

Chemical vapour deposition of corrosion-resistant TiN film to the inner walls of long steel tubes

HIDEAKI ITOH, KAICHIRO KATO, KOHZO SUGIYAMA

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464, Japan

A uniform TiN film was coated on to the inner walls of long steel tubes by moving a chemical vapour deposition furnace along the tubes. The moving direction of the furnace from outlet side to inlet side gave a more homogeneous coating than the reverse moving direction. The TiN-coated steel tube (inside diameter 10 mm) was obtained under the following conditions; peak deposition temperature 1050°C, total flow rate of reactant gas ($\text{TiCl}_4 + \text{N}_2 + \text{H}_2$) $\sim 6.0 \text{ ml sec}^{-1}$, moving velocity of the furnace 2.8 mm min^{-1} . The inner wall of the coated tube showed high corrosion resistance for dipping in 6N HCl aqueous solution for 17 h.

1. Introduction

Corrosion-resistant ceramic coating to the inner walls of long tubes is one of the most promising techniques to give an economical corrosion-resistant tube. Titanium nitride (TiN) is a coating material which is highly resistant to corrosion by strong acids. It is known that TiN can be coated on many kinds of steel substrates by chemical vapour deposition (CVD) at temperatures higher than 950°C. However, a uniform coating with constant film thickness along the axial direction of a long tube is rather difficult to obtain, because the film thickness decreases (usually exponentially) with increasing axial distance x from the inlet of the reactant gas [1, 2]. In fact, we confirmed that the film thickness and texture of the deposit change from place to place, and they varied also as a function of total gas stream velocity [3].

In the present study, uniform coating of TiN to the inner walls of long steel tubes was performed using a CVD furnace which moved with a constant velocity along the axial direction of a steel tube. This paper relates the deposition conditions of TiN, the film thickness distribution and the film structure, as well as the corrosion resistance of the coated specimens.

2. Experimental procedure

Fig. 1 shows the flow system of the CVD apparatus. The reactant gas mixture for deposition of TiN is composed of TiCl_4 , N_2 and H_2 . H_2 gas was purified by permeation through palladium film, while N_2 gas was deoxygenated by activated copper and dehydrated by concentrated H_2SO_4 and P_2O_5 . TiCl_4 vapour was saturated in the H_2 gas at a given temperature (30 to 70°C) and was carried to the deposition zone of the furnace. In order to prevent oxidation of the outer wall of the steel tube, argon gas (flow rate 5 ml sec^{-1}) was flowed into the clearance between the outer face of the steel tube and the inner face of the quartz sleeve in the furnace. A bypass for argon inert gas or reactant gas

was set, so that a steady flow of the reactant gas could easily be switched from the bypass to the main tube at the start of the TiN deposition run.

The equipment of the moving CVD furnace is illustrated in Fig. 2. A small furnace on a track was moved along rails of 100 cm length, which were inclined at 2.7°. A substrate steel tube was inserted into the furnace, which was pulled up or released by a low-speed motor at a given velocity (0.25 to 1.0 cm min^{-1}) via a molybdenum wire. A weight of 400 g connected to the other end of the track helped to stabilize the furnace movement.

