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Pulsed chemical vapour infiltration of TiN into a fine silica capillary sealed at one end

K. SUGIYAMA, Y. KURISU
Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-01, Japan

A fused-silica capillary sealed at one end of 1–100 μm inner diameter was used as a substrate, and the thickness distribution of deposits on the inner wall was surveyed using pressure-pulsed chemical vapour infiltration and the source gas system $TiCl_4$–N_2–H_2. All distribution curves had a minimum near the inlet, and had a maximum at a variable depth depending on the deposition temperature. The thickness ratio $L(x)/L(out)$ ($L(x)$ is the thickness of deposit at a depth of x mm from the mouth, $L(out)$ is the thickness on the outer wall of the capillary) varied with deposition temperature, inner diameter of the capillary, length of the capillary and so on. In the case of TiN infiltration, a temperature reduction to 850 °C was effective to infiltrate to a deep zone.

1. Introduction

Among the chemical vapour infiltration (CVI) processes, isothermal CVI [1–3] requires an operation time as long as 300–500 h although the process has the merit of obtaining the same size and shape in the desired products. In contrast, forced CVI [4–6] shortens the operation time to 20–30 h but the shape of preforms is limited to cubic or cylindrical in order to flow through the source gas; expensive mechanical processing is therefore necessary for shaping. In the pressure-pulsed CVI process (pulses CVI) [7–11], sequential steps of evacuation of vessel, instantaneous introduction of source gas, and holding to allow deposition are repeated. By-product gas in the fine pores or clearances is removed during the evacuation step, and fresh source gas is instantaneously put there in the next step. Thickness distribution curves can be roughly estimated by assuming the flow-in speed of gas, temperature changes of gas and inner wall during flowing into the capillary, radial diffusion of reactant and so on [12]. However, precise analysis of the deposition in pulse CVI is very difficult because of the time- and depth-dependent temperature changes of the inner wall and the flow-in gas. In the present paper, the effects of various factors on the deposition profiles are described using fine silica capillaries sealed at one end and TiN as a model deposit.

2. Experimental procedure

Fig. 1 shows the pulse CVI apparatus. In a wire cage hung from the bottom of the inner tube, a fused silica capillary sealed at one end was held. The temperature of the capillary zone was measured by a chromel–alumel thermocouple inserted into the zone. Keeping the temperature of the zone in the range of 850–950 °C, $TiCl_4$ (5%)–N_2 (32%)–H_2 gas was instantaneously introduced into the vessel up to 700 torr, and after 1 s of hold-time the gas was evacuated below 1 torr using a dual evacuation system. These sequential steps were repeated 2000 times; thereafter, the capillary was buried in resin and polished to half-thickness so as to expose the maximum cross-section along the capillary axis. The thickness distribution of the TiN deposit on the inner wall (Fig. 2) and the average thickness of the deposit on the outer surface of the capillary were read from SEM (Hitachi S-510) images of the cross-section.

3. Results and discussion

3.1. Effect of temperature and inner diameter on the thickness distribution

Using capillaries with an inner diameter of 55–67 μm, the effect of deposition temperature on the thickness distribution was surveyed for three levels of temperature, 950, 900 and 850 °C, the thickness distributions of which are shown in Figs 3–5, respectively. In these figures the distribution curves are plotted as thickness ratio versus distance from the capillary mouth; the former is defined as $L(x) \times 100/L(out)$, where $L(x)$ is the thickness of deposit on the inner wall of the capillary at a position x mm from the capillary mouth, and $L(out)$ is the average thickness of the deposit on the outer surface of the capillary. All curves have a minimum near the mouth, and also have a maximum at a variable depth depending on the deposition temperature. The sudden shrinkage of the path of flowing gas at the capillary mouth causes a pressure drop at points near the mouth, and this pressure drop induces the deposition minimum there. Cold gas from a reservoir at room temperature is instantaneously introduced into the reaction vessel, so the temperature of the gas is far below the average temperature of the vessel and the capillary. The gas is heated up to reaction temperature during its flow into the capillary

