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# Preparation of titanium nitride coated powders by rotary powder bed chemical vapour deposition

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Titanium nitride coated powders were prepared by rotary powder bed chemical vapour deposition (CVD) in which a powder in a rotary specimen cell was heated by infrared radiation in a reactant gas stream. Titanium powder covered with TiN or $Ti_2N$ thin film was obtained by diffusion coating treatment of titanium particles (grain size 10 to 50 μm) at 900 to 1000° C and 0.5 to 1.0 atm for 60 min in a nitrogen stream. TiN was coated on to the surface of scaly graphite particles (grain size 30 to 100 μm or 100 to 1000 μm) as well as titanium particles by CVD in the reactant system $TiCl_4$–$N_2$–$H_2$ at 900° C and 1 atm for 40 min. The uniformity of the coating (composition and film thickness) and the dispersability of the coated particles were considerably promoted by rotating the powder bed at about 90 r.p.m. compared with non-rotary powder bed CVD.

## 1. Introduction

Metallic or ceramic powders which are coated by various kinds of inorganic material are important as starting powders for the development of new composite materials [1, 2]. Fluidized bed chemical vapour deposition (CVD) is well known as a general coating technique from the vapour phase on to a powder surface [3–6]. However, the stabilization of the fluidized bed is an essential problem and a large quantity of fluidizing gas is required, which limits the wide applications of fluidized-bed CVD to the coating of powders [5, 7, 8].

In the present paper, a rotary powder bed CVD apparatus was designed with the purpose of developing a more applicable CVD coating technique for powders [9]. Titanium nitride was chosen as a typical coating material for CVD [10, 11]. Two kinds of CVD coating were carried out: by the diffusion treatment of titanium powder in a nitrogen stream, and by CVD using a reactant system of $TiCl_4$–$N_2$–$H_2$ on to graphite and titanium powders. The source powder conditions (grain size, morphology) and treatment conditions (temperature, gas flow rates, pressure, rotation speed, etc.) were correlated to the uniformity of the composition, crystallinity or film thickness, and the dispersability of the coated powders.

## 2. Experimental procedure

Fig. 1 shows a schematic diagram of the rotary powder bed CVD apparatus. An infrared radiation forcusing furnace was used for heating the powder specimen (0.5 to 1.5 g), which was placed in a rotary quartz specimen cell (inside diameter 17 mm) at the centre of a transparent quartz reactor (inside diameter 38 mm). The specimen temperature at the furnace centre was measured by a calibrated thermocouple that was attached to the outer wall of the reactor. When specimen temperatures were 900 and 1200° C, for example, the temperatures of the outer wall were 720 and 1000° C, respectively. The specimen cell was connected to the rotary shaft at the inlet-side manifold, which was rotated at a given rotation speed (0 to 500 r.p.m.). Argon gas (flow rate about 20 ml min$^{-1}$) was streamed from the inlet side to protect the magnetic fluid seal. A reactant gas mixture ($TiCl_4$–$N_2$–$H_2$) was introduced at the manifold port and streamed mainly into the rotary specimen cell and partly into the outside space of the specimen cell in the reactor. A diffusion pump was arranged to evacuate the reactor system to $10^{-5}$ torr before and after the run. A liquid nitrogen trap and a rotary pump were attached to the outlet-side manifold in order to make low-pressure CVD possible.

Granular titanium powders (grain size 10 to 50 μm) and natural scaly graphite powders (grain size: fine 30 to 100 μm, coarse 100 to 1000 μm) were used as source powders to be coated. The source powder in the specimen cell was degassed under $10^{-3}$ torr and then pretreated in an argon flow for 1 h. The pretreated powder was subsequently coated with titanium nitride by the diffusion coating of titanium powder in a nitrogen stream or by normal-pressure CVD of graphite and titanium powders in the reactant system $TiCl_4$–$N_2$–$H_2$. TiN-coated powder was taken out of the reactor after the post-treatment under vacuum ($10^{-5}$ torr).