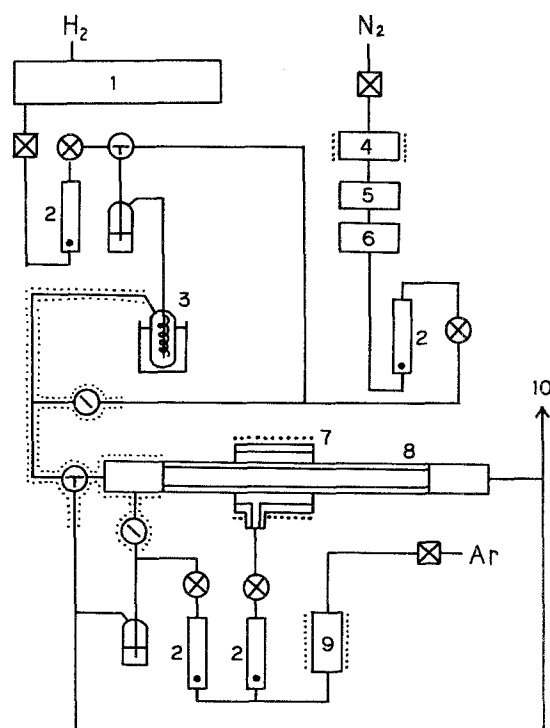


Figure 1 Flow system of the experimental apparatus: (1) hydrogen purifier, (2) flow meter, (3) TiCl_4 saturator, (4) activated copper, (5) conc. H_2SO_4 , (6) P_2O_5 , (7) movable CVD furnace, (8) steel tube, (9) titanium sponge, (10) exhaust.

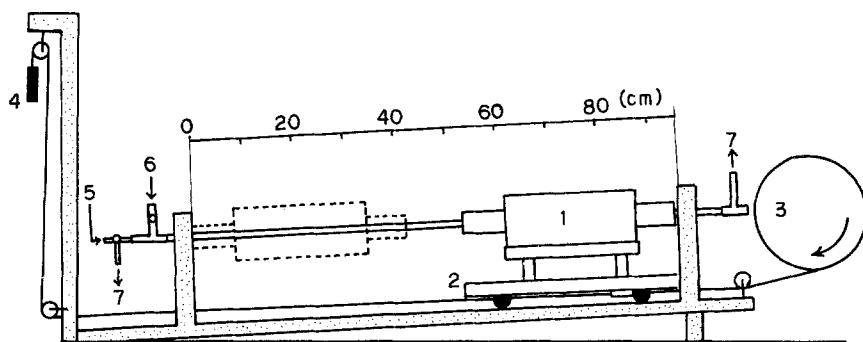


Figure 2 Equipment for moving the CVD furnace: (1) CVD furnace, (2) track, (3) motor, (4) weight, (5) reactant gas mixture ($\text{TiCl}_4 + \text{N}_2 + \text{H}_2$), (6) argon, (7) exhaust.

Low-carbon steel tube (STS-35: $C \leq 0.25\%$) was used as the substrate tube, the inside and the outside diameters of which were 10 and 12 mm, respectively. Prior to a coating experiment, the tube was soaked in an ultrasonic cleaner bath (containing 0.1N HCl aqueous solution) for 50 min to remove the rust. The tube was then washed with water and ethyl alcohol, after which it was set on the CVD equipment and was dried at 200 to 250°C by moving the furnace in an argon atmosphere.

3. Results and discussion

3.1. Deposition conditions of TiN films

The temperature profile in the CVD furnace is shown in Fig. 3, where the furnace is kept stationary at the peak temperature of 1050°C. The temperature distributes along the length. The central region with a length of about 12 cm corresponds to the deposition zone of TiN, which is above 950°C in the furnace. The peak temperature of 1050°C is considered to be optimum for this type of moving CVD furnace to deposit a fine-grained TiN. Table I shows the influences of total flow rates and TiCl_4 concentrations on the thickness of TiN film, where the flow rate ratio of N_2/H_2 was kept constant at unity. It was found by preliminary experiments that the moving rate (0.28 to 0.36 cm min^{-1}) of the furnace had only a minor influence on the film thickness distribution or the TiN texture, while the moving direction affected greatly the deposition behaviour of TiN as described below.

3.2. Film thickness distribution

To evaluate the uniformity of the film thickness along the axial direction, the thickness of the deposited TiN film at each position was measured by optical microscopy and the film thickness distribution profile was

plotted. Fig. 3 shows the profile in the case of using a stationary furnace, when the linear flow velocity of the total reaction gas is 32 cm sec^{-1} (at an average temperature of 1000°C) and the deposition reaction time is 90 min. The curve shows a typical film thickness distribution for a stationary furnace. A maximum thickness can be seen at the inlet side of the reaction gas, where the temperature is rising up to the peak; the curve then has a shoulder near the central part of the furnace, and decreases gradually at the outlet side ($x > 22 \text{ cm}$) of the furnace.