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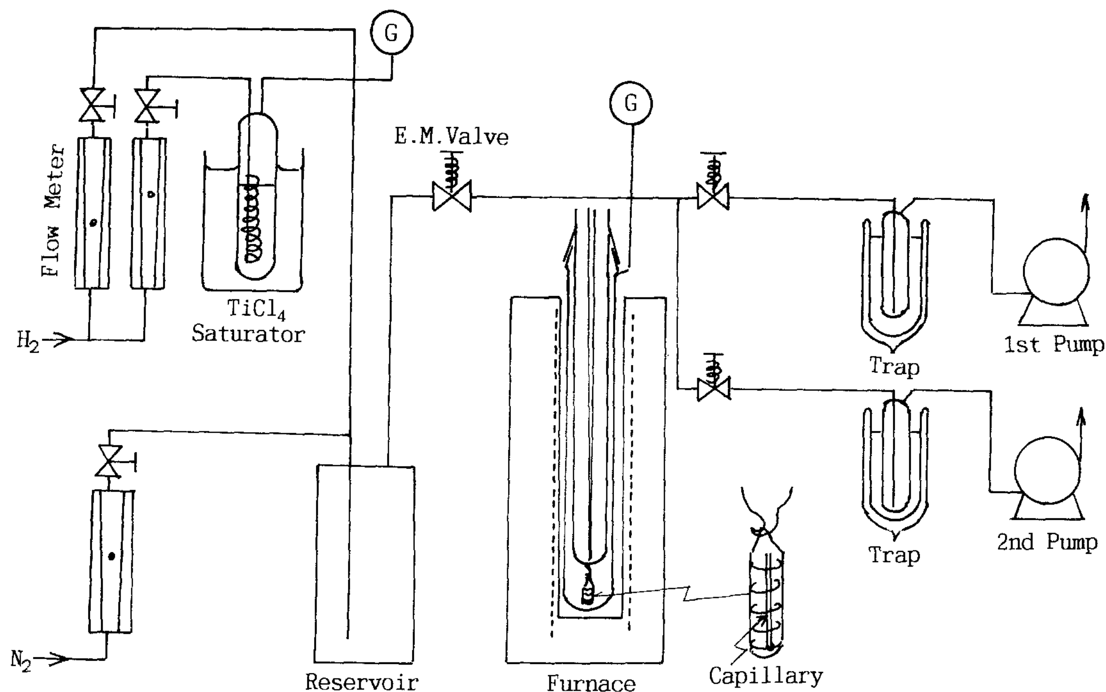

Figure 1 Apparatus for pulse CVI of TiN into a fine silica capillary sealed at one end.

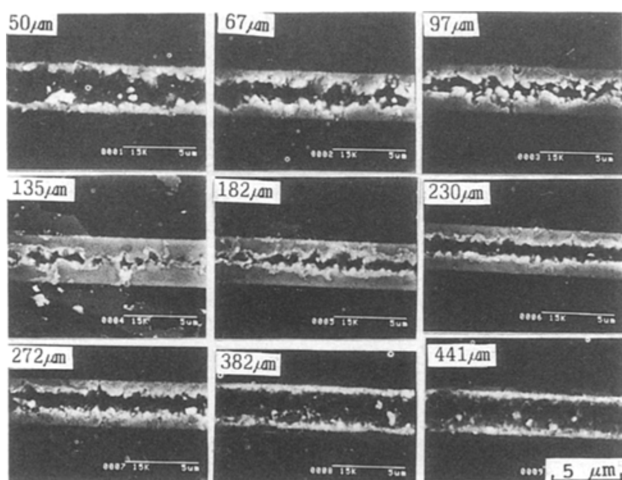

Figure 2 Thickness distribution of TiN deposit (3.3 μm inner diameter). Figures in photos are the depth from the capillary mouth. $TiCl_4$ 4%, 950 °C, 2000 pulses.