The coated powder was analysed by X-ray diffraction and observed by scanning electron microscope (SEM). The specific surface area of the source or coated powder was measured by the BET method.

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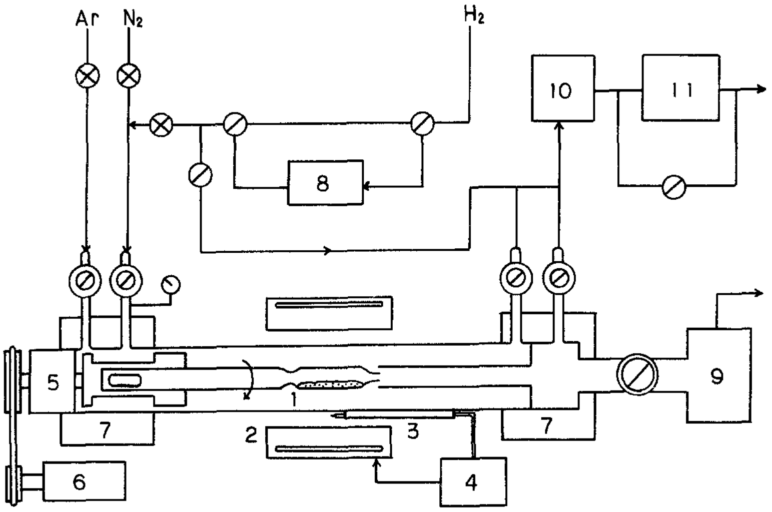

*Figure 1* Schematic diagram of rotary powder bed CVD apparatus: (1) rotary specimen cell, (2) infrared radiation furnace, (3) thermocouple, (4) temperature controller, (5) seal, (6) motor drive, (7) manifold, (8) $TiCl_4$ evaporator, (9) diffusion pump, (10) liquid nitrogen trap, (11) rotary pump.

## 3. Results and discussion

### 3.1. Diffusion coating of titanium nitride on to titanium powder

Fig. 2 shows X-ray diffraction patterns of the diffusion-coated titanium powder, where the treatment time was kept constant at 60 min. At a treatment temperature as low as 900° C (see Fig. 2a) the diffraction lines of titanium, $Ti_2N$ and TiN can be identified, among which the intensities for $Ti_2N$ are higher than those for titanium or TiN. All the lines of titanium disappear, however, at the higher treatment temperature of 1100° C (see Figs 2b and c) due to the formation of a thicker TiN coating film. Weak lines corresponding to $Ti_2N$ can be observed at a treatment pressure of 0.5 atm and nitrogen flow rate of 60 ml min$^{-1}$. It is speculated from Figs 2a to c that a $Ti_2N$ intermediate layer would be in existence between the titanium core and the TiN coated outer layer [12].

The difference between the coated powders made with rotary powder bed (90 r.p.m.) and by a non-rotary bed (0 r.p.m.) was minor, although in the latter case the intensities for TiN were slightly weaker and a peak splitting at higher diffraction angle was observed, as shown in Fig. 2d. A small amount of $TiN_x$, which has a slightly lower lattice constant, coexists with stoichiometric TiN in the case of non-rotary powder bed CVD.

