JOURNAL OF MATERIALS SCIENCE 26 (1991) 258–262

Preparation of AlN–Al_2O_3 fibre composites using chemical vapour infiltration

ISAO KIMURA, NORIYASU HOTTA, MASAHIRO ISHII, MASATO TANAKA
Department of Chemical Engineering, Faculty of Engineering, Niigata University, Niigata 950-21, Japan

Vapour-phase reaction of $AlCl_3$ and NH_3 at 800 to 1000 °C was performed, and AlN produced was made infiltrate an Al_2O_3 fabric to form AlN matrix–Al_2O_3 fibre composites. The composites were characterized by observation of the appearances and by analyses with X-ray diffraction and scanning electron microscopy. The matrices of the composites prepared at above 900 °C had lustrous, smooth surfaces and revealed the preferred orientation to *c*-axis. The composite was constituted by the substrate layer and the surface layer. The fibres in the substrate layer were covered with radially-grown, columnar AlN grains with a maximum height of 15 μm. The surface layer was a dense AlN film 50 μm thick. Both the layers interlocked each other with mediation of the radially-grown AlN grains covering the fibres. The formation mechanism of the composites was deduced from the morphology. The wettability with a molten dental alloy was very low.

1. Introduction

On casting alloys some constituent may be oxidized selectively, resulting in decrease in precision of the dimensions, increase in the surface roughness, loss in age hardening, and so on [1, 2]. These instances are serious problems in the field of prosthodontics. Coatings of corrosion-resistant ceramics on parts contacting the alloy can be effective in the improvement of the properties. It has been reported previously [3–5] that a coating of nitride ceramics on a wax pattern inhibits the dental alloys from being oxidized. The aim of the present study is the improvement of crucible materials.

Crucibles made of alumina (Al_2O_3) or mullite are unfavourable for uses where contamination of the contents is severely restricted, because of their inferior resistance to corrosion. It is well known that aluminium nitride (AlN) ceramics have excellent resistance to corrosion [6–8], but they are poor in sinterability and costly to fabricate. In addition, they are brittle and are broken easily by mechanical shock. Coatings of the ceramic on a relatively inexpensive substrate can give us some advantages that corrosion resistance of the substrate is improved and that the sintering operation of the nitride powder is omissible. Moreover, it is expected that using a ceramic fabric as a substrate allows articles to be light and tough.

A nonconventional method, by which a ceramic matrix is made up in a ceramic fibre preform to prepare ceramic matrix–ceramic fibre composites, is referred to as chemical vapour infiltration (CVI). In this work the AlN matrix was formed on an Al_2O_3 fabric substrate using a form of CVI. The reason why the Al_2O_3 fabric was selected is that it is the most inexpensive of continuous ceramic fibres available at the present time.

2. Experimental procedures

Sources of AlN were commercially available, granular $AlCl_3$ (purity 98.0%) and NH_3 gas (purity 99.9%). Nitrogen gas (purity 99.999%) was used as the carrier gas, the protective gas and the diluent gas. An Al_2O_3 fabric, woven by twilling yarn of 960 fibres whose properties from its catalogue are listed in Table I, was used as the fibre preform. Fig. 1 shows the Al_2O_3 fabric. The fabric seems macroscopically to be tightly woven, but it is observed microscopically that the distance between the fibres is sparse in places.

A schematic illustration of the reactor assembly is shown in Fig. 2. Mullite tube measuring 42 mm inner diameter and 1000 mm long was used as the reactor. The $AlCl_3$-feeding tube is a concentrically double tube, heated with a ribbon heater to prevent gaseous $AlCl_3$ from depositing prior to the vapour-phase reaction. The fabric was cut down to 25 mm by 25 mm, set in a graphite frame with a lean of 60°, and placed at 10 mm apart from the $AlCl_3$-feeding nozzle. $AlCl_3$ was heated at 150 to 200 °C to be sublimed and carried by a nitrogen stream through the inner tube of the feeding tube into the centre of the furnace. Nitrogen gas was passed also through the outer tube of the feeding tube to protect the nozzle from being blocked by a bulky AlN. NH_3 was diluted with nitrogen and fed