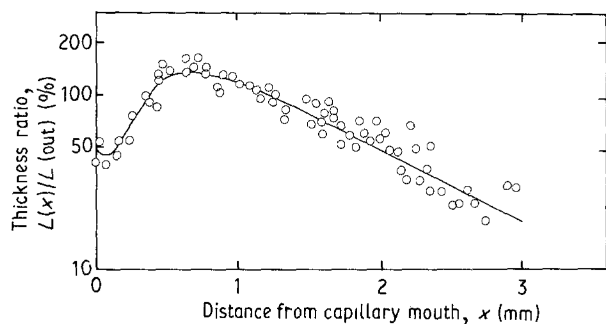

Figure 3 Thickness distribution of TiN deposit; i.d. = 55 μm, capillary length 20 mm, 950 °C, 2000 pulses. $L(x)$ is the thickness of deposit at the depth of x mm, $L(out)$ is the average thickness of deposit on outer surface of capillary.

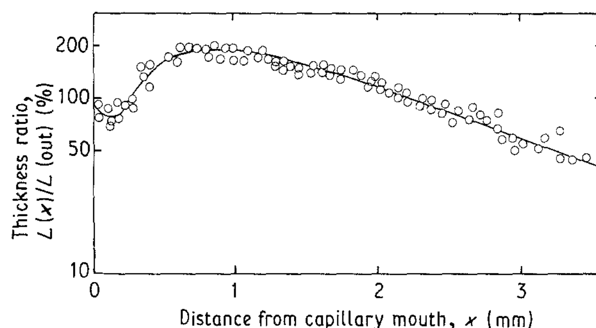

Figure 4 Thickness distribution of TiN deposit; i.d. = 55 μm, capillary length 20 mm, 900 °C, 2000 pulses.

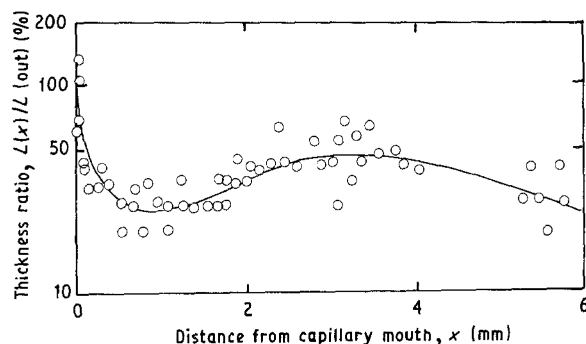

Figure 5 Thickness distribution of TiN deposit; i.d. = 67 μm, capillary length 20 mm, 850 °C, 2000 pulses.

so that a deposition maximum may be formed at some depth from the capillary mouth. Recently Nakanishi *et al.* [13] have reported on the reaction kinetics of TiN from the same gas system as that in the present paper, in which they determined an activation energy change from 102 to 50 kJ mol^{-1} in the temperature range 880–900 °C. The very slow deposition rate at

850 °C (Fig. 5) compared with those at 900 or 950 °C (Fig. 3 or 4) can be explained by an accelerating reduction of the deposition rate with decrease of reaction temperature.

The heat transfer from the outer surface to the inner one through the capillary wall, the thickness of which is 100–500 μm depending on the capillary diameter, affects the thickness distribution profile of the deposit. Above 900 °C, the thickness maximum of the deposit reaches about 200% of $L(x)/L\,(out)$, and this means that a considerable portion of the reactant carried by flow into deep zones of the capillary reacts before reaching a depth of 3 mm (Fig. 3) or 5 mm (Fig. 4). On the other hand, at 850 °C (Fig. 5) the thickness maximum is 50–70%, which means that the temperature difference between the inner and outer surfaces of the capillary makes a large difference to the reaction rate at this temperature.

3.2. Case of very thin capillary

In the above section, capillaries with an inner diameter of 55–67 μm were used. The flow mode in these cases was roughly estimated as viscous flow. In the case of a thin capillary the inner diameter of which was below about 5 μm, the flow mode was estimated as molecular flow. In order to check the effect of the difference of flow mode, capillaries with an inner diameter of 1 μm were tested. Figs 6 and 7 show the thickness distribution obtained at 900 and 850 °C, respectively. In these figures, the ordinate is shown as the full extent of the inner diameter, 1 μm. At 900 °C the gas penetration path has been blocked at the mouth, and is nearly closed at about 100 μm from the mouth. At 850 °C, the mouth opens widely yet, however, the gas penetration path is nearly closed at about 80 μm from the mouth. It is supposed that the difference of flow mode does not seriously affect the thickness distribution.