Fig. 4 shows the film thickness distribution profile, when the furnace was moved from the inlet to the outlet side at a velocity of 2.8 mm min^{-1} . The deposition conditions are as follows; peak temperature 1050°C; flow rates N_2 3.0 ml sec^{-1} , H_2 3.0 ml sec^{-1} , TiCl_4 0.03 ml sec^{-1} (0.99%); moving distance of the furnace 52.5 cm; total deposition run time 189 min. The temperature distribution profiles at the start and finish are also shown. According to this figure, the TiN film thickness increases abruptly at the axial position $x = 15 \text{ cm}$, and then proceeds to the maximum value of 11.5 μm at $x = 30 \text{ cm}$. As the furnace moves, the film thickness decreases to about 9 μm and has a rather constant value at $45 \text{ cm} \lesssim x \lesssim 70 \text{ cm}$.

Fig. 5 shows the film thickness distribution profile when the furnace was moved from the outlet to the inlet side. The deposition conditions and the furnace moving conditions were the same as in Fig. 5 for the plots indicated by circles, whereas the plots indicated by triangles (moving velocity 3.6 mm min^{-1}) were obtained under the following conditions; peak temperature 1050°C; flow rates N_2 2.5 ml sec^{-1} , H_2 2.5 ml sec^{-1} , TiCl_4 0.05 ml sec^{-1} (0.99%); moving distance 53 cm; total deposition run time 148 min. The figure indicates that the distribution curve is trapezoid-

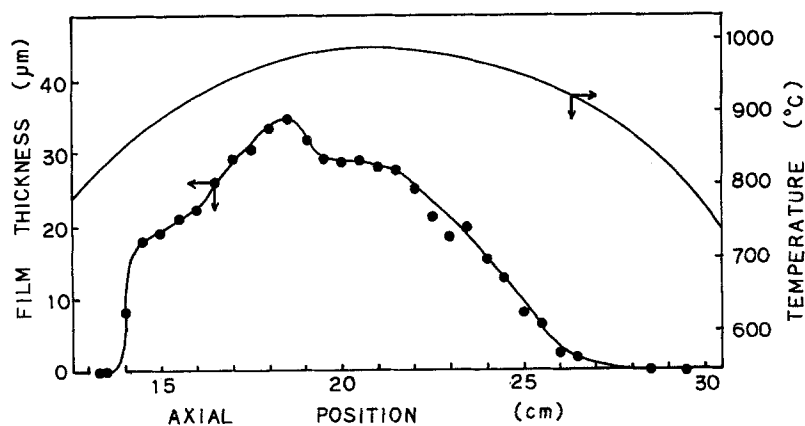


Figure 3 Temperature profile and film thickness distribution using stationary CVD furnace; reaction time 90 min, total gas velocity 32 cm sec^{-1} .

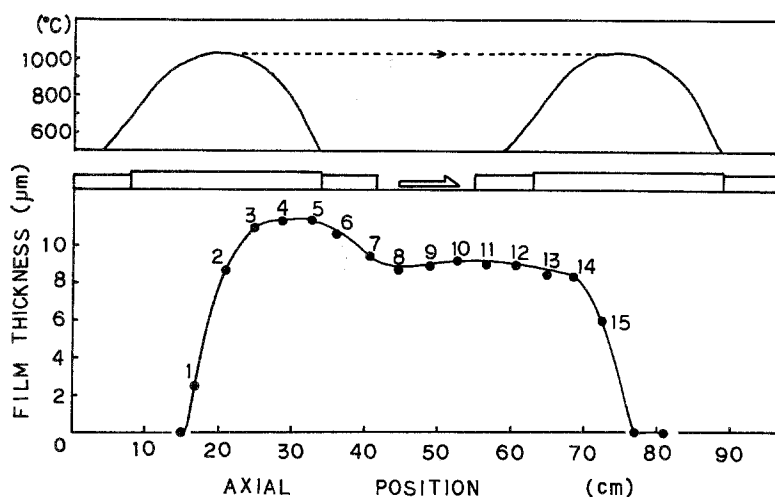
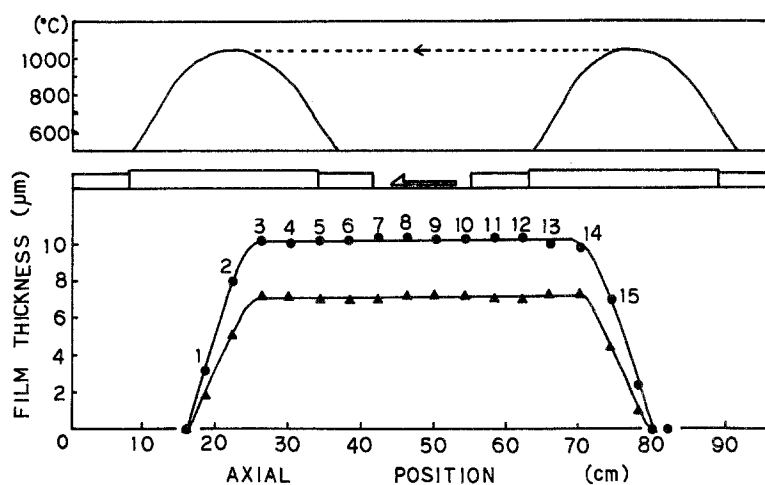


