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# Preparation of Y-TZP/$Al_2O_3$ whisker preform by an *in situ* method

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*In situ* growth of $Al_2O_3$ whiskers into the matrix of Y-TZP (yttria-doped tetragonal zirconia polycrystals) was examined in order to prepare Y-TZP/$Al_2O_3$ whisker preform for the composites. Various shapes of $Al_2O_3$ particles were grown by the reaction of $Al_2O_3$ and $AlF_3$ powders with moist nitrogen or oxygen gases at high temperature. They showed a trend to change the particle shapes from massive → rhombohedron → whisker → platelet as the processing temperature was increased. These particles, however, grew only on the surface and not inside the pellets It was found necessary to introduce the carrier gas inside the pellets for particle growth to occur internally. $Al_2O_3$ whiskers can be synthesized inside the pellets by mixing with an organic space-forming agent having a relatively large particle size.

## 1. Introduction

It is well known that ceramics composites containing dispersed highly anisotropic particles such as whiskers or platelets, show enhancement of fracture toughness owing to the toughening mechanisms of crack deflection and/or pull-out of whiskers [1]. Therefore, a variety of composites have been examined to date which are mainly prepared by a conventional mixing method. Recently, some attempts have been made to develop a new process using an *in situ* chemical reaction to form the required shape of particles in the specimens. Yamada *et al.* [2] prepared a mixture of $Si_3N_4$ powders and SiC whiskers by an *in situ* method; this mixture was used as starting material for the preparation of $Si_3N_4$/SiC whisker composites. Amorphous $SiO_2$ and carbon black were used as the raw materials for the SiC whiskers which were mixed with NaCl (a space-forming agent), and $Si_3N_4$ powders. *In situ* whiskering treatment was performed at 1600 °C for 1 h and a mixture of $Si_3N_4$ powder and SiC whiskers was obtained. Okada *et al.* [3] reported the preparation of Y-TZP/mullite whisker composites by a similar method. In this case, pellets were formed from the mixed powders of mullite precursor xerogel and Y-TZP, and fired with $AlF_3$ powders in an air-tight container. *In situ* mullite whisker growth was achieved in the compacted specimens by firing at 1000–1200 °C. The whiskered specimen was further fired at higher temperatures and nearly fully dense Y-TZP/mullite whisker composites were obtained. Although the precise formation mechanism of mullite whiskers was uncertain, hydrolysis of $AlF_3$ and the formation of HF gas were considered to play an important role in whisker formation. The fracture toughness of the composites was found to show an increase with increasing aspect ratio of the mullite whiskers. Recently, an *in situ* whisker preparation method using a liquid-phase sintering process was reported in various ceramics [4–6]. The fracture toughness of $Si_3N_4$ prepared by this method was found to be enhanced from 6 MPa $m^{0.5}$ to 12 MPa $m^{0.5}$ as the diameter of the rod-like $Si_3N_4$ particles increased [4]. A certain relation was found between the fracture toughness and the size of the particles, with fracture toughness increasing proportionally to the square root of the diameter of the rod-like $Si_3N_4$ particles.

The mechanical properties of $ZrO_2/Al_2O_3$ composites have been examined by several workers [7–9] and a good level of bending strength was reported for the composites. However, the mechanical properties of the composites are unsatisfactory on two counts: first the fracture toughness, which exhibited an apparently unsatisfactory level compared with the good level of bending strength, and second, the mechanical properties of this composites which were presumed to degrade at high temperature, because both zirconia and alumina ceramics show heavy degradation of the mechanical properties at high temperature. If the dispersed $Al_2O_3$ particles were replaced by whiskers instead of equiaxed shaped particles, an improvement of fracture toughness and also high-temperature mechanical properties could be expected by the dispersion of whiskers owing to the toughening mechanisms mentioned above.

Various preparation methods have been reported for the synthesis of $Al_2O_3$ whiskers. A variety of the synthesis methods using high-temperature chemical reactions has been reported to date, including reactions between $Al_2O_3$ powders and hydrogen gas [10], aluminium metal and water vapour [11], $AlCl_3$ and water vapour [12], and $AlF_3$ and water vapour [13].