TABLE I Properties of the continuous Al_2O_3 fibre

Colour	Colourless
Chemical composition	Al_2O_3 80% SiO_2 20%
Density	3.1 g cm^{-3}
Diameter	10 μm
Tensile strength	1670 MPa
Tensile modulus	167 GPa

0022–2461/91 $03.00 + .12

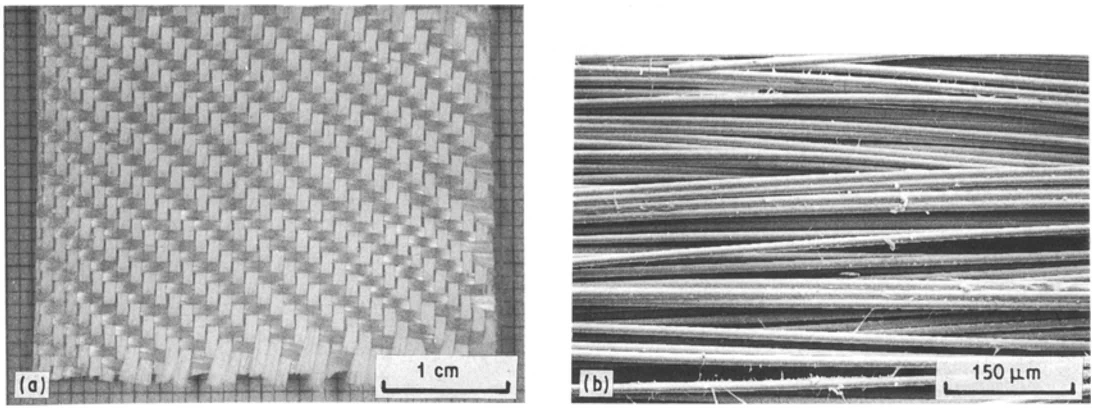

Figure 1 (a) Al_2O_3 fabric. (b) Higher magnification of (a).

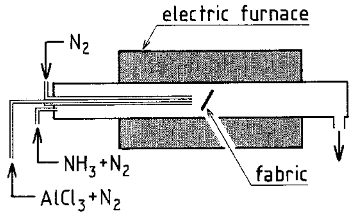

Figure 2 Schematic illustration of the reactor assembly.

into the reactor through another tube. The reaction conditions are listed in Table II.

The phase and the crystallinity of the composites were analysed by powder X-ray diffraction. The surface and cross-sectional structures were examined by scanning electron microscopy. A dental alloy (composition: Au 12%, Ag 45%, Pd 20%, Cu 18%, else 5%; melting point: 930 °C; size: 7 mm × 4 mm × 1 mm) placed on the composite was heated at 1100 °C for 1 h in an argon stream to be melted, and then the wettability was observed by the naked eye.

3. Results

3.1. Appearance

The composites obtained had quite different appearances from the upstream side, faced with the $AlCl_3$-feeding nozzle, to the downstream side.

For the upstream side the appearance altered with preparation temperature as summarized in Table III. The composite prepared at 800 °C had a rough surface, on which bulky deposits have been grown irregularly. These deposits were hard, and they firmly cohered with the matrix surface. The composite prepared at 900 °C had a smooth, lustrous surface. The matrix looked to be a transparent film. The composite prepared at 1000 °C presented an appearance much the same as one at 900 °C, but the transparency and the luster were relatively reduced. As mentioned below, the luster and the transparency are closely related to the microstructures. NH_3 concentration had little effect on the appearance, though the transparency has somewhat diminished at NH_3 concentrations except 20 vol%.

On the downstream side a white powdery product was deposited. The appearance was not altered with preparation temperature or NH_3 concentration. Cohesion of this product with the fabric was not so firm that a part of it was able to be scraped off even by a spatula.

Thus, as it was regarded that NH_3 concentration was not a significant factor, the following experiments were made with fixing it at 20 vol%.