Figure 4 Film thickness distribution profile along the axial direction. Moving direction of CVD furnace: from inlet side to outlet side, moving velocity 2.8 mm min^{-1} , total deposition run time 189 min.

Figure 5 Film thickness distribution profile along the axial direction. Moving direction of CVD furnace: from outlet side to inlet side, moving velocity (●) 2.8 mm min^{-1} , (▲) 3.6 mm min^{-1} .



shaped and the film thickness is highly uniform in a long range of the deposited tube, except for the steep increase or decrease in thickness on the inlet or outlet side, respectively.

3.3. Film texture and adherence

Identification of the deposits and the crystallographic features of the TiN film were investigated by X-ray diffraction. Fig. 6 shows X-ray diffraction patterns of the deposits taken from various parts of the inner wall, in the case of using a stationary furnace. Comparing Figs. 3 and 6, the (220) preferred orientation is confirmed at the substrate position $15 \text{ cm} < x < 20 \text{ cm}$. The X-ray patterns with low preferred orientations were obtained at the inlet side (Fig. 6a) and the outlet side (Figs. 6d and e) of the furnace. A purple film, presumably a lower chloride of titanium, was deposited on the up-stream wall ($9 \text{ cm} < x < 11 \text{ cm}$). However, this film was amorphous and could not be

identified by X-ray diffraction. On the other hand, the deposit on the downstream wall ($34 \text{ cm} < x < 36 \text{ cm}$) was found to be $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ as shown in Fig. 6f.

Scanning electron microscope (SEM) photographs of the TiN film surface are shown in Fig. 7, obtained at various positions of the stationary CVD furnace. Fine blade-like crystallites appear at the position $x = 14.5 \text{ cm}$, where the deposition temperature is as

TABLE I Film thickness (μm) of TiN as a function of total flow rate and TiCl_4 concentration*

Total flow rate (ml sec^{-1})	TiCl_4 (%) and N_2/TiCl_4 (bracketed)		
	0.99 (50.0)	1.48 (33.3)	1.96 (25.0)
4.1	—	7.0	—
5.1	7.0	8.5	9.0
6.1	10.0	10.0	10.5

*Peak temperature 1050°C , moving velocity 3.6 mm min^{-1} .