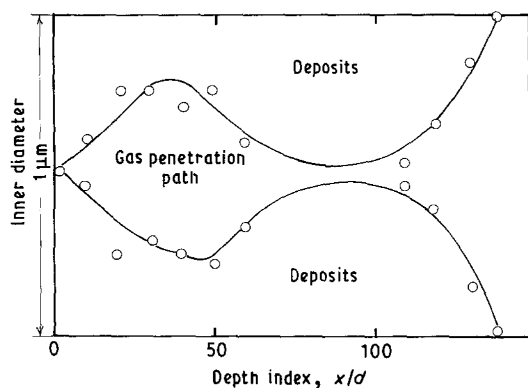

Figure 6 Thickness distribution of deposit in a fine capillary of 1 μm inner diameter. Depth index x/d is the ratio of depth, x, to the inner diameter, d. 900 °C, capillary length 1 mm, 2000 pulses.

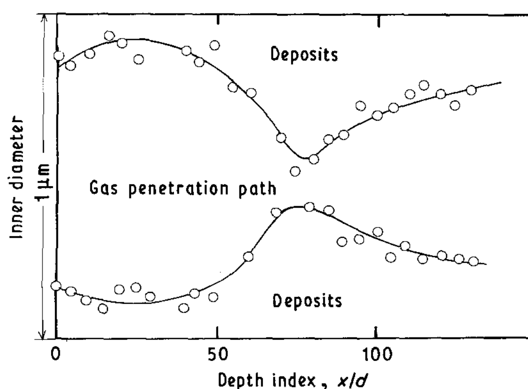

Figure 7 Thickness distribution of deposit in a fine capillary of 1 μm inner diameter; 850 °C, capillary length 1 mm, 2000 pulses.

3.3. Difference of heat conduction of capillary model from those of porous or particulate preforms

In previous experiments [9], we found that an SiC matrix can be deposited by pulse CVI from the gas system CH_3SiCl_3–H_2 into porous carbon plate (700 μm thick) with a pore distribution of 0.2–0.5 μm, in which deposition is initiated from half-thickness (350 μm deep) when a cold-wall type furnace is used. The reason why deposition initiates from the deepest zone is considered to be that the temperatures of gas and capillary wall are too low to react near the mouth; on the other hand, at deep zones they remain in the temperature range in which deposition is possible, even though it is slow. An analogous result was also obtained when a hot-wall type furnace was used [7, 10], in which the temperature change during a pulse is supposed qualitatively to be as shown in Fig. 8. In the present experiments, the temperature of the outer surface of the capillary may be nearly equal along the capillary length; therefore the heating up of gas just flowing into the capillary may be much faster than in the case of porous carbon plate. This suggests that the infiltration to deep levels of fibrous, particulate or porous preforms is much easier than in the present experiments.

3.4. Effect of capillary length on thickness distribution

During the flow-in step in each pulse, deposition on to

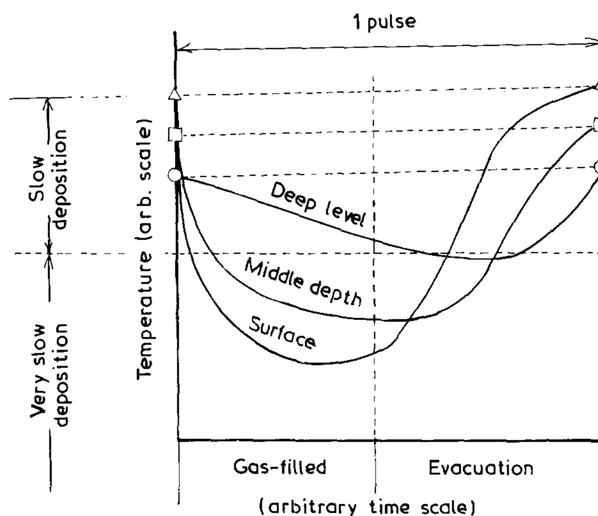

Figure 8 A concept of the reason why infiltration initiates from the deepest level when a porous plate or particulate preform is used as a substrate.