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In addition to these methods, Jagota and Raj [14] reported a unique preparation method. They prepared a thin film of alumina xerogel seeded with $\alpha$-$Al_2O_3$ fine particles by the sol–gel technique. $Al_2O_3$ whiskers, 40–60 nm in diameter and $\sim 10\,\mu m$ in length, were formed by calcination at 900–1200 °C. Among the various synthesis methods, that using the hydrolysis reaction of $AlF_3$ was considered to be the most suitable for our purpose, because the processing temperature used this method to synthesize the whiskers could be lower than in the other methods. In this work, an *in situ* whiskering technique was examined to prepare a preform of Y-TZP/$Al_2O_3$ whisker for composites.

## 2. Experimental procedure

The starting materials used were 3 mol % $Y_2O_3$-doped TZP (TZ-3Y: Tosoh Corp. Ltd) with an average particle size of 0.1–0.3 μm, high-purity $Al_2O_3$ powder (AKP-30: Sumitomo Chemicals Co. Ltd) with an average particle size of 0.3–0.5 μm, and $AlF_3$ powder (Morita Chemicals Co. Ltd). Polyethylene fibres (SK60: Toyobo Co. Ltd) and polymethylmethacrylate spheres (MBX: Sekisui Chemical Industry Co. Ltd) were used as organic space-forming agents because they burnt at relatively low temperature leaving a space in the pellets as a result. The average size of the former agent was 10 μm diameter and 1–2 mm long. The latter was spherical in shape and three particle-size ranges with average particle sizes of 5, 12 and 30 μm, respectively, were used.

The composition of the specimens was varied within the ranges of $Al_2O_3$ = 0–20 wt %, $AlF_3$ = 0–20 wt %, and Y-TZP = 60–100 wt %. The mixtures were compacted to pellets of 10 or 20 mm diameter by a uniaxial press at pressures of 2.94–98 MPa. These pellets were whiskered using two types of furnace as schematically shown in Fig. 1. The whiskering treatment was performed within the following range of conditions; firing temperature 540–1250 °C, heating rate 5 °C $min^{-1}$, duration 2 h, flow rate of a carrier gas 0–38 ml $min^{-1}$. The carrier gas was supplied directly from the cylinders and the flow rate was controlled by a needle valve. $H_2O$ vapour was introduced to the flow line by bubbling the carrier gas through water at room temperature. The carrier gas used for the synthesis was moist nitrogen in furnace A and moist oxygen in furnace B. The reason for using moist oxygen in the latter case was to burn out the organic space-forming agent dispersed in the pellets.

The outer surface and inner (fractured) surfaces of the heat-treated specimens were observed by scanning electron microscopy (MSM-9, Akashi Seisakusho Co. Ltd).

## 3. Results and discussion

### 3.1. Reaction in furnace A

The following experimental factors were examined: (1) flow rate of the carrier gas ($F_{gas}$); (2) forming pressure of the pellet ($P_{form}$); (3) $Al_2O_3$ content in the specimen ($C_{Al_2O_3}$); (4) $AlF_3$ content in the specimen ($C_{AlF_3}$); (5) firing temperature, $T_f$. The standard conditions were set at $F_{gas}$ = 19 ml $min^{-1}$, $P_{form}$ = 4.9 MPa, $C_{Al_2O_3}$ = 5 wt %, $C_{AlF_3}$ = 10 wt %, and $T_f$ = 1250 °C. In order to examine the influence of each parameter on the formation of $Al_2O_3$ particles, only one of the above parameter at a time was varied within the instrumental restrictions.

Experiments with $F_{gas}$ = 0, 4.7, 19, and 38 ml $min^{-1}$ were performed. The formation of $Al_2O_3$ whiskers, 10–30 μm long, and/or platelets of $\sim 10\,\mu m$, were observed for $F_{gas}$ = 4.7 and 19 ml $min^{-1}$, but no formation of highly anisotropic particles was observed for $F_{gas}$ = 0 and 38 ml $min^{-1}$. Therefore, it was deduced that $F_{gas}$ was not very sensitive to the particle shape of the $Al_2O_3$ particles formed but that a moderate flow

