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

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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 TiCl₄–N₂–H₂. 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 \( L(x)/L(\text{out}) \) (\( L(x) \) is the thickness of deposit at a depth of \( x \) mm from the mouth, \( L(\text{out}) \) 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, TiCl₄ (5%)–N₂ (32%)–H₂ 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 \( L(x) \times 100/L(\text{out}) \), 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 \( L(\text{out}) \) 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.
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 photo are the depth from the capillary mouth. TiCl₄ 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, \( L(\text{out}) \) 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