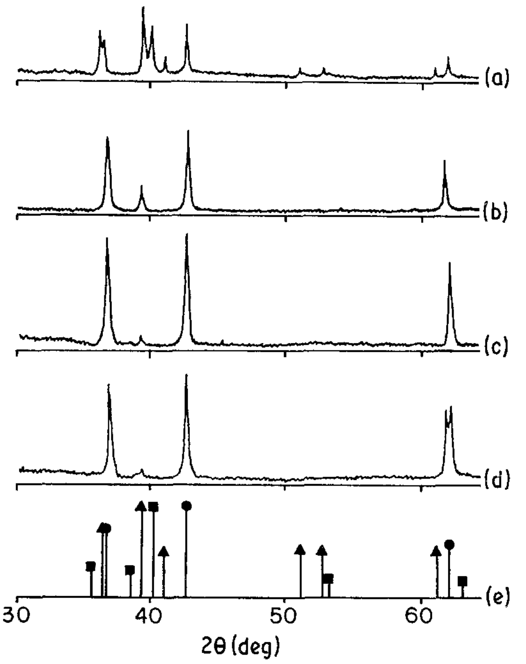

*Figure 2* X-ray diffraction patterns (Cu*Kα* radiation) of diffusion-coated titanium powder treated for 60 min. Treatment conditions: (a) 900° C, $N_2$ 50 ml min$^{-1}$, 1 atm, 90 r.p.m.; (b) 1100° C, $N_2$ 60 ml min$^{-1}$, 0.5 atm, 90 r.p.m.; (c) 1100° C, $N_2$ 200 ml min$^{-1}$, 1 atm, 90 r.p.m.; (d) 1100° C, $N_2$ 200 ml min$^{-1}$, 1 atm, 0 r.p.m.; (e) JCPDS file data for (●) TiN, (▲) $Ti_2N$, (■) titanium.

SEM photographs of the surface appearance of a titanium particle and a coated particle are shown in Figs 3a and b. The diffusion-coated powder was yellow-coloured and clearly distinguished from the source titanium powder. Fine network deposits were observed in the magnified coated surface (Fig. 3b) with reference to the smooth titanium surface (Fig. 3a).

### 3.2. CVD of TiN on to graphite powder

Fig. 4 shows X-ray diffraction patterns of TiN-coated graphite powder obtained by CVD in the $TiCl_4$–$N_2$–$H_2$ system. The following CVD parameters were kept constant: reactant gas flow rates $TiCl_4$ 3 ml min$^{-1}$, $N_2$ 200 ml min$^{-1}$, $H_2$ 250 ml min$^{-1}$; pressure 1 atm; reaction time 40 min; rotation speed 90 r.p.m. TiN can be identified together with a large amount of graphite at the specimen temperature of 900° C for both coarse and fine powders. In case of CVD on to fine powder, however, the intensities of TiN diffraction lines are lower than those of the coarse powder. The colour of the coated powder was dark yellow, which is caused by the coating of a thinner TiN film. On the other hand, a yellow or golden yellow coloured thick TiN coating was obtained on the coarse powder, since the coarse powder has a six times smaller surface area than the fine powder as will be shown later in Fig. 8. At a specimen temperature as low as 800° C, the intensities of TiN lines decreased and $TiN_x$ with a poor nitrogen concentration was found to coexist with stoichiometric TiN.

As far as the uniformity of coating along the rotary shaft axis direction is concerned, a considerable dependence on the treatment temperature was observed. A highly crystalline TiN was deposited on the upstream side at 1000° C, with decreasing crystallinity on the downstream side. A uniform coating on to the powder in the whole range of cell geometry was obtained at 900° C.