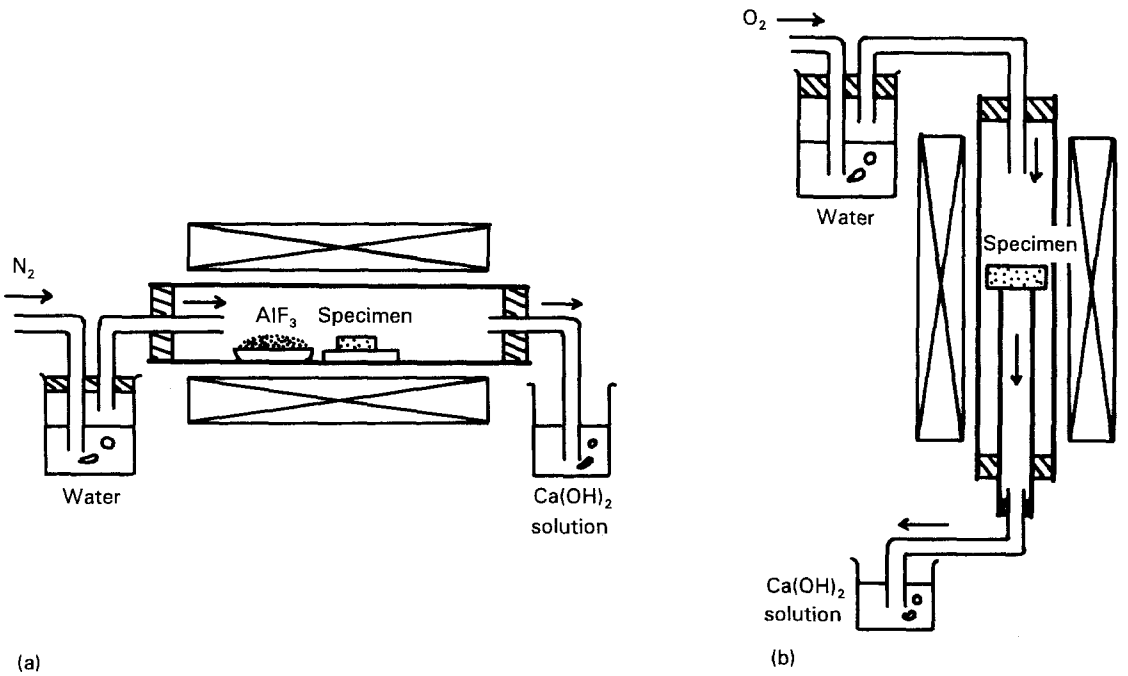


*Figure 1* Schematic illustrations of (a) furnace A and (b) furnace B used in this study.

rate of carrier gas was an appropriate condition for the formation of highly anisotropic particles. Because no highly anisotropic particles were formed for $F_{gas} = 0$, the presence of moisture was considered to be an essential condition for the growth of $Al_2O_3$ whiskers. On the other hand, the reason for no formation of whiskers under high $F_{gas}$ conditions was attributed to the rapid expenditure of $AlF_3$, which sublimed at high temperature, by the too fast flow rate of the carrier gas.

$P_{form}$ was related to the green density of the compacts and, thus, to the permeability of the carrier gas. The pellets were prepared under the four different $P_{form}$ conditions at pressures of 4.9, 9.8, 19.6, and 49 MPa.

The formation of $Al_2O_3$ whiskers was observed only in the specimen prepared at the lowest pressure, $P_{form} = 4.9$ MPa. Platy particles, together with octahedral particles (50–100 μm), were formed in the specimen prepared at $P_{form} = 9.8$ MPa. Only equiaxed particles were observed in the specimens prepared at still higher $P_{form}$ conditions. Because the green density of the specimen prepared at $P_{form} = 4.9$ MPa was low and relatively large pores remained in the pellets, it was inferred that this packing state, which had higher permeability than that prepared at higher $P_{form}$, was suitable for whisker formation.

For the $C_{Al_2O_3}$, two different contents, i.e. 5 and 20 wt %, were examined and the formation of whiskers was observed under both conditions. Therefore, the effect of this factor was decided to be small. The $AlF_3$ contents were varied as $C_{AlF_3} = 5$, 10 and 20 wt %. For $C_{AlF_3} = 5$ wt %, tiny whiskers 2–5 μm in length and equiaxed massive particles around 5 μm in size were formed. Whiskers 10–20 μm long were obtained for $C_{AlF_3} = 10$ wt %. The formed particle shape changed to platelets, 5–10 μm in size, as $C_{AlF_3}$ increased to 20 wt %. Therefore, the $C_{AlF_3}$ content was found to influence particle shape, but the $C_{Al_2O_3}$ did not.

