, the crystallographic orientation of which is (111)[110], are detected simultaneously.

Figure 4 shows pole figures of chemically polished and TiN-coated areas inside a single giant secondary recrystallized Goss grain (single crystal). In (100)_{Si-steel} pole figure (b') of the chemically polished area, the crystallographic orientation of the silicon steel is (011)[100], where the peak shape of two (200) poles shows a round-shape.

In contrast, in the (111)_{TiN} pole figure (a) of the TiN films, the crystallographic orientation of the dominant texture of the TiN films is (111)[110], and in (100)_{Si-steel} pole figure (b) of the silicon steel, the dominant texture of silicon steel is (011)[100]. It should be noticed that

Fig. 5. Ti atoms on (111)_{TiN} crystallographic planes which are arranged on (011)_{Si-steel} crystallographic planes of (011)[100] single crystal of silicon steel.

Table 1. JCPDS of TiN and α -Fe and marks of poles in pole figures of TiN and α -Fe.

TiN (38-1420)*				α -Fe (06-0696)*			
d(Å)	Int.	hkl	Mark**	d(Å)	Int.	hkl	Mark**
2.4492	72	111	▲	2.0268	100	110	○
2.1207	100	200	■	1.4332	20	200	□
1.4997	45	220	●	1.1702	30	211	
1.2789	19	311		1.0134	10	220	

* JCPDS

** Notation of poles in pole figures

the texture formation in the TiN-coated area is in good agreement with that of Fig. 2, where the peak shape of conjugated peaks of two (200) poles of silicon steel and two (220) poles of the TiN films manifests an elliptical shape.

4. Discussion

4.1. Preferential Formation of Thin Films TiN-coated on the Surface of (011)[100] Single Crystal of Silicon Steel

In past study, thin-film X-ray diffraction measurement was mainly used to identify the structure and preferential formation of TiN.⁹⁾ The texture formation and its orientation relative to the dual structure of the TiN films and iron matrix were not investigated because simultaneous measurement by X-ray diffraction would have been required. It should be emphasized that, in the present experiment, both pole figures of the TiN films and of the

iron matrix were obtained by simultaneous measurement of the TiN films and iron matrix by X-ray diffraction in the same sample. Strong strength of TiN in the X-ray diffraction measurement was detected from the epitaxial growth of TiN vapor-deposited on the surface of the (011)[100] single crystals of the silicon steel samples. In particular, because plasma coating of TiN by the HCD method produces a stronger (111) peak⁹⁾ than other plasma coating methods, it should be noted that the pole figures of TiN in Figs. 2 and 3 showed a distinctive texture formation with a strong (111) peak of TiN. It is also considered that the strong texture formation of (111)_{TiN} on the surface of a (011)[100] single crystal of silicon steel by HCD method can be achieved due to plasma coating at a high ionization rate of 43%¹⁰⁾ using a low voltage (40 V) and large current (500 A), and is known to give a fine and smooth TiN films with good adhesion. This is also supported by the fact that ion plating by the EB + RF method shows a lower ionization of 6%,¹⁰⁾ and their TiN films produces comparatively strong (200), (111), and (220) peaks, and weak (311) and (222) peaks.

4.2. Orientation Relationship between TiN Films and (011)[100] Single Crystal

TiN has a NaCl structure having a lattice constant of 4.24 Å, where Ti and N atoms are arranged alternately. In plasma coating of TiN by this HCD method, it is considered that the TiN films can obtain nearly Ti/N = 1 from the measurement of atomic percent by EPMA.⁹⁾ Also, from the present experimental results of the texture formation of the TiN films, it is evident that the dominant texture of (111)_{TiN} formed preferentially on the surface of a (011)[100] single crystal of silicon steel. In the atomic arrangement of the (111) crystallographic plane of TiN, the layers of Ti and N atoms are formed alternately.

When the (111)_{TiN} pole figure of the TiN films and the (100)_{Si-steel} pole figure of the (011)[100] single crystal of the silicon steel sample were measured simultaneously, it is considered that the orientation relationship between the (111) crystallographic plane of the TiN and the (110) single crystal of the silicon steel can be expressed as: $(1\bar{1}1)_{\text{TiN}} // (011)_{\text{Si-steel}}, [110]_{\text{TiN}} // [100]_{\text{Si-steel}}$.

Figure 5 shows schematic Ti and Fe atoms of $(1\bar{1}1)_{\text{TiN}}$ and $(011)_{\text{Si-steel}}$ crystallographic planes. The misfit from

the ideal geometric orientation relationship is 4.5 %, where the $[110]_{\text{TiN}}$ direction of the $(1\bar{1}1)_{\text{TiN}}$ plane is 0.299 nm and the $[100]_{\text{Si-steel}}$ direction of the $(011)_{\text{Si-steel}}$ plane is 0.286 nm.

It should be noted that the TiN films deposited onto the surface of (011)[100] single crystal of silicon steel showed very good misfit within several percents, in which the difference of the thermal expansion coefficients of the ceramic TiN films and silicon steel sheet, after cooling from 700°C (plasma coating temperature) to room temperature, strongly tensions the near-surface of the TiN-coated silicon steel sheet.

5. Conclusion

Pole figures of the TiN films and the related (011)[100] single crystal of silicon steel sheet samples were measured simultaneously using the SSD auto pole figure method. The following results were obtained.

- (1) TiN showed a very distinct $(1\bar{1}1)[110]$ texture, and that of the single crystal showed a $(011)[100]$ texture.
- (2) The orientation relationship between the TiN film and silicon steel substrate is considered to be expressed as: $(1\bar{1}1)_{\text{TiN}} // (011)_{\text{Si-steel}}, [110]_{\text{TiN}} // [100]_{\text{Si-steel}}$.
- (3) The TiN films deposited onto the surface of (011)[100] single crystal of silicon steel showed very good misfit within several percent.

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