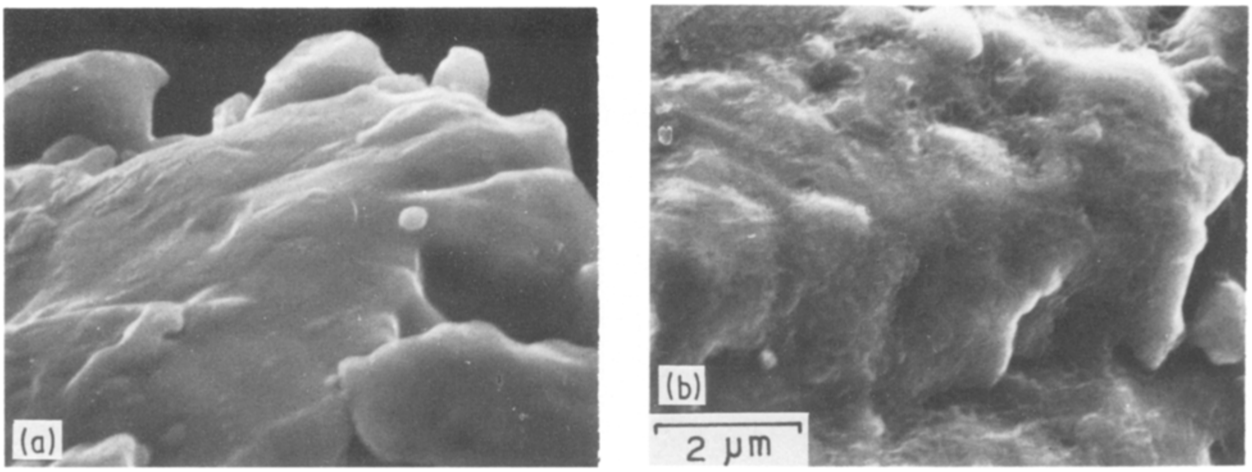

*Figure 3* SEM photographs of surface appearance of (a) source titanium particle and (b) diffusion-coated titanium particle. Treatment conditions: 1100° C, $N_2$ 200 ml min$^{-1}$, 1 atm, 60 min, 90 r.p.m.

Fig. 5 shows a cross-section and the surface appearance of TiN-coated coarse graphite powder, where the treatment conditions are the same as for the specimen in Fig. 4b. TiN film with a thickness of 0.5 to 1.0 $\mu$m was homogeneously coated on a scaly graphite grain, as shown in Fig. 5a. The surface microstructure of the coated film is composed of aggregates of fine TiN deposits with a grain size of about 1 $\mu$m (Fig. 5b).

### 3.3. CVD of TiN on to titanium powder

Fig. 6 shows SEM photographs of the appearance of TiN-coated titanium particles obtained by CVD in the $TiCl_4$–$N_2$–$H_2$ system. The coating conditions are the same as those in Fig. 5. A uniform coating of TiN on a single particle of titanium (diameter about 30 $\mu$m) is found in case of rotary powder bed CVD with a rotation speed of 90 r.p.m. (see Fig. 6a). On the other hand, agglomeration of titanium particles occurred in the case of the non-rotary powder bed CVD (see Fig. 6b), and TiN was probably deposited on these agglomerated particles having irregular surfaces. Uniformity of coating and dispersability of the coated powder are promoted by an increased degree of contact between the reaction gas and the particle surface in the rotary specimen cell.