The $T_f$ values examined were 540, 610, 940, 1020, 1150, and 1250 °C. The shapes of the formed particles changed considerably on changing $T_f$. Fig. 2 shows scanning electron micrograph of the surface of specimens treated at various temperatures. The formation of the whiskers was recognized in specimens prepared at 940, 1020 and 1150 °C. In particular, the whiskers were dominantly formed in the specimen prepared at $T_f = 1020$ °C. This formation condition was very different on various points from that reported by Hayashi *et al.* [13]. For example, the water vapour pressure they examined ranged from $8 \times 10^{-3}$ to $5 \times 10^{-1}$ torr (1 torr = 133.322 Pa), in which the optimum value was $1 \times 10^{-1}$ torr, whereas that used here was around 18 torr and much higher than the values reported by Hayashi *et al.* [13]. The synthesis experiments of Hayashi *et al.* [13] were all performed at 1400 °C although the principal sublimation reaction of $AlF_3$ started to occur as low as ~ 800 °C. The much higher partial pressures of $H_2O$ and $AlF_3$ atmospheres in this study compared with that reported by Hayashi *et al.* [13] were considered to be effective in lowering the formation temperature of the whiskers. From TEM observation, these whiskers were revealed to be elongated to ⟨1 0 0⟩ and the developed side plane was {0 0 1}. Four types of orientation relations for $Al_2O_3$ whiskers have been reported [15]. Their elongation directions were ⟨0 0 1⟩ in the C type, ⟨1 1 0⟩ in the $A_1$ type, ⟨1 0 0⟩ in the $A_2$ type, and ⟨1 1 3⟩ in the A/C type. The whiskers obtained in this