3.2. X-ray diffraction pattern

Fig. 3 shows X-ray diffraction patterns of the composites. A pattern of an AlN powder [9] is also shown for reference. The Al_2O_3 fabric showed no diffraction. In any composites obtained only diffraction lines of AlN were recognized. The diffraction intensity and width for the upstream side of the composite prepared at 800 °C were nearly the same as those of the powder. Unlike this, the composites prepared at 900 and 1000 °C revealed a sharp and intense (0 0 2) line, indicative of the preferred orientation to *c*-axis and high crystallinity.

On the other hand, diffraction lines for the downstream side of any composites were recognized to be similar to those of the AlN powder. This indicates that the powdery deposit was an AlN powder.

TABLE II Preparation conditions

Preparation temperature	800 to 1000 °C
$AlCl_3$ feed rate	0.25 g min^{-1}
NH_3 flow rate	100 to 400 cm^3 min^{-1}
N_2 flow rate	200 cm^3 min^{-1} as carrier gas of $AlCl_3$ 200 cm^3 min^{-1} as protective gas 200 to 500 cm^3 min^{-1} as diluent gas of NH_3
Total flow rate of NH_3 and N_2	1000 cm^3 min^{-1}

TABLE III Appearances of the upstream side of the composites prepared at an NH_3 concentration of 20 vol %

Preparation temperature (°C)	800	900	1000
Colour	White	Colourless to faint yellow	Faint yellow
Transparency	No	Clear	Rather clear
Luster	No	Fine	Slight
Surface condition	Rough Bulky deposit	Smooth	Smooth

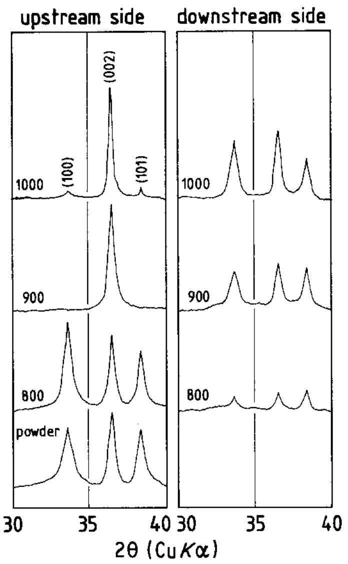

Figure 3 X-ray diffraction patterns of the composites. The numbers on diffraction lines designate preparation temperatures. The AlN powder was synthesized by CVD at 1100 °C.

3.3. Surface structure

It is found from microphotographs in Fig. 4 that a composite presenting more a lustrous and more transparent appearance had a denser structure. The matrix of the composite prepared at 800 °C was not dense. Many cracks were observed between massive grains 50 to 80 μm in size. These grains are regarded as having been formed by aggregating clusters, 5 to 20 μm, of fine particles less than 1 μm.

In the composite prepared at 900 °C, though some cracks existed, the surface was smooth and dense. It seems to be an assemblage of domes, called a corn structure [10]. The matrix of the composite prepared at 1000 °C appeared at first as if scale-like grains were stacked, but actually it was constructed by well-grown columnar grains. There existed some hollows in the surface owing to difference in length of each grain.

3.4. Cross-sectional structure

Fig. 5 shows cross section of the composite presented in Fig. 4b. It is regarded as being constituted by two regions, a substrate layer indicated by A and a surface layer on the upstream surface indicated by B.

In the substrate layer each fibre was covered with radially-grown, columnar AlN grains. The length of them were about 15 μm at the upstream side and decreased with coming toward the downstream side. These grains have met each other in places to form a continuous matrix, not quite dense. Some voids were left where distances between fibres were relatively long.

The surface layer was an AlN film about 50 μm thick. Although there are a few voids near the boundary to the substrate layer, it was dense for the most part. These columnar grains seem to be grown preferentially to certain axis direction. This feature is consistent with the result from X-ray diffraction.

Its growth rate was found at a very rough estimation to be 50 plus 15 μm per 40 min, or 1.6 μm min^{-1}. This value is larger than those of 0.2 to 1 μm min^{-1} by an ordinary CVD through vapour-phase reaction of $AlCl_3$ and NH_3 at normal pressure [11–14].

In any composites the surface layer interlocked with the substrate layer so firmly that they were never separated off.