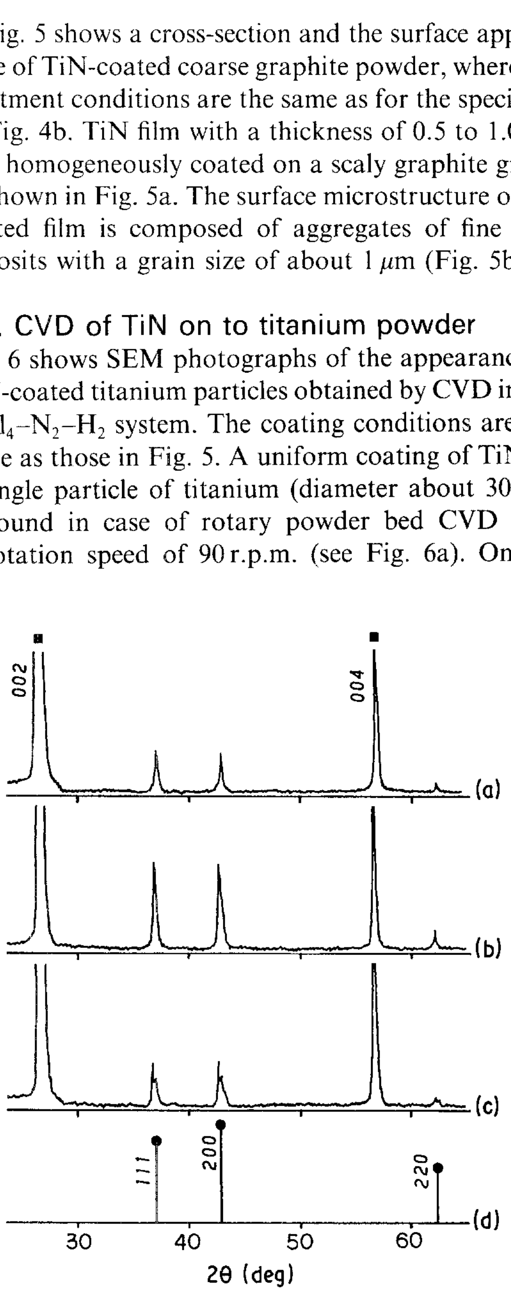

*Figure 4* X-ray diffraction patterns of TiN-coated graphite powder treated by CVD in the $TiCl_4$–$N_2$–$H_2$ system. Treatment conditions: $TiCl_4$ 3 ml min$^{-1}$, $N_2$ 200 ml min$^{-1}$, $H_2$ 250 ml min$^{-1}$, 1 atm, 40 min, 90 r.p.m. (a) 900° C, fine graphite powder; (b) 900° C, coarse graphite powder; (c) 800° C, coarse graphite powder; (d) JCPDS file data. (●) TiN, (■) graphite.

An SEM photograph of a cross-section of a TiN-coated particle, which was embedded into the epoxy resin, is shown in Fig. 7. A few smaller particles attached to a large particle with a diameter of about 30 $\mu$m are observed. A homogeneous TiN coating with a constant film thickness of 1 to 2 $\mu$m can be seen on the surface of the titanium metal. A crack can be observed in Figs 6a and 7, which may be attributed to the difference in thermal shrinkage between the titanium metal and the TiN-coated layer during the cooling process after CVD treatment.

### 3.4. Surface area of TiN-coated powder

Fig. 8 shows the BET surface area of the TiN-coated powders against treatment temperature, in comparison with that of the source powder. It is apparent that the surface area of the diffusion-coated powder is almost the same as the source titanium powder (see ⬢* in Fig. 8), as suggested from the surface appearance of the coated powder in Fig. 3b. However, the surface area of the TiN-coated titanium powder produced by CVD in the $TiCl_4$–$N_2$–$H_2$ system increased on account of the deposition of fine TiN grains with a large surface area. On the other hand, the surface area of the TiN-coated graphite powder decreases with increasing temperature up to 900° C. The infiltration of TiN into the pores of graphite particles is considered to decrease the surface area. Above 1000° C, the surface area of the coated fine graphite powder increased, probably due to the increased deposition of TiN on to the TiN-coated surface.

## 4. Conclusions

Titanium nitride coated titanium and graphite powders were prepared by using a rotary powder bed CVD apparatus. The following two kinds of CVD coating system were investigated to obtain uniform coatings