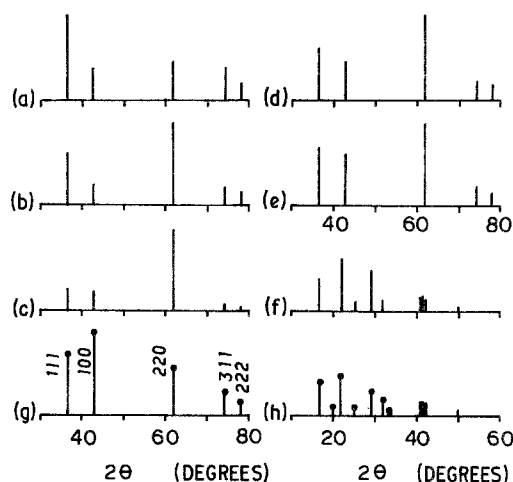


Figure 6 X-ray diffraction patterns ($\text{CuK}\alpha$ radiation) of deposited surfaces in the stationary CVD furnaces. Substrate position (cm): (a) 14.2 to 15.1, (b) 16.4 to 17.3, (c) 18.3 to 19.5, (d) 22.0 to 22.9, (e) 24.3 to 25.2, (f) 34.0 to 36.0, (g) ASTM-TiN, (h) ASTM- $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$.

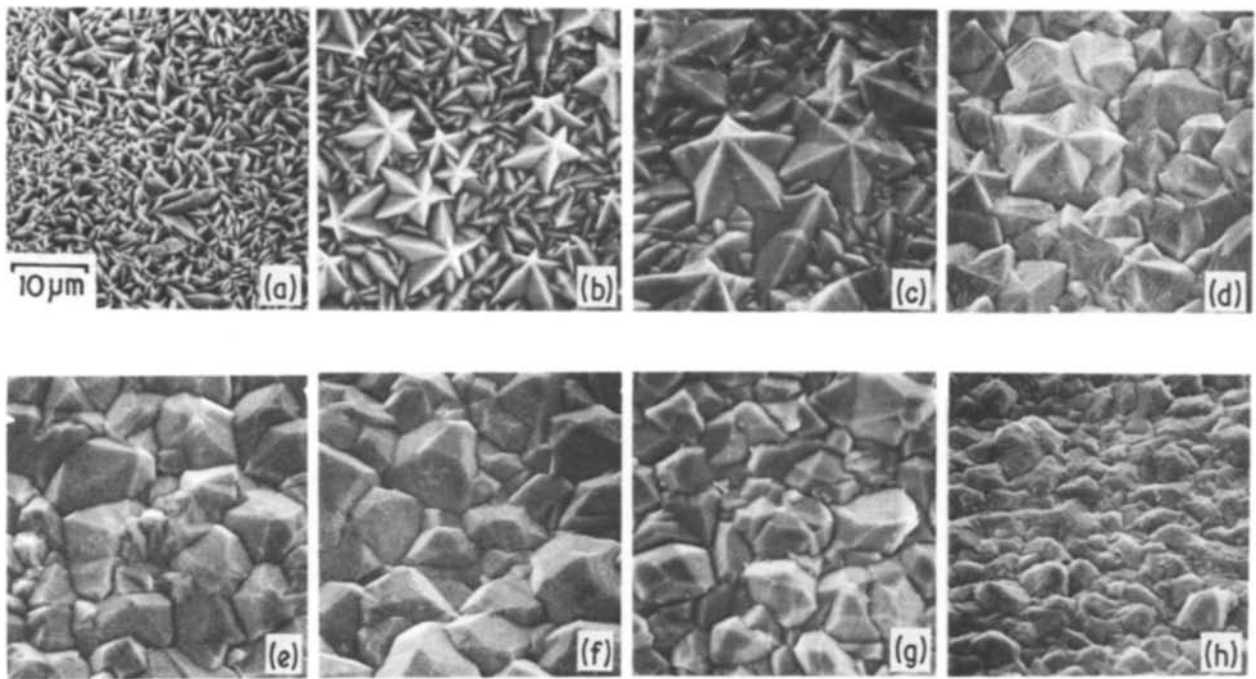


Figure 7 Variation of TiN surface textures in the stationary CVD furnace. Substrate position (cm): (a) 14.5, (b) 15.5, (c) 16.5, (d) 18.0, (e) 20.0, (f) 21.5, (g) 23.5, (h) 25.0.

low as 950°C . Star-like crystallites can be seen at $15\text{ cm} < x < 17\text{ cm}$, and they grow to stonewall-like crystallites at $19\text{ cm} < x < 21.5\text{ cm}$ with their sizes getting smaller as the deposition position shifts to the outlet side.

