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Nitridation of the sol–gel derived TiO_2 coating films and the infrared ray reflection

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The titanium nitride coating film was prepared on the SiO_2 glass substrate by ammonolysis of titanium dioxide coating film formed by sol–gel method. The X-ray diffraction (XRD) pattern indicated that it is cubic titanium nitride with a lattice parameter, a_0, of 0.4231 nm. The obtained titanium nitride is non-stoichiometric (TiN_x $x \leq 1$) because the value, 0.4231 nm, is smaller than the stoichiometric one (0.4240 nm). The coating film show very high infrared (i.r.) reflectance in the wavelength region of 2–8 μm.

1. Introduction

In recent years, much attention has been paid to the high functional thin film. A large number of research and development on ceramic coating films has been carried out, for example, for transparent electrode (solar cell) [1], photo-electrochemical film [2], high temperature superconductor [3, 4], hybrid film [5], etc. The preparation methods of ceramics thin film are divided into two categories. One is vapour phase reaction, such as CVD and PVD. The other is liquid phase reaction, such as the sol–gel method [6–8].

The sol–gel method is one of the newer methods for synthesizing fine ceramics materials. A lot of investigations has been carried out on ceramics coating by this method [6–8]. This process consists of the hydrolysis of an alcoholic-metal-alkoxide solution. Coating sol is easily prepared by controlling hydrolysis the conditions. The obtained coating film is very porous, and easily changes to the nitride by heating in ammonia gas atmosphere (ammonolysis) [9, 10].

Nitride ceramics have become increasingly interesting because of their high chemical durability, high melting temperature and extreme hardness. Titanium oxide (TiO_2) has been widely used as a coating film, for example on halogen lamp as energy-saving film [11], the titanium nitride film has only been used as a protective film due to their excellent mechanical properties. However, the excellent physical properties should also be used, for example, in the field of heat wave reflector.

In the present study, the technique of ammonolysis of sol–gel derived TiO_2 coating film was applied to the fabrication of titanium nitride coating films. In addition, the heat wave reflective properties were investigated.

2. Experimental procedure

2.1. Preparation of TiO_2 coating films

Titanium tetraisopropoxide, $Ti(O\text{–}iC_3H_7)_4$ (Wako Chemical Co.) was used as a starting material. Diethanolamine (DEA) as a stabilizing agent [12] for hydrolysis, was first diluted with half of the prescribed amount of C_2H_5OH (99.5%), then the titanium tetraisopropoxide (TTIP) was added to this solution. After 0.5 h the mixture of H_2O and remaining C_2H_5OH was added drop-wise to the solution while stirring. The amount of each chemical in the present study was TTIP : H_2O : C_2H_5OH : DEA = 1 : 3 : 5 : 1 in the molar ratio. The solution was aged for 3 h at room temperature to complete the hydrolysis of TTIP. Fig. 1 shows the flow chart of the preparation procedure of TiO_2 coating sol.

The TiO_2 sol thus obtained was coated on the SiO_2 glass substrate using a dip-coating technique [13, 14]. The substrate was thoroughly cleaned in an ultrasonic vibrator with acetone, and was dipped into the sol and withdrawn vertically at a constant velocity of 0.16 mm s^{-1}. After drying for 5 min in air, the coated substrate was heated at 500 °C for 10 min in air. Viscosity of coating sol was measured by a B-type viscometer (Tokyo Keiki Co.), and the thickness was determined with a profilometer (TENCOR Co.).

2.2. Nitridation of TiO_2 coating films

The TiO_2 coating films were nitrided in a flow of NH_3 gas. A heating schedule is shown in Fig. 2. After a silica reaction tube was filled with N_2 gas, the TiO_2 coating films were heated up to 1100 °C at a heating rate of 5 °C min^{-1} in a flow of NH_3 gas, and kept for 5 h. The sample was then furnace cooled in a flow of N_2 gas. The film was characterized by X-ray diffraction.

2.3. Measurement of i.r. reflection

I.r. reflectance of ammonolysis products was measured by Infrared Spectrophotometer (Simazu Co.) in the wavelength region of 2–20 μm. Evaporated aluminium film was used as a standard.