the inner wall of the capillary takes place. The longer the capillary length, the thicker the film thickness near the capillary mouth, because the total amount of source gas which flows into the capillary is proportional to the capillary length. A similar relation can be seen between the thickness of the deposit near the mouth and the inner diameter of the capillary. In Figs 9 and 10, the relationships between the thickness distribution of the deposit and the ratio of length, L, to inner diameter, d, are shown at 950 and 850 °C, respectively. As expected, the distribution curves are flatter at 850 °C than at 950 °C; however, the thickness distributions at 950 °C are flat near the capillary mouth when L/d is sufficiently large such as 1600 or 4600. At 850 °C, the slow deposition rate contributes to the flat distribution, although the finer the inner diameter, the faster the falling rate of thickness with increase of depth.

3.5. Effect of heat conductivity on the thickness distribution

SUS 316 tube was used as a metallic capillary, the inner diameter of which was 50 μm. Fig. 11 shows the thickness distribution curves compared with those of silica capillary with a similar inner diameter. It is clearly seen from the figure that the thickness distribu-

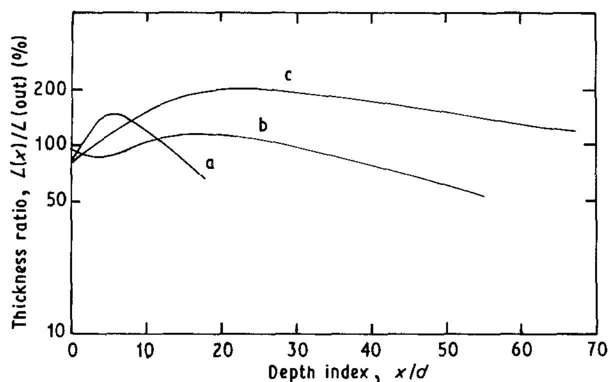

Figure 9 Dependence of thickness distribution on capillary length (L); 950 °C, 2000 pulses. (a) L/d = 620, i.d. = 4.2 μm; (b) L/d = 1600, i.d. = 4.1 μm; (c) L/d = 4600, i.d. = 3.4 μm.

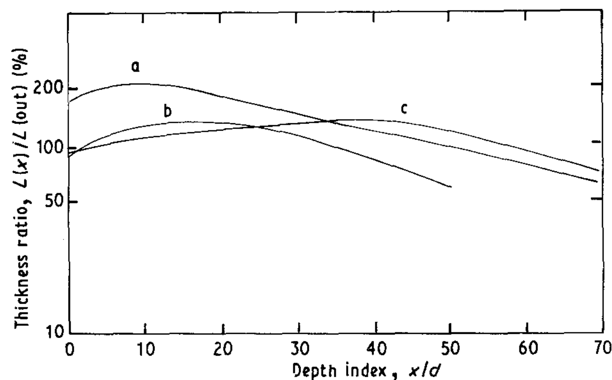

Figure 10 Dependence of thickness distribution on capillary thickness and length; 850 °C, 2000 pulses. (a) L/d = 1400, i.d. = 2.5 μm; (b) L/d = 650, i.d. = 4.6 μm; (c) L/d = 620, i.d. = 6.0 μm.