Fig. 8 shows the textures of the deposits obtained by moving the furnace from the inlet to the outlet (the photograph numbers correspond to those of the deposition positions indicated in Fig. 4). These photographs seem to reflect the history of the texture change by moving the furnace, i.e. the deposits are composed

of stonewall-like deposits on which smaller blade-like crystallites are deposited on their tops (see Fig. 8 ③ and ⑤). However, coarse nodular deposits are found in the downstream region ($40\text{ cm} < x < 70\text{ cm}$), where the film thickness exceeds the maximum value of $12\text{ }\mu\text{m}$ as shown in Fig. 4. These abnormal deposits were obtained when the furnace moved along the steel wall where the $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ had deposited in the downstream region (see Fig. 6). Therefore, the formation of iron chloride was considered to help the development of the nodule-like deposits.

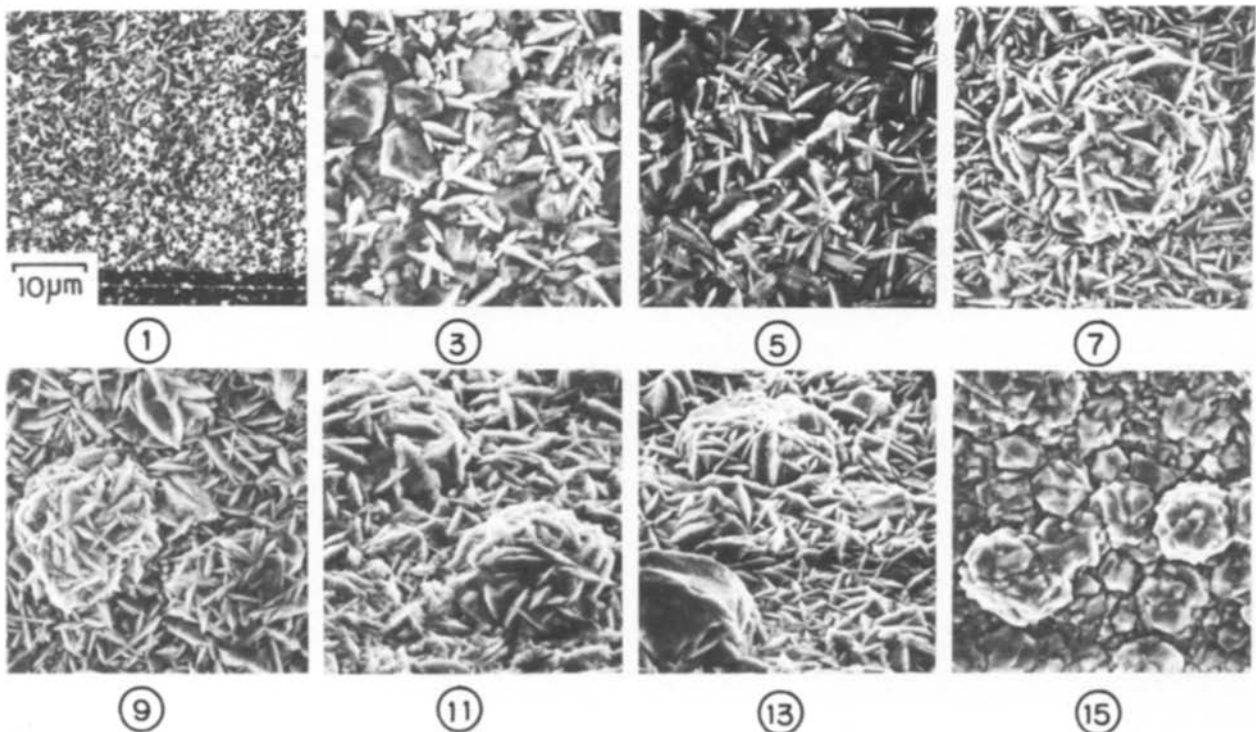


Figure 8 Variation of TiN surface textures along the axial direction. Moving direction of CVD furnace: from inlet side to outlet side. (The number of each photo corresponds to that shown on the curve in Fig. 4.)

