Pergamon

NanoStructured Materials, Vol. 4, No. 5, pp. 497-506, 1994
Copyright © 1994 Elsevier Science Ltd
Printed in the USA. All rights reserved
0965-9773/94 $6.00 + .00

0965-9773(94)00029-8

VAPOR PHASE MANUFACTURE OF POROUS TiN DEPOSITS ON/IN POROUS SUPPORTS

J.P. Dekker*† and **J. Schoonman***

*Laboratory for Applied Inorganic Chemistry
Delft University of Technology, Julianalaan 136
2628 BL Delft, The Netherlands

†Energy Research Foundation The Netherlands (ECN)
Westerduinweg 3, 1755 ZG Petten, The Netherlands

(Accepted May 1994)

Abstract—*Particle Precipitation aided Chemical Vapor Deposition (PP-CVD) is a modification of the conventional CVD process. In PP-CVD an aerosol is formed in the gas phase at an elevated temperature, and particles are deposited on a substrate surface. The synthesis of titanium nitride (TiN) using titanium tetrachloride vapor, nitrogen, ammonia, and hydrogen is studied. TiN is formed by a heterogeneous reaction involving a titanium containing species and nitrogen, whereas simultaneously a TiN aerosol is formed by a reaction involving ammonia. Dense columnar microstructures are formed in the absence of a temperature gradient. At low temperature differences between substrate and gas phase only dense microstructures with virtually equiaxed grains are observed. Porous coherent layers are found in experiments, where larger temperature differences are applied. The observed interconnection of the particles originates from a heterogeneous reaction. A further increase in temperature difference between the susceptor and the gas phase only leads to loose powder deposits.*

INTRODUCTION

Gas phase synthesis techniques have a variety of potential applications in membrane and catalysis technology. Production methods for a porous inorganic membrane and for a catalyst monolith will be given as illustrative examples. For the formation of porous inorganic deposits on/in porous supports, a combination of a gas to particle conversion and a Chemical Vapor Deposition (CVD) process is used. With this modified hot-wall CVD process it is possible to control the microstructure of the layer by a controlled deposition of submicron particles on the substrate. In this so-called Particle Precipitation aided CVD (PP-CVD) an aerosol is formed at an elevated temperature, and the particles are deposited on the substrate surface by introducing an external force for particle deposition, such as thermophoresis, electrophoresis, or forced flow. Particle precipitation on the substrate surface will result in a loose powder deposit, which has a poor mechanical stability. In order to obtain a coherent porous layer consisting of interconnecting submicron particles the deposit should be sintered, or a heterogeneous reaction should occur simultaneously to interconnect the individual particles. Thus, the PP-CVD process consists of three steps, *i.e.* particle formation, particle deposition, and interconnection or sintering of the particles as illustrated in Figure 1.

The PP-CVD process has been introduced by the group of Komiyama (1-5). The driving force for particle deposition was thermophoresis. Dense to highly porous layers were obtained depending upon experimental conditions. The microstructure of the layers seemed to be determined by a combination of particle deposition, sintering, and heterogeneous reaction. In all cases, the uniformity in film thickness in the axial direction of the tubular reactor was very poor, because of the strong depletion of reactant in the gas phase. The group of Yamamoto has deposited silicon nitride particles on a porous substrate by electrophoresis or a forced flow (6-8). Afterwards, the precipitated powders were sintered to form a porous layer.

The reactant mixture used in the PP-CVD process has to serve as a source for the powder formation as well as for the heterogeneous reaction. In principle, two separate reaction routes, *i.e.* one for the powder formation and one for the heterogeneous reaction, should be used. Formation of layers by a heterogeneous (CVD) reaction is well documented (9-12). The criteria for the synthesis of a solid in the gas phase for a given chemical mixture are not well understood. However, as a first approximation, the formation of a solid seems to be determined by the thermodynamic