3.5. Wettability with an alloy

The corrosion resistance of the composite was briefly evaluated by observing its wettability with a dental alloy. On melting, the dental alloy became spherical as if it were a drop of mercury. The contact angle was observed to be greater than 150°, indicative of low wettability. No change was recognized at the surface of the composite, and it appears to have been not contaminated.

4. Discussion

It is known that more rapid deposition at lower temperature can induce greater residual stress [15], which often causes unfavourable phenomena such as cracking and breaking down. The cracks observed in Fig. 4 were generated probably by residual stress, due to the difference between the matrix and the fibre in thermal expansion. In a case where cracks are generated in a film deposited on a flat substrate it is frequently possible to separate off the film easily. The firm interlocking between the surface layer and the substrate layer in the composites may be due to mediation of the radially-grown grains covering the fibres.

From observation of the microstructures the formation mechanism of the composite may be deduced as follows. The apparatus and the operation employed in this study were approximately the same as those in a previous study [9, 16, 17], in which it was demonstrated that a fine AlN powder is synthesized through homogeneous nucleation. Hence, it is pertinent to regard the species infiltrating the fabric as ultrafine AlN particles or AlN nuclei.

The ultrafine AlN particles, which are produced in the vapour phase by the homogeneous nucleation, infiltrate the fabric and deposit on a fibre surface in an early step. Their crystallographic directions are random so far. Since the growth to *c*-axis is more rapid than to *a*-axis, the columnar grains are formed subsequently, and the only grains whose *c*-axes are perpendicular to the fibre can grow successively. While growing, these grains come in contact with neighbouring ones to form the continuous matrix.

As the upstream surface is buried by the matrix, the ultrafine AlN particles cannot infiltrate the fabric any further. Growth of the surface layer, therefore, proceeds in a later step, where the only grains whose *c*-axes are perpendicular to the substrate layer grow at above 900 °C. It is known [18] that such a structure results from sufficiently rapid surface diffusion. Since at 800 °C the diffusion is probably slow, the ultrafine AlN particles may sediment without preferring specific crystal lattice site. At lower temperatures the contribution of the heterogeneous nucleation is not negligible so that secondary growth can occur on