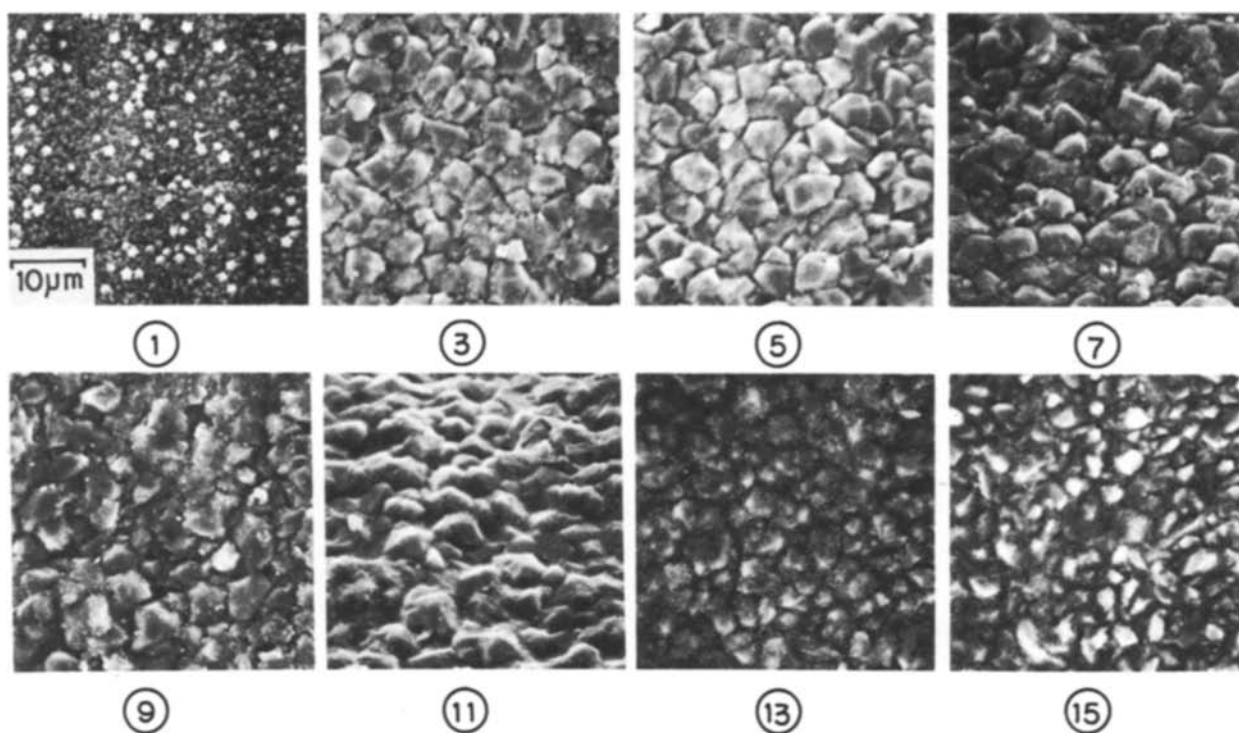


Figure 9 Variation of TiN surface textures along the axial direction. Moving direction of CVD furnace: from outlet side to inlet side. (The number of each photo corresponds to that shown in the curve in Fig. 5.)

Fig. 9 shows the variation of surface texture when the furnace was moved from the outlet to the inlet side. As suggested from Fig. 7, rather homogeneous stonewall-like deposits are seen on most of the top surface. The surface of each grain is not even, however, because very fine deposits grew when the low-temperature zone (900 to 950°C) of the furnace at the outlet side was passing the as-deposited surfaces. It is apparent by comparison of Figs. 8 and 9 that the uniformity of TiN film thickness and texture is better in the case of moving the furnace from outlet to inlet than in the reverse case.