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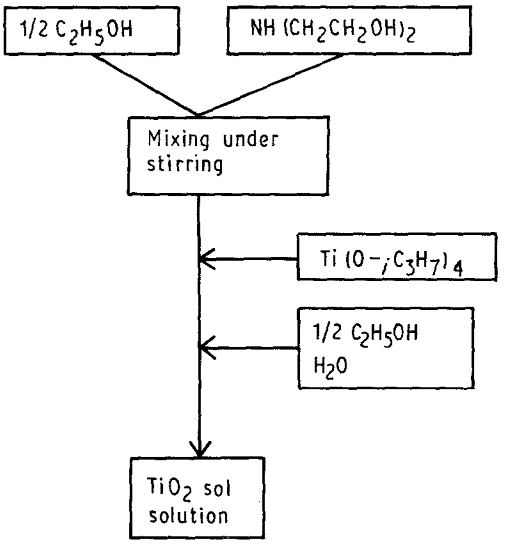

Figure 1 Schematic diagram for preparation of a coating sol solution.

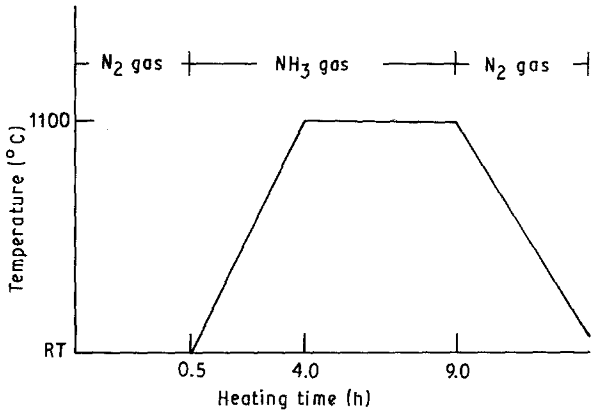

Figure 2 Heating schedule of coating film.

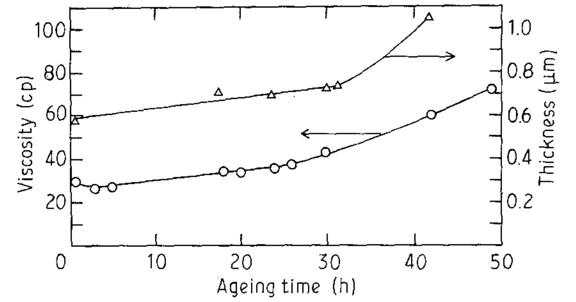

Figure 3 Relation of the thickness of coating film and viscosity of sol with ageing time.

3. Results and discussion

3.1 Effect of ageing time on viscosity and thickness

The TiO_2 sol solution was aged in air at room temperature. Fig. 3 shows the relation between the viscosity of sol solution and ageing time. The viscosity slightly increases with ageing time until 30 h, and from sol of this range the homogeneous coating films were prepared. After 30 h, the viscosity increases rapidly, and film obtained from this sol showed a number of cracking.

In Fig. 3, the variation of film thickness prepared by single process with ageing time is also shown. The thickness increases with the increasing viscosity. The range which the homogeneous film was obtained, was below about 0.6 μm. The film of more than 0.6 μm was not homogeneous because of the cracks.

From these results, ageing time of the sol of 3 h was adapted in this study, because this sol showed the smallest viscosity, thus it was most suitable for coating.

3.2. Characterization of ammonolysis products

3.2.1. X-ray diffraction

The X-ray diffraction pattern of the titanium nitride film obtained is shown in Fig. 4. The titanium nitride prepared by ammonolysis shows cubic symmetry with lattice parameter, a_0, of 0.4231 (1) nm which is smaller than the value of stoichiometric titanium nitride (0.4240 nm) [ASTM 6–642]. This means that the obtained titanium nitride film is non-stoichiometric with the composition TiN_x $x \leq 1$. The same phenomenon has been reported by Kamiya *et al.* for the ammonolysis products of sol–gel derived TiO_2 coating films on Al_2O_3 substrate [13].