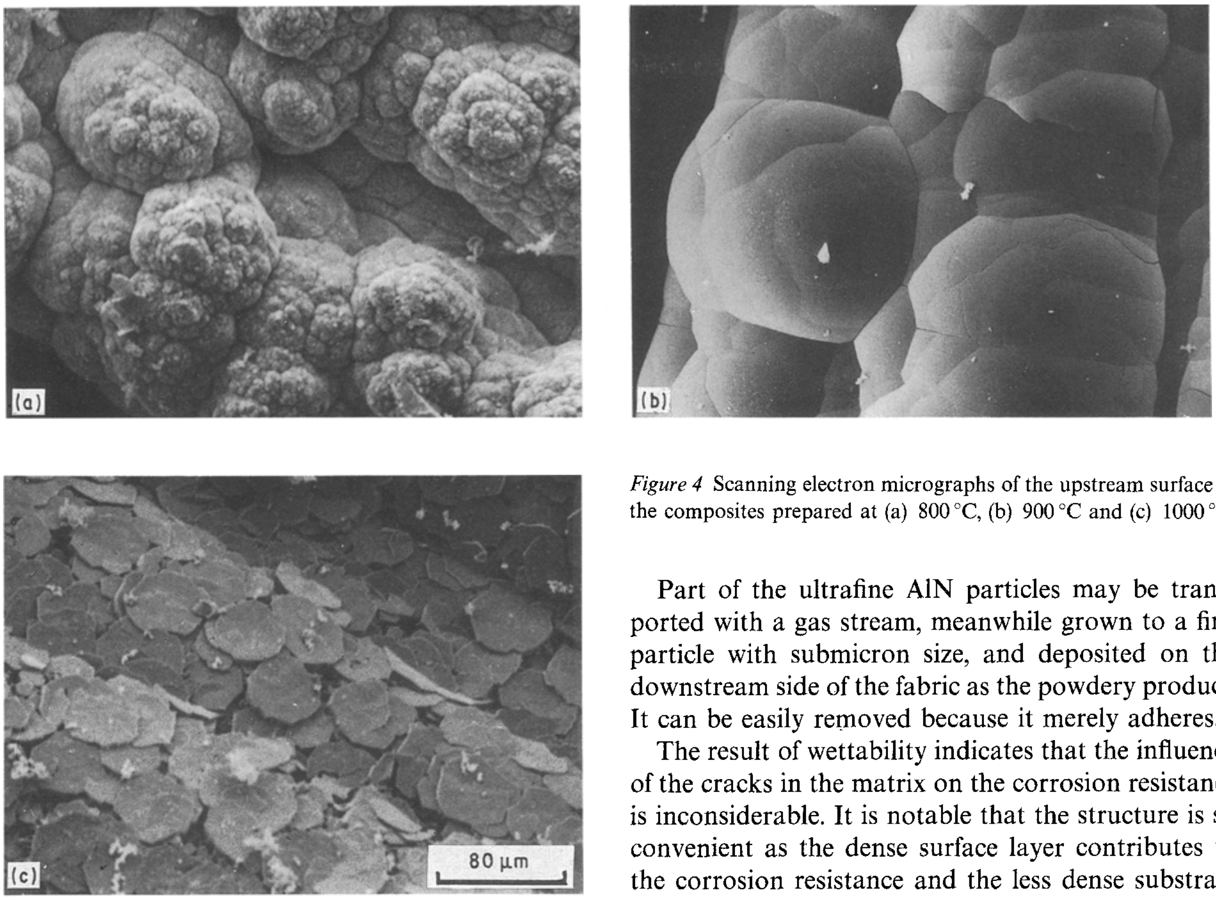

Figure 4 Scanning electron micrographs of the upstream surface of the composites prepared at (a) 800 °C, (b) 900 °C and (c) 1000 °C.

a particle produced by the homogeneous nucleation [6, 14]. The bulky deposits, in addition to the roughness of the surface, on the composite prepared at 800 °C are formed most likely owing to the secondary growth.

Part of the ultrafine AlN particles may be transported with a gas stream, meanwhile grown to a fine particle with submicron size, and deposited on the downstream side of the fabric as the powdery product. It can be easily removed because it merely adheres.

The result of wettability indicates that the influence of the cracks in the matrix on the corrosion resistance is inconsiderable. It is notable that the structure is so convenient as the dense surface layer contributes to the corrosion resistance and the less dense substrate layer contributes to the light weight. These suggest the possibility of the composites being applicable as new crucible materials or chemical insulators.

5. Conclusion

The composites prepared in this study consisted of two regions, the surface layer and the substrate layer.