Fig. 10 shows the difference in the cross-sectional textures of the films obtained by the two moving directions. The adherence of the TiN film to the carbon steel substrate was excellent in most of the specimens, except when adherence was prevented by the deposition of lower chlorides such as $TiCl_n$ ($n = 2$ to 3) at a special position on the upper stream where the gas composition for the initial reaction was unfavour-

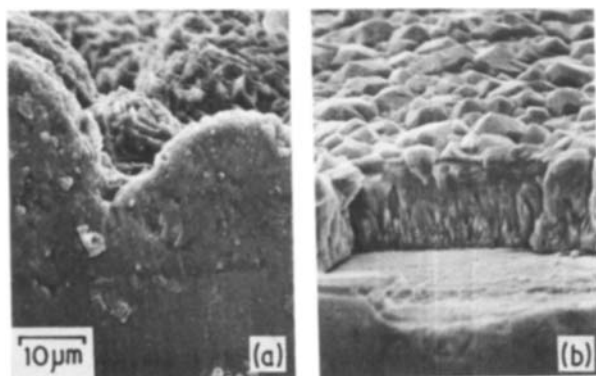


Figure 10 Cross-sectional texture of deposited TiN. Moving direction: (a) from inlet side to outlet side, (b) from outlet side to inlet side.

able. This problem was solved by using the bypass to prepare a steady flow of reactant gas prior to the run.

3.4. Corrosion resistance test in acid solutions

A corrosion resistance test of TiN-coated tubes was carried out using 6N HCl aqueous solution as a corrosion reagent. The test tubes were 5 cm in length, and were cut from a long coated tube. The lower end of each tube was embedded into a vinyl chloride stopper, and fixed with epoxy resin. 3.5 ml of the 6N HCl solution was then poured into each tube, and was left standing for 17 h. Table II shows the summarized results of this test, where the weight changes of specimens at various deposition positions are indicated as well as the blank test result using an uncoated steel tube. It is concluded from the table that the coated tubes have excellent corrosion resistance against acid. The observed minor decreases in weight could be caused by acid cleaning of the adhering dirt on the TiN film surface. If the film contained cracks or pinholes, the steel tube might have been corroded by acid penetration through their boundaries. This verifies the complete coverage of the steel tube inner wall by TiN film. In fact, an analogous test using aqua regia (1:3 $HNO_3:HCl$) also showed no corrosion of the steel

TABLE II Corrosion test result in 6N HCl aqueous solution for 17 h

Axial position (cm)	Specimen length (cm)	Weight loss (mg)
25 to 30	4.9	2
35 to 40	4.9	4
45 to 50	5.1	2
55 to 60	4.9	1
65 to 70	4.7	3
Blank test	5.0	446

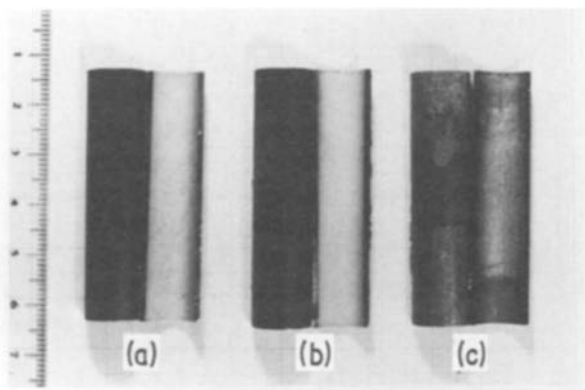


Figure 11 The surface appearance of inner (right) and outer (left) walls of three tubes: (a) coated tube before corrosion test, (b) coated tube after corrosion test, (c) uncoated tube (blank test) after corrosion test.

tube. Fig. 11 shows the surfaces of the inner and outer walls of the tubes, which are the coated specimens before and after the corrosion test, and the uncoated (blank) test specimen.

4. Conclusion

From the series of TiN coating experiments described

above, it is concluded that a uniform film-thickness distribution is available especially when the furnace is moved from the outlet side to the inlet side of a long steel tube. This distribution curve was obtained by the integration of the film-thickness profile of the stationary furnace. The adherence of the film to the steel substrate was excellent, as verified by no observation of cracks or pinholes after the corrosion resistance test in acid solutions. Such a tight coverage is considered to be caused by the fact that the shrinkage of the inner TiN film is less than that of the outer steel tube substrate.

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