3.2.2. I.r. reflection

The i.r. reflection pattern of the obtained TiN_x coating film is shown in Fig. 5. It can be seen that this film shows very high i.r. reflectance in the wavelength

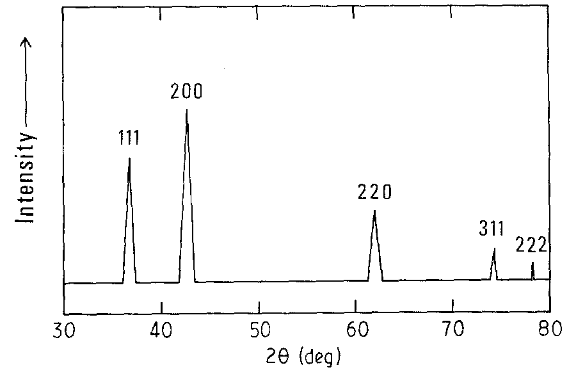

Figure 4 X-ray diffraction pattern of ammonolysis product.

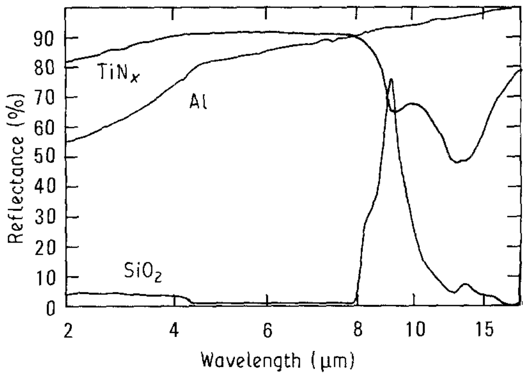

Figure 5 I.r. reflection pattern of obtained TiN_x coating film.

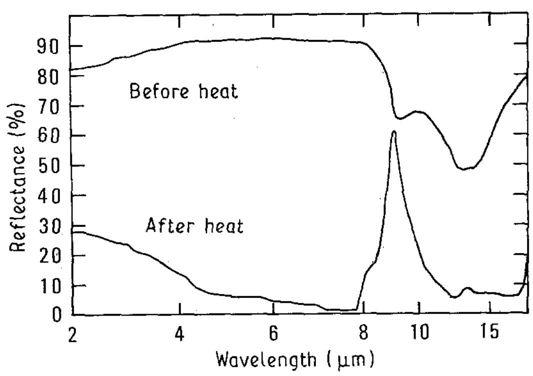

Figure 6 I.r. reflections of TiN_x coating films before and after heat treatment.

region of 2–8 μm, this range is much higher than the value of commercial aluminium plate. In Fig. 6 the i.r. reflectance of heated TiN_x coating film is shown (800 °C, 10 min in air), the intensity of which is much smaller than the non-heated TiN_x coating film in all the wavelength regions studied.

4. Conclusion

4.1. Nitridation process of TiO_2 coating films

The nitridation of the sol–gel derived TiO_2 coating films may be proceeded by the reaction of NH_3 with reduced TiO_2 as shown below [9].

$$NH_3 \rightarrow 1/2\,N_2 + 3/2\,H_2 \qquad (1)$$

$$2TiO_2 + H_2 \rightarrow Ti_2O_3 + H_2O \qquad (2)$$

$$TiO_2 + H_2 \rightarrow TiO + H_2O \qquad (2)$$

$$Ti_2O_3 + NH_3 \rightarrow 2TiN + 3H_2O \qquad (3)$$

$$2TiO + 2NH_3 \rightarrow 2TiN + 2H_2O + H_2 \qquad (3)$$

In this study, the coating film was coloured black after heat treatment at 500 °C, which may be due to the carbon remaining from DEA. It can be assumed that the residual carbon in the TiO_2 film may act as a catalyst for the nitridation. TiO_2 is also reduced by carbon through the reaction (2′) as follows. It may proceed simultaneously with reaction (2).

$$TiO_2 + C(CO) \rightarrow TiO + CO(CO_2) \qquad (2')$$

$$2TiO_2 + C(CO) \rightarrow Ti_2O_3 + CO(CO_2) \qquad (2')$$

4.2. I.r. reflection property of TiN_x coating film

TiN_x coating film show very high i.r. reflectance, especially in the wavelength region of 2–8 μm. Consequently, TiN_x coating film is a promising material as an i.r. reflector. However, TiN_x coating film was sensitive to air at high temperature (above 500 °C), and gradually transformed to TiO_2 [14]. Oxidation of TiN_x decreased the i.r. reflectance, equivalent to the SiO_2 glass (see Figs. 5 and 6). To maintain the good reflectance properties of TiN_x, preventative treatments for oxidation will be required, such as SiO_2 coating or other composite materials.

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