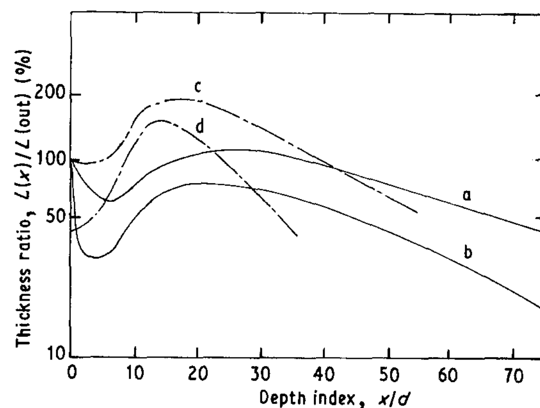

Figure 11 The effect of heat conductivity on thickness distribution; capillary length = 20 mm, 2000 pulses. (a) SUS 316, 900 °C, i.d. = 50 μm; (b) SUS 316, 950 °C, i.d. = 50 μm; (c) fused silica, i.d. = 55 μm, 900 °C; (d) fused silica, i.d. = 55 μm, 950 °C.

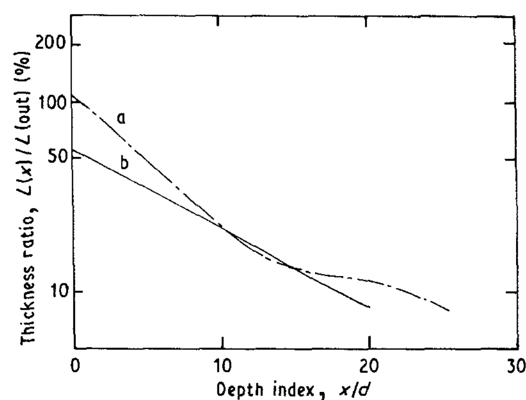

Figure 12 Thickness distribution of TiC; 950 °C, $TiCl_4$ 5%, C_3H_8 1%, 2000 pulses, capillary length = 20 mm. (a) i.d. = 12 μm, (b) i.d. = 59 μm.

tion of the deposit in SUS 316 capillary is flatter than that in silica capillary. The reasons are considered to be that, firstly, the high heat-conduction of SUS 316 through the capillary wall leads to effective cooling of the whole capillary when cold source gas is introduced instantaneously; the thickness distribution curve therefore becomes similar to that of silica capillary with deposition at a lower temperature. Another reason for the flattening is considered to be that the inner wall of SUS 316 is smoother to flow than that of silica tube because TiN crystals hardly nucleate on the silica surface, so that crystallites are apt to grow coarsely; in contrast, nucleation of TiN is easy on the metallic surface.

3.6. Comparison of TiN and TiC

Suitable CVD conditions for TiN and TiC are markedly different from each other, especially in the temperature dependence of deposition rate. From a gas mixture of $TiCl_4$–C_3H_8–H_2, sound films of TiC can be deposited above 920 °C, below which deposits contain TiC of low crystallinity, lower chlorides of titanium and carbon phases. Above 920 °C, the deposition rate of TiC steeply increases. On the other hand, crystalline TiN deposits can be seen at above 800 °C, and the

deposition rate gradually increases with increase of temperature. Fig. 12 shows the thickness distribution curves of TiC in capillaries with inner diameters of 12 and 59 μm. Comparing Figs 3 and 12, it can be seen that the thickness of TiC film drops faster near to the mouth than that of TiN. For pulse CVI to deep levels, the temperature has to be set to a value considerably lower, at which the deposition rate is very slow. However, the deposition rate and the quality of TiC films change markedly at around 920–950 °C, so the scope for control of temperature is only limited.

4. Conclusions

The effects of various factors on the thickness distribution of deposits along the depth in the pulse CVI process were surveyed using silica capillary sealed at one end as a substrate and TiN as a model deposit, and the following results were obtained.

1. All thickness distribution curves had a minimum near the capillary mouth and had a maximum at a variable depth depending on the deposition temperature.

2. By lowering the temperature from 900 to 850 °C, the distribution curve was markedly flattened.

3. The longer the capillary length, or the greater the inner diameter of the capillary, the flatter the thickness distribution.

4. Notable differences of thickness distribution could not be seen between molecular flow (1 μm i.d.) and viscous flow (50 μm i.d.).

5. TiC is more difficult to infiltrate homogeneously than TiN.

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