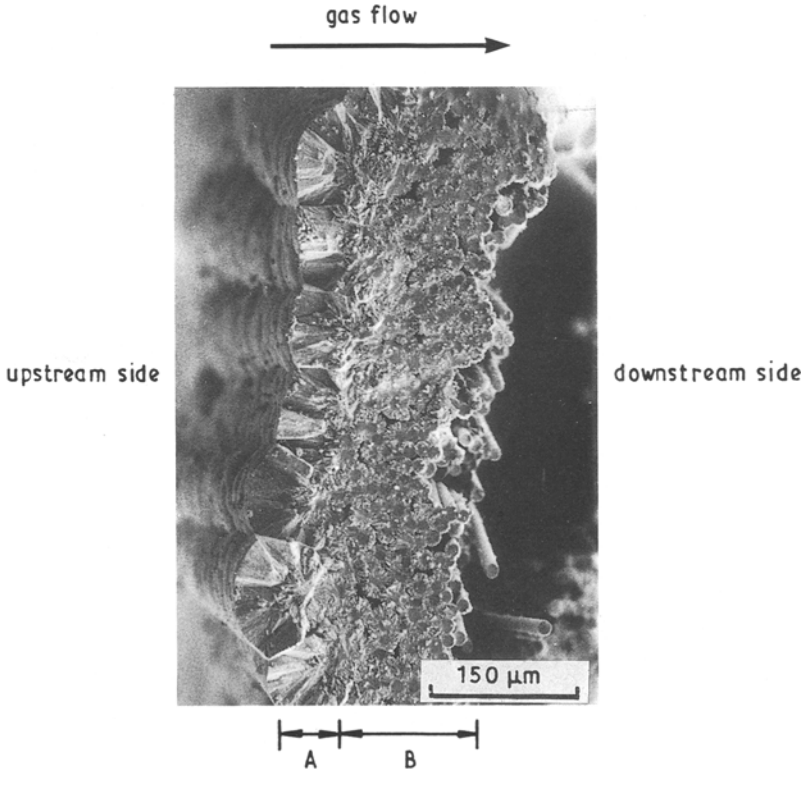

Figure 5 Scanning electron micrograph of the cross section of the composite prepared at 900 °C. (A) substrate layer, (B) surface layer.

The surface layer was a dense AlN film, and it showed little wettability with a molten alloy. The substrate layer was composed of Al_2O_3 fibres, surrounded with an AlN matrix. Some voids, existing in it, suggest that the strength of the composite would not be so high as that of materials made by CVI reported previously. This, however, is not disappointing at all, because outstandingly high strength is not necessarily demanded for the purpose of this study. If anything, they may contribute to the lightweight nature of the composite.

Although the composites obtained were tabular in shape, they do not have to be limited to simple shapes. Preforming the ceramic fabric will enable them to have any shape. This is one advantage of using CVI.

Acknowledgement

The authors thank Denki Kagaku Kogyo K. K. for supplying the Al_2O_3 fabric.

References

1. H. OHNO, *J. Jpn Soc. Dental Appar. Mater.* **17** (1976) 297.
2. H. OHNO, *ibid.* **17** (1976) 313.
3. M. KANATANI, S. NOMURA, K. ISHIOKA, N. HOTTA and I. KIMURA, *J. Jpn Prosthodont. Soc.* **32** (1988) 43.
4. M. KANATANI, S. NOMURA, K. ISHIOKA, N. HOTTA, I. KIMURA and T. KANATANI, *Quintessence Dental Technol.* **13** (1988) 289.
5. M. KANATANI, S. NOMURA, K. ISHIOKA, N. HOTTA and I. KIMURA, *J. Jpn Prosthodont. Soc.* **33** (1989) 64.
6. G. LONG and L. M. FOSTER, *J. Amer. Ceram. Soc.* **42** (1959) 53.
7. K. M. TAYLOR and C. LENIE, *J. Electrochem. Soc.* **107** (1960) 308.
8. S. MATSUO, K. KOMEYA and Y. MATSUKI, *Yogyo-Kyokai-Shi* **73** (1965) 73.
9. I. KIMURA, N. HOTTA, H. NUKUI, N. SAITO and S. YASUKAWA, *J. Mater. Sci.*, **24** (1989) 4076.
10. K. NIIHARA and T. HIRAI, *ibid.* **11** (1976) 593.
11. A. J. NOREIKA and D. W. ING, *J. Appl. Phys.* **39** (1968) 5578.
12. W. M. YIM, E. L. STOFKO, P. J. ZANZUCCI, J. I. PANKOVE, M. ETTENBERG and S. L. GILBERT, *ibid.* **44** (1973) 292.
13. M. P. CALLAGHAN, E. PATTERSON, B. P. RICHARDS and C. A. WALLACE, *J. Cryst. Growth* **22** (1974) 85.
14. J. BAUER, L. BISTE and D. BOLZE, *Phys. Status Solidi A* **39** (1977) 173.
15. E. A. IRENE, *J. Electron. Mater.* **5** (1976) 287.
16. I. KIMURA, N. HOTTA, H. NUKUI, N. SAITO and S. YASUKAWA, *J. Mater. Sci. Lett.* **7** (1988) 66.
17. I. KIMURA, N. HOTTA, H. NUKUI, N. SAITO and S. YASUKAWA, *Nippon Seramikkusu Kyokai Gakujutsu Ronbunshi* **96** (1988) 206.
18. D. P. STINTON, T. M. BESMANN and R. A. LOWDEN, *Amer. Ceram. Soc. Bull.* **67** (1988) 350.

Received 14 November
and accepted 1 December 1989