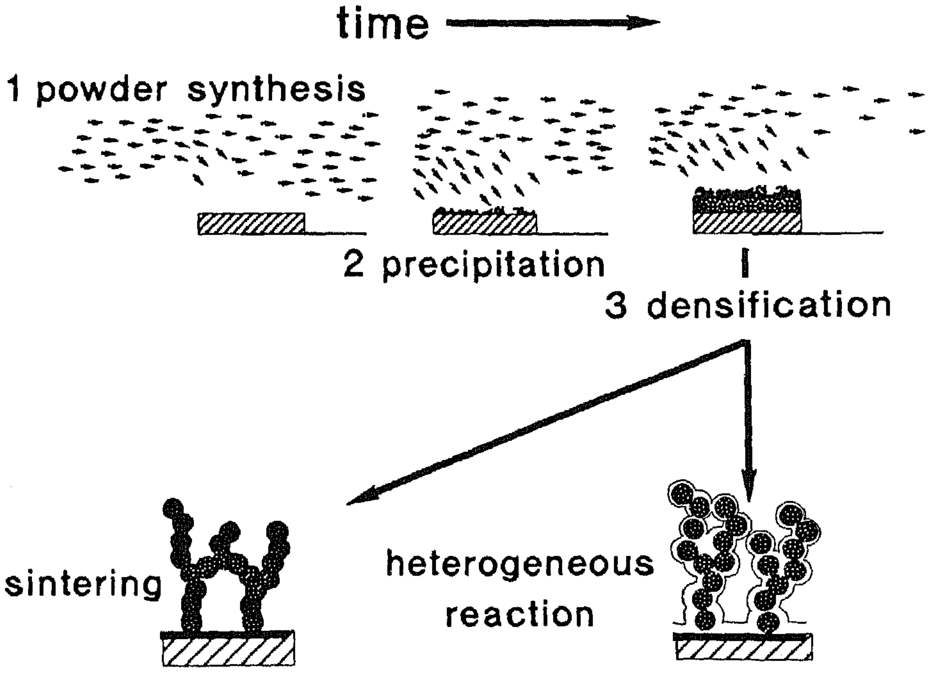


Figure 1. The principle of the three stages of the PP-CVD process.

equilibrium constant. Kato *et al.* (13) observed a tendency between powder formation (of nitrides and carbides) and the equilibrium constant. In general, a homogenous reaction will only occur if the equilibrium constant of the reaction is high enough. We have investigated the formation of porous deposits of titanium nitride (TiN) on/in porous supports by the PP-CVD process (14-16). TiN has been chosen to investigate the possibilities of the PP-CVD process, because it is possible to synthesize TiN aerosols as well as TiN layers at the same reaction temperature and reactor pressure using different nitrogen containing reactants. A heterogeneous reaction is necessary to interconnect the precipitated particles, because TiN has a poor sinterability. A TiN aerosol can be formed using titanium tetrachloride ($TiCl_4$), ammonia, and hydrogen (H_2),

$$2\,TiCl_4(g) + 2\,NH_3(g) + H_2(g) \rightarrow 2\,TiN(s) + 8\,HCl(g) \qquad [1]$$

whereas $TiCl_4$, H_2 and nitrogen (N_2) can only react on a surface to form TiN,

$$2\,TiCl_4(g) + N_2(g) + 4\,H_2(g) \rightarrow 2\,TiN(s) + 8\,HCl(g) \qquad [2]$$

The pores between the precipitated particles, which originate from the first reaction, should be entirely or partly filled by the solid deposit of the second reaction. It is expected that the layers formed have different porosities, depending on the ratio of particle precipitation rate over heterogeneous reaction rate. The driving force for powder deposition on the substrate can be thermophoresis, diffusion, or gravitation, depending on the particle size. Thermophoresis is used as a driving force for particle deposition for the formation of porous layers on porous supports. These porous TiN layers which are electronically conducting can be used as membranes for electro-filtration. No additional driving force for particle deposition is applied for the deposition in alumina foams. These high surface foams might be attractive as catalyst monoliths.

EXPERIMENTAL ASPECTS

A schematic drawing of the gas distribution system of the CVD apparatus is given in Figure 2. Hydrogen is bubbled through heated liquid $TiCl_4$ in order to saturate the hydrogen stream with reactant vapor. The reactants for homogeneous reaction, *i.e.* NH_3 and $TiCl_4$ are introduced into the reactor separately, and the two flows are mixed in the high temperature zone of the reactor. Two reactor configurations have been used, *i.e.* one reactor in which porous layers are formed on tubular porous alumina tubes, and one reactor in which porous layers are formed in disc-shaped alumina foams.

Deposits on Porous Supports

For the deposition of particles on porous tubes, thermophoresis is used as the driving force for particle deposition. In this case, the susceptor for positioning and cooling the substrate consists of a hollow quartz tube closed at one end. It is positioned in the middle of the reactor as illustrated in Figure 3. The tubes are slid over the cooled susceptor. The substrates have an inner diameter of 9 mm, an outer diameter of 15 mm, a length of 15 mm, an average pore size of 4.5 μm, and a porosity of 40 percent.

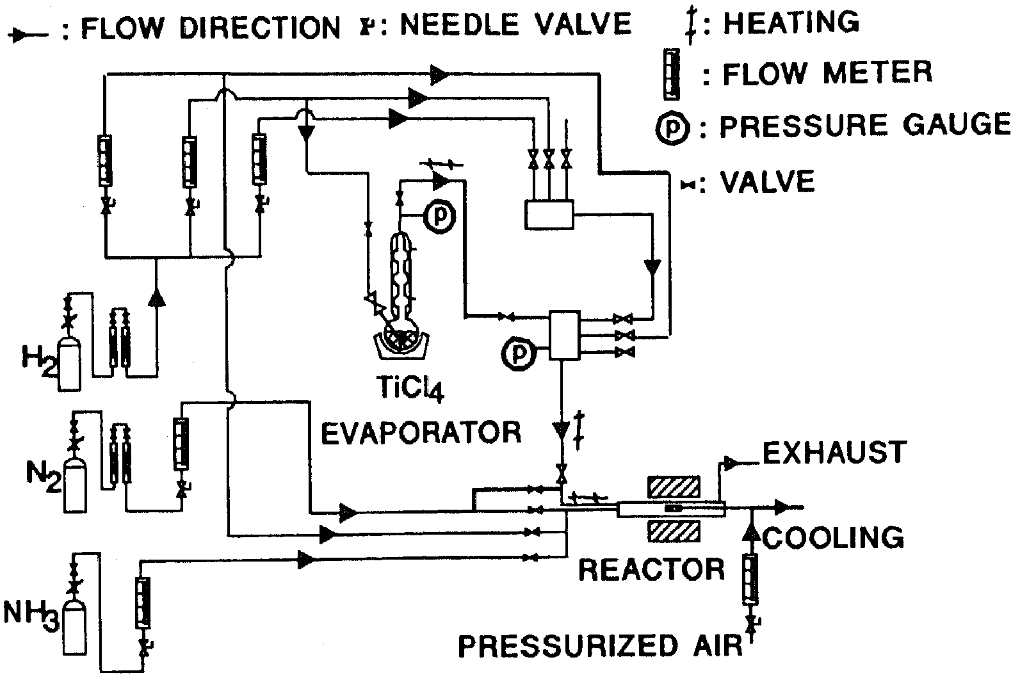


Figure 2. A schematic drawing of the gas distribution system of the CVD apparatus.

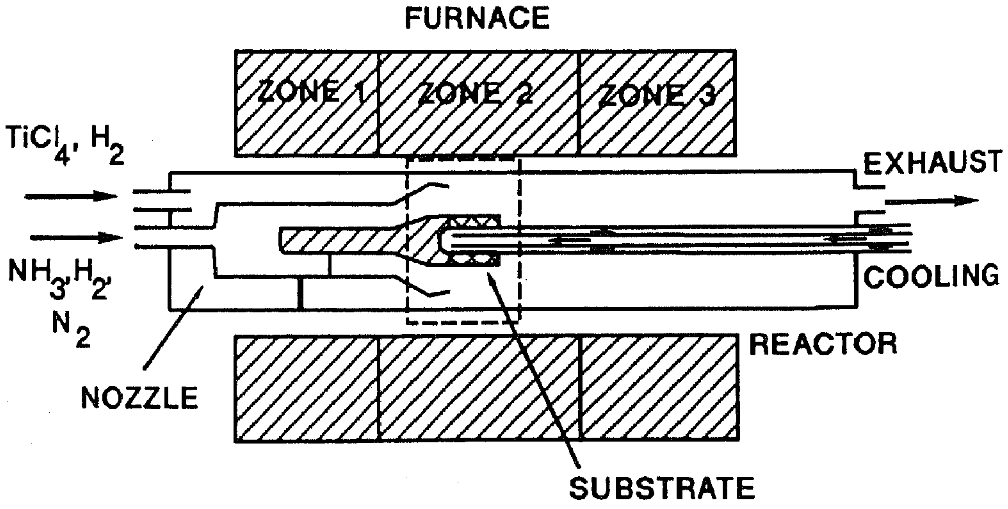


Figure 3. A schematic drawing of the reactor for the deposition of porous layers on porous tubes.

TABLE 1
Typical Process Parameters for the Synthesis of TiN by PP-CVD.

Ammonia flow			Titanium flow		
NH_3	13.5	μmole/s	$TiCl_4$	35.9	μmole/s
N_2	0.448	mmole/s	H_2	0.93	mmole/s
H_2	0.162	mmole/s	total	0.97	mmole/s
total	0.624	mmole/s			
Reaction time	3600	s	Temp. difference	0-38	K
Reaction temp.	923-1023	K	Reactor pressure	1 x 10^5	Pa

The cooling of the susceptor is regulated by an externally controlled flow of pressurized air. The reaction temperature is varied from 923 K to 1173 K, and the temperature difference between gas phase and substrate is varied from 0 K to 38 K. Temperatures are measured with chromel-alumel thermocouples as illustrated in a blown- up part of the center of the reactor in Figure 4. The reaction temperature is measured at the end of the gas distribution nozzle (A1 in Figure 4). The temperature of the gas phase is measured 15 mm above the substrate (A2 in Figure 4), and the temperature of the substrate is measured with a thermocouple mounted on the surface of the substrate (A3 in Figure 4). Typical experimental conditions are summarized in Table 1.

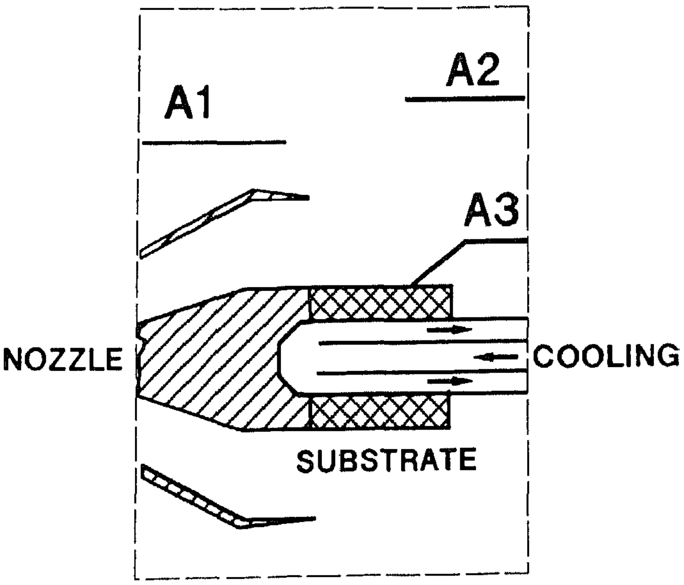


Figure 4. A schematic drawing of a blown-up part of the center of the reactor for the deposition of porous layers on porous tubes.

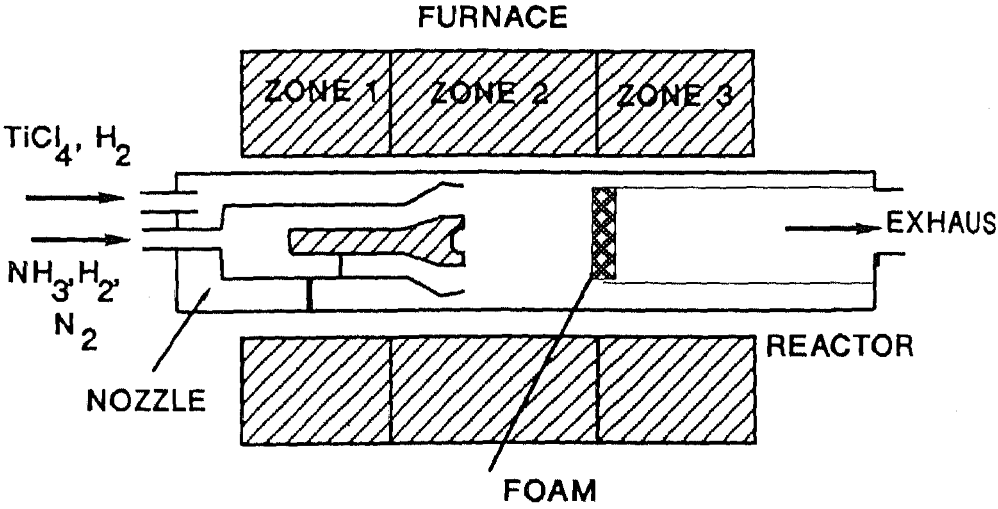


Figure 5. Schematic drawing of the reactor for the synthesis of high surface area foams.

Deposits on Alumina Foams

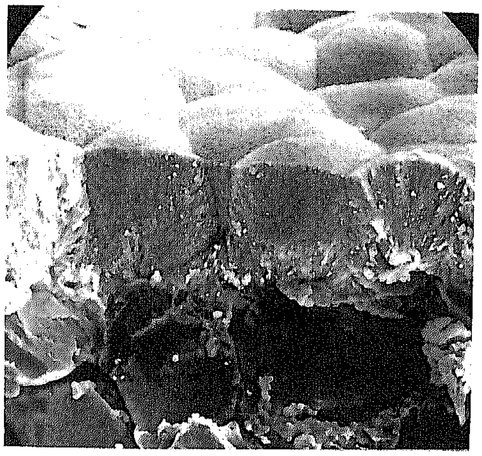
Preliminary experiments have been performed to produce a high surface area foam. In this case, the reactant flow is forced through the foam as illustrated in Figure 5. The foams have a diameter of 42 mm and a thickness of 13 mm. These open-cell foams have a porosity of more than 80 percent and a pore radius of 0.4 mm. It is expected that a considerable amount of the particles in the gas phase will deposit on the cellular walls of the foam. Here, no additional driving force for particle deposition is necessary because of the relative high surface area-volume ratio. Similar process conditions have been used as described for the deposition of layers on porous tubes. All deposits are studied using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis.

RESULTS AND DISCUSSION

In all cases, the deposits consist of crystalline TiN, as identified by X-ray diffraction analysis. Particle size analyses of samples taken from the gas phase indicate that the mean primary particle size varies between 100 and 200 nm, and the geometric standard deviation varies between 1.1 and 1.3 (16,17).

Deposits on Porous Supports

All deposits had a uniform thickness over the entire length of the support. Three types of deposits are observed, *i.e.* dense layers, coherent porous layers, and loose powder deposits. In the absence of cooling, the experimental configuration is identical to a conventional CVD reactor, and the contribution of the particles to the growth rate is expected to be low, because the diffusion rate of the particles in the gas phase is very small. Dense layers with faceted columnar grains are



Figures 6. SEM micrograph of a cross-section of a TiN layer with virtually equiaxed grains, which is typical for layers grown with a small temperature difference. The reaction temperature was 923 K, and the temperature difference was 3 K.

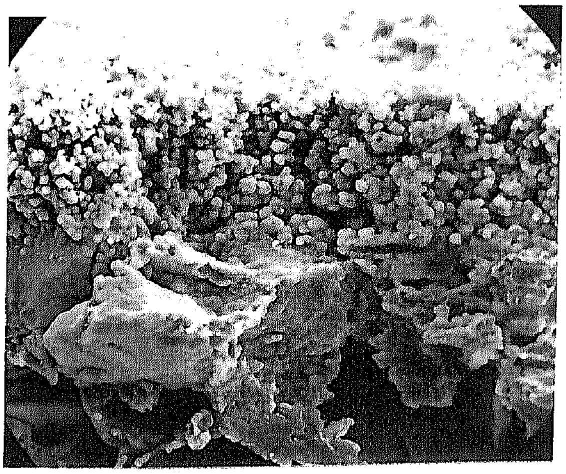


Figure 7. SEM micrograph of a cross-section of a porous TiN layer, which is typical for layers grown at intermediate temperature differences. The reaction temperature was 973 K, and the temperature difference was 16 K.

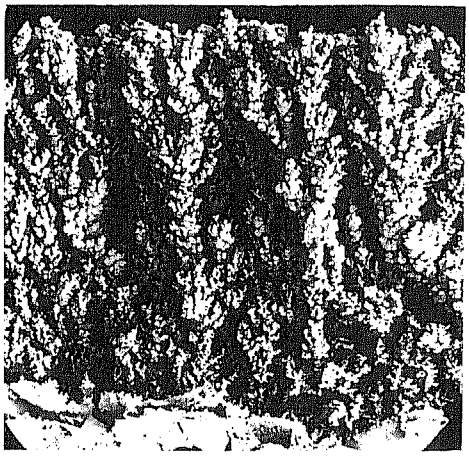


Figure 8. SEM micrograph of a cross-section of a loose TiN powder deposit. This deposit is grown at a reaction temperature of 1023 K, and at a temperature difference of 38 K.

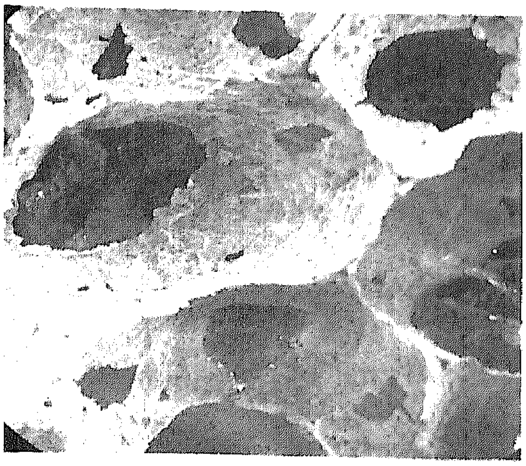


Figure 9. SEM micrograph of a cross-section of an Al_2O_3 foam.

observed which are typical for CVD reactions. A small temperature difference of only a few degrees has a considerable effect on the microstructure of the layers. The columnar structure disappears, and the average grain size is considerably smaller. A cross-section of a layer typical for the synthesis experiments with a small temperature gradient is presented in Figure 6. Apparently, the introduction of a small temperature difference favors a renucleation at the surface, and as a result virtually equiaxed grains are formed.

A further increase in the temperature gradient will result in an increase in the particle deposition rate. A cross-section typical for the synthesis experiments with a temperature gradient of more than 5 K, and a reaction temperature of 923 K or 1023 K is presented in Figure 7. The observed interconnection of the particles has to originate from a heterogeneous reaction. Apparently, under these conditions the heterogeneous reaction rate is high enough, with respect to the particle precipitation rate, to interconnect the precipitated particles; whereas the heterogeneous reaction rate is not high enough to fill the voids between them. Consequently, this results in the formation of a porous layer by the PP-CVD process. The synthesis of such mechanically stable porous layers of a material with a poor sinterability is unique. To our knowledge no other type of synthesis process is capable of making porous TiN layers at such a low temperature. Only a small window with respect to temperature gradient and reaction temperature has been found in which porous coherent layers can be deposited. Temperature differences of more than 20 K only lead to loose powder deposits as illustrated in Figure 8.

Deposits in Alumina Foam

At a high temperature, a forced gas flow is applied through the porous foam. The flow contains an aerosol as well as reactants for a heterogeneous reaction. The aerosol deposition in the foam is determined by a combination of inertial compaction and diffusion. Simultaneously, there is a heterogeneous reaction on the precipitated particles and on the cellular walls of the foam which gives the system an improved mechanical stability. As a result, an open-cell structure with a high porosity and a high specific surface area is formed. A SEM micrograph of a cross-section of a bare foam is given in Figure 9. In Figure 10, SEM micrographs with increasing magnification (A→B→C→D) of a cross-section of one foam with a TiN deposit are presented as an illustrative example. After synthesis, a highly porous monolith is formed with a specific surface area of approximately 20 m^2/g and a virtually unchanged fluid resistance. No gradient in the amount of deposited material over the thickness of the samples is observed.

CONCLUSIONS

In all cases, the deposits consist of crystalline TiN. Without cooling, the experimental configuration for the formation of a porous layer on a support is identical to a conventional CVD reactor. Dense layers with faceted columnar grains without any particles incorporated have been observed under these conditions. A small temperature difference of only a few degrees has a considerable effect on the microstructure of the layers. The columnar structure disappears, and the average grain size is considerably smaller. A further increase in the temperature gradient results in an increase in the particle deposition rate, and hence in the formation of a porous layer. Temperature differences beyond 20 K only lead to loose powder deposits. If there is a forced flow through a porous preform, similar layer can be deposited on the inside of the preform. It is shown

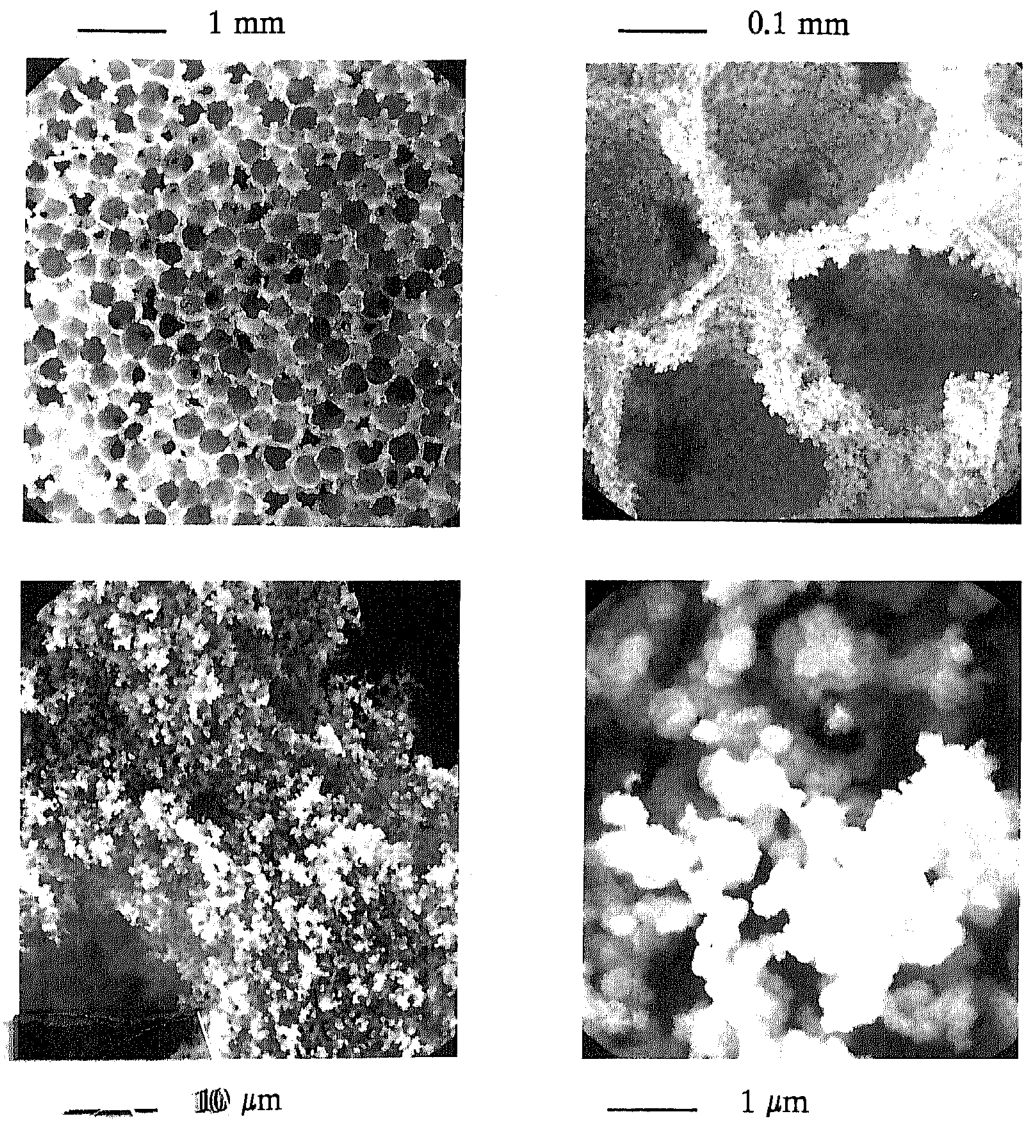


Figure 10. SEM micrographs with increasing magnification of an Al_2O_3 foam with precipitated TiN particles on the cellular walls of the foam.

that a highly porous monolith can be formed with a specific surface area of approximately 20 m^2/g. Because of the combination of the low fluid resistance of these foams and its high surface area, these modified foams might be a promising monolith for catalysis.

REFERENCES

1. Y. Shimogaki and H. Komiyama, Chem. Lett., 267 (1986).
2. Y. Shimogaki and H. Komiyama, *New Materials Processing*, World Congress III of Chemical Engineering, Tokyo Japan (1986) p. 258.
3. Y. Shimogaki and H. Komiyama, Yogyo-Kyokai Shi 95, 70 (1987).
4. T. Osawa and H. Komiyama, *New Material s Processing*, World Congress III of Chemical Engineering, Tokyo Japan (1986) p. 250.
5. H. Komiyama and T. Osawa, Jpn. J. Appl. Phys. 24, L795 (1985).
6. H. Yamamoto, T. Nomura, and S. Masuda, Kona 8, 12 (1990).
7. H. Yamamoto, Rep. Asahi Glass Foundation 59, 323 (1991).
8. S. Yamada and H. Yamamoto, Jpn. Kokai Tokkyo Koho, JP 05 85, 855 (1993).
9. H.O. Pierson, *Handbook of Chemical Vapor Deposition (CVD)*, Noyes (1992).
10. C.E. Morosanu, *Thin Films by Chemical Vapour Depostion*, Elsevier (1990).
11. F.S. Gallasso, *Chemical Vapor Deposited Materials*, CRC Press, Boca Raton (1991).
12. M.L. Hitchman and K.J. Jensen, *Chemical Vapor Deposition*, Academic Press (1993).
13. A. Kato, J. Hojo, and Y. Okabe, Mem. Fac. Eng. Kyushi Univ. 41, 319 (1981).
14. J.P. Dekker, P.J. van der Put, H.J. Veringa, and J. Schoonman, *Proc. Int. Conf. Ceramics: AUSTCERAM* 92 (Bannister M.J., ed.),Vol. 1, CSIRO Publications, Melbourne Australia (1992) p. 787.
15. J.P. Dekker, P.J. van der Put, H.J. Veringa, and J. Schoonman, Aerosol Sci. and Techn. 19, 549 (1993).
16. J.P. Dekker, *CVD techniques for the synthesis or modification of porous ceramics*, Thesis, Delft University of Technology (1994).
17. J.P. Dekker, P.J. van der Put, H.J. Veringa, and J. Schoonman, J. Mater. Chem., accepted (1994).