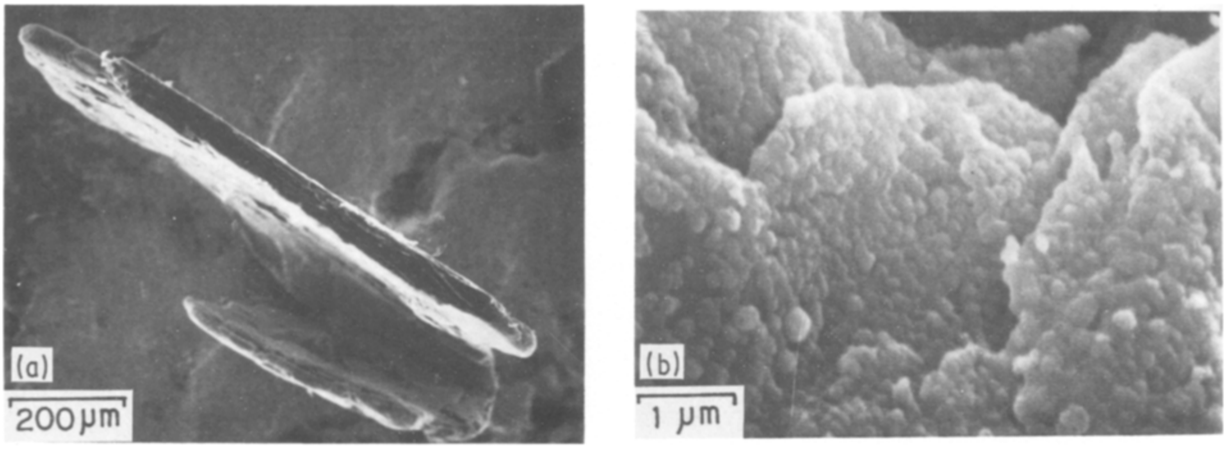

*Figure 5* SEM photographs of (a) cross-section and (b) surface appearance of TiN-coated coarse graphite powder. Treatment conditions: 900° C, 1 atm, 40 min, 90 r.p.m.

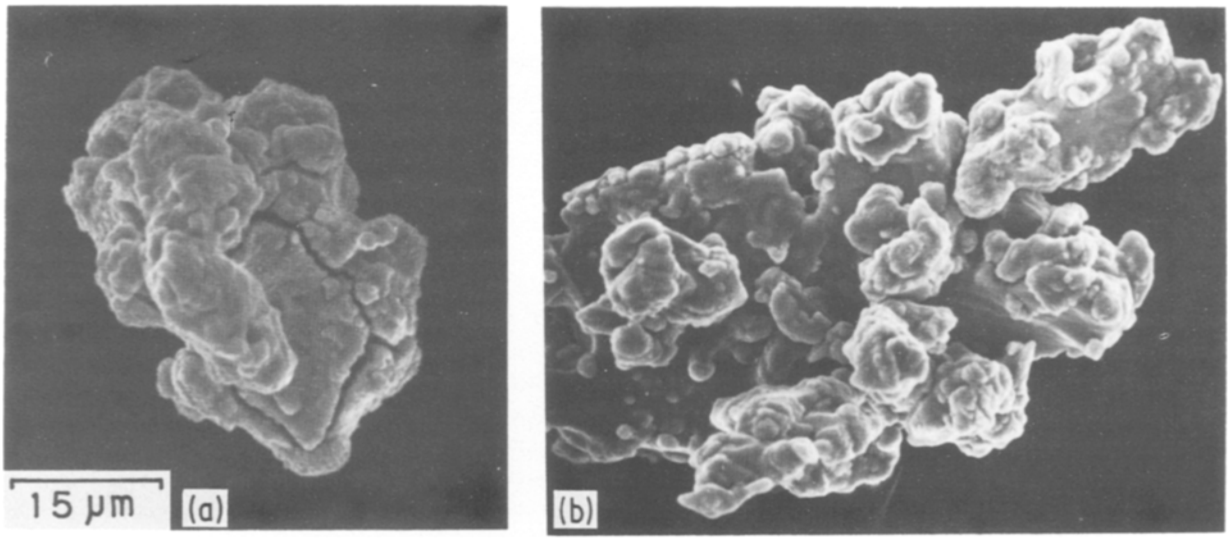

*Figure 6* SEM photographs of the appearance of TiN-coated particles treated by CVD in the $TiCl_4$–$N_2$–$H_2$ system: (a) rotary powder bed CVD (90 r.p.m.) and (b) non-rotary powder bed C.V.D.; treatment conditions 900° C, 1 atm, 40 min.