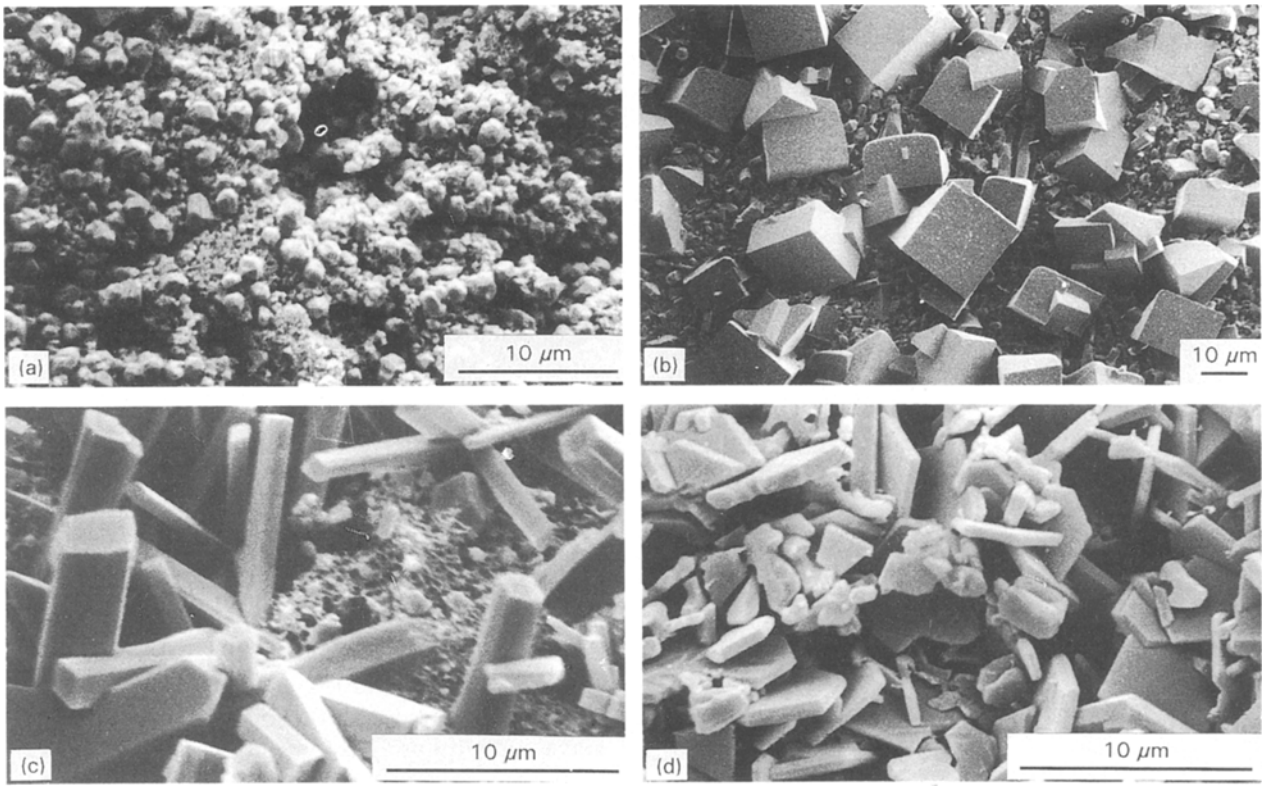


*Figure 2* (a–d) Scanning electron micrographs of the surface of specimens after whisker treatment at various firing temperatures. (a) 610 °C, (b) 940 °C, (c) 1020 °C, (d) 1150 °C.

study were, therefore, found to be grouped to the $A_2$ type. Under the low $T_f$ conditions, equiaxed particles were formed dominantly and the formation of cube-like rhombohedral particles was observed in the specimen prepared at $T_f = 940\,°C$. The crystal planes of these particles were found to be indexed by the {1 0 1}. On the other hand, platy particles were dominantly formed in specimens prepared under high $T_f$ conditions. The developed basal plane of these particles was {0 0 1}. As a result, these data are summarized in relation to $T_f$ as shown in Fig. 3. A certain trend of particle shape change with $T_f$ can be observed: massive → rhombohedron → whisker → platelet in turn, as $T_f$ increases.

During the whiskering treatment, no obvious particle-shape change was observed for Y-TZP throughout this study. However, grain growth of $ZrO_2$ was sometimes observed after treatment at high temperatures above 1200 °C. A considerable amount of $ZrO_2$ was found to transform to the monoclinic phase from the tetragonal phase in the specimens treated at that temperature. Therefore, it was necessary to avoid whiskering treatment at temperatures higher than 1200 °C.

The refractory materials used in the reactor, which was exposed to the corrosive gases at high temperature, were alumina ceramics made from high-purity alumina. HF gas evolved in the reaction was especially corrosive and reactive to the silica component. Therefore, when mullite ceramics were used instead of alumina ceramics, the corrosive gases attacked the mullite and contamination of the $SiO_2$ component occurred in the specimens. The formation of zircon and also mullite was observed in the specimens in this case. The lower temperature region in the reactor was sometimes contaminated with glassy phase for the same reason. Although the exact formation mechanism was uncertain, sometimes very large and thin films of zirconia, as shown in Fig. 4, were formed on the surface of the specimens. They were flexible and easily curved because they were very thin.

Thus, the formation of $Al_2O_3$ whiskers was achieved in this study, although the optimum experimental conditions required to form the whiskers were largely different from those reported elsewhere [13]. However, the highly anisotropic particles formed were

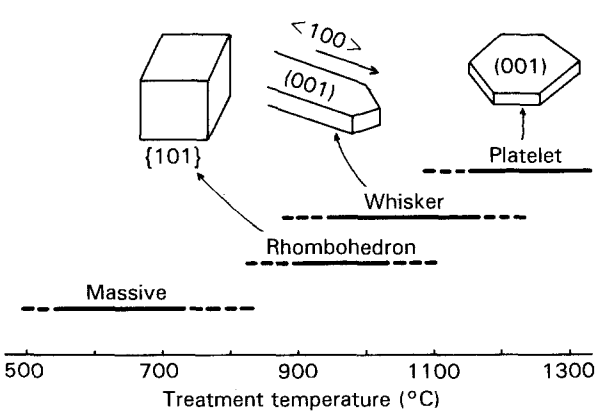


*Figure 3* Relationship between the particle shapes formed and the firing temperature.


*Figure 4* Scanning electron micrograph of the surface of a specimen treated using a mullite tube.

mostly restricted to the vