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# Application of CVD method on grain-oriented electrical steel

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**Abstract**

Application of CVD method on grain-oriented electrical steel has been studied. Iron loss of grain-oriented electrical steel can be improved by thermal residual stress based on difference in thermal expansion between ceramic coating and steel substrate. Tensile stress on steel sheet enhances easy magnetization in the rolling direction. Required properties for the ceramic film are low thermal expansion, high elastic modulus and good adhesion, and nitride or carbide films are favorable from this point. For this purpose, TiN was deposited from a gas mixture of $TiCl_4$, $H_2$ and $N_2$ using thermal CVD process at atmospheric pressure. $TiCl_4$ was introduced into the reactor chamber by using $H_2$ as a carrier gas. The deposition behavior of TiN was well explained by Langmuir–Hishelwood model taking the effect of HCl formation into account. High temperature deposition of TiN brought about strong tensile stress and achieved the extremely low iron loss. Deposition thickness of 1 μm was sufficient to keep superior adhesion and magnetic properties after stress relief annealing, 1073 K, 3 h in $N_2$ atmosphere.


*Keywords:* Grain-oriented electrical steel; Iron loss; CVD; Thermal residual stress

## 1. Introduction

Grain-oriented electrical steel is mainly used for core material in transformers and other electrical machinery and equipment. It is 3%Si–Fe polycrystalline material with near (110)[001] orientations and shows very low core loss in the rolling direction.

It is well known that application of tensile stress to the electrical steel sheet is effective for reducing iron loss [1]. When the thermal expansion coefficient of the surface film formed at high temperature is lower than that of the steel sheet, a tension is given to the steel sheet during the cooling process owing to the difference in contraction between the steel and the surface film. Insulation coating with low thermal expansion coefficient have therefore been developed and applied for grain-oriented electrical steel [2].

Thermal residual stress was formulated by Moses et al. [3]. In the case that the coating is thinner than steel sheet, it is simplified as follows,

$$\sigma_m = \frac{2A_c E_c(\alpha_m - \alpha_c)\Delta T}{A_m} \tag{1}$$

where $\alpha_m$ and $\alpha_c$ are the thermal expansion coefficient with m and c denoting for steel substrate and coating respectively, $A_m$ and $A_c$ are cross sectional area. $E_c$ is the average value of Young's modulus over the cooling range. Carbides or nitrides with high Young's moduli and low thermal expansion coefficient as a coating film have been investigated by ion plating on polished electrical steel sheet [4].

Since the effect of surface morphology on magnetic properties is large, smoother surface is desired when the tension coating is applied [5].

In this paper, application of titanium compound coating by thermal CVD on grain-oriented electrical steel has been studied.

## 2. Experimental details

The sheet samples were prepared from products of 0.23 mm thick grain-oriented electrical steel sheet, cut down to a size of 280 × 30 mm, and strain-relief annealed for 7.2 ks at 1073 K. The size of the specimens was chosen in accordance with the standard for single sheet tester (SST), which is usually applied for magnetic measurements. The magnetic properties are expressed by the iron loss at 1.7 T, 50 Hz: W17/50 (W/kg).

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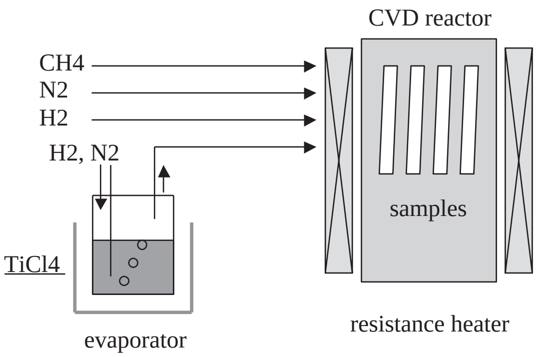


Fig. 1. Schematic diagram of CVD apparatus.

The conventional insulation coating of the electrical steel sheets was removed by dipping the sheet in a NaOH solution, and then the oxide film was removed by dipping them in an HCl solution. Finally the surface of sheet samples was chemically polished by dipping them in a HF–$H_2O_2$ solution.

The apparatus for thermal CVD is shown in Fig. 1. Four sample sheets were simultaneously processed in a vertical Inconel reactor heated to 1173–1423 K by an electric resistance heater.

TiN was deposited from a $TiCl_4$–$N_2$–$H_2$ gas mixture and TiC was deposited from a $TiCl_4$–$CH_4$–$H_2$ gas mixture for 1 to 10 min. The saturation temperature of $TiCl_4$ was 333–368 K. $TiCl_4$ was introduced into the reactor by using $H_2$ as a carrier gas.

The surface microstructure and texture of the deposited film were investigated using SEM. The film thickness was determined by the cross sectional observation. The crystallographic orientation of the film was examined using EBSP (electron back scattering diffraction patterns).

## 3. Results

### 3.1. Magnetic properties

The iron loss W17/50 measured in the sample sheets with TiN film are shown in Fig. 2. The value of W17/50 decreased with increasing TiN film thickness. It is considered that the decrease of the iron loss value is caused by the thermal residual stress based on difference in thermal expansion between TiN film and steel sheet. The amount of tensile stress by TiN film was calculated from the curvature of the substrate steel sheet with TiN only on one of the two sides. It was verified to be almost equivalent to the value estimated from Eq. (1).

The Iron loss consists of hysteresis loss (Wh) and eddy current loss (We). The former depends on crystal orientation, amount of impurities and surface and interfacial roughness, and the latter depends on sheet thickness, electrical resistivity and magnetic domain wall displacement. Fig. 3 shows a typical change in iron loss with successive process of TiC deposition, which showed similar tendency with TiN.

It should be noted that Wh hardly changed and We was reduced greatly by CVD treatment. When TiC is deposited on chemical polished surface, the smoothness was kept unchanged while strong tensile stress was applied on the steel sheet effectively. Neither insulation coating nor strain-relief annealing gave adverse effects. After strain-relief annealing, the adhesion of TiC was improved.

### 3.2. Deposition behavior

Fig. 4 shows the effects of the $TiCl_4$ and $N_2$ concentrations on the deposition rate of TiN. The balance was $H_2$. Deposition rate of TiN showed a maximum at a certain gas composition and started to decrease with excessive supply of $TiCl_4$ or $N_2$ gas. The deposition rate reached a maximum when $N_2/TiCl_4$ ratio approached 30. The chemical composition of TiN maintained stoichiometry regardless of the gas mixture condition.

With increasing deposition temperature, deposition rate increased. Activation energy obtained from the Arrhenius plot is 39.7 kcal/mol, which is slightly larger than previous studies [6,7].

### 3.3. Morphology

In the initial stage of TiC deposition, heteroepitaxial growth on grain-oriented electrical steel was observed as shown in Fig. 5. Sample sheet can be almost regarded as a single crystal with (110) surface. As a result of examining the relationship between the two crystal orientations by EBSP, TiC (111)[110]//3%Si–Fe (110)[001] relation was found as shown schematically in Fig. 6. The length of 15 times of the lattice spacing in [001] direction on 3%Si–Fe (110) is nearly equal to 7 times that in [110] on TiC (111). The length of 4 times of [110] lattice spacing on 3%Si–Fe is close to 3 times that in [112] on TiC. While in the case

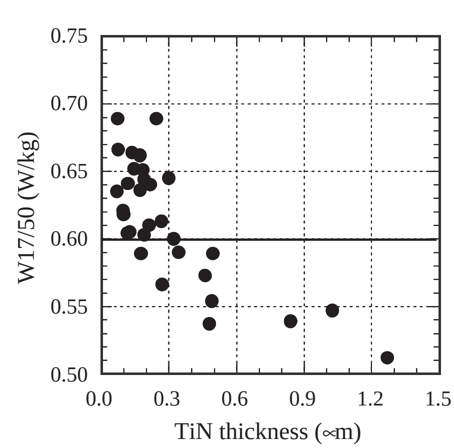


Fig. 2. Effect of TiN thickness on iron loss W17/50.