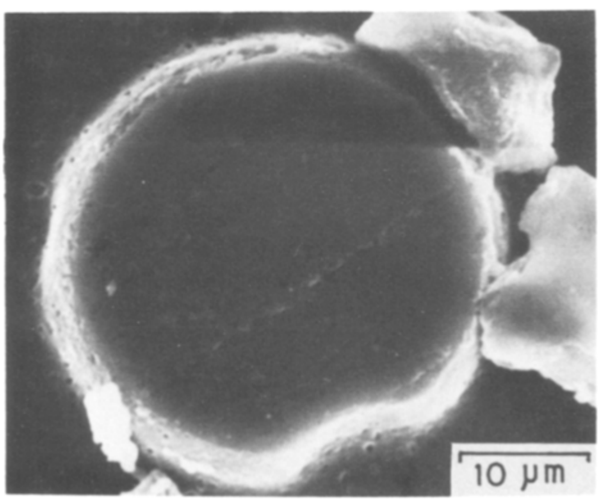

*Figure 7* SEM photograph of cross-section of TiN-coated particle treated by rotary powder bed CVD.

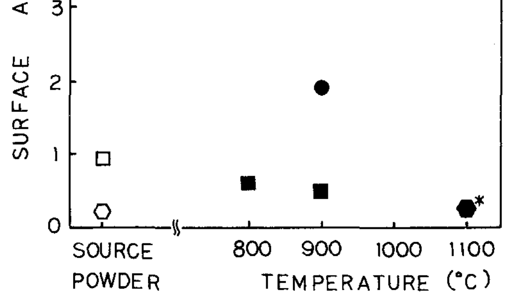

*Figure 8* BET surface area of source powder and coated powder treated at various temperatures: (○, ●) fine graphite powder, (□, ■) coarse graphite powder, (⬡, ⬢) titanium powder (⬢* diffusion coating).

on to powders having different grain sizes and morphologies:

1. Titanium powder covered with titanium nitride (TiN or $Ti_2N$) was obtained by diffusion-coating of titanium particles at 900 to 1100° C and 0.5 to 1.0 atm for 60 min in a nitrogen stream.
2. TiN-coated graphite or titanium powder was obtained by CVD in the $TiCl_4$–$N_2$–$H_2$ system at 900° C and 1 atm for 40 min.

It is suggested from these results that rotary powder bed CVD may be recommended as a versatile coating technique of inorganic compounds on to various kinds of powder.

## References

1. D. HULL, "An Introduction to Composite Materials" (Cambridge University Press, Cambridge, 1981) p. 1.
2. J. M. BLOCHER Jr, *J. Vac. Sci. Technol.* **11** (1974) 680.
3. C. F. POWELL, J. H. OXLEY and J. M. BLOCHER Jr, "Vapor Deposition" (Wiley, New York, 1966) p. 12.
4. R. W. KIDD, M. F. BROWNING and J. M. RUSIN, in Proceedings of 7th International Conference on CVD (Electrochemical Society, Inc., Princeton, 1979) p. 563.
5. C. M. HOLLABAUGH, R. D. REISWIG, L. A. WAHMAN and R. W. WHITE, *J. Nucl. Mater.* **57** (1975) 325.
6. P. WAGNER, L. A. WAHMAN, R. W. WHITE, C. M. HOLLABAUCH and R. D. REISWIG, *ibid.* **62** (1976) 221.
7. C. E. HAMRIN Jr and E. M. FOSTER, in Proceedings of Conference on CVD of Refractory Metals, Alloys and Compounds (American Nuclear Society, Inc., Hinsdale, 1967) p. 243.
8. G. HSU, R. HOGLE, N. ROHATGI and A. MORRISON, *J. Electrochem. Soc.* **131** (1984) 660.
9. C. L. YAWS and G. F. WAKEFIELD, *Ceram. Bull.* **51** (1972) 857.
10. K. SUGIYAMA, K. KINBARA and K. SUGIYAMA, *Thin Solid Films* **112** (1984) 357.
11. H. ITOH, K. KATO and K. SUGIYAMA, *J. Mater. Sci.* **21** (1986) 751.
12. G. V. SAMSONOV and A. P. EPIK, "Coating of High-Temperature Materials", Part 1 (Plenum, New York, 1966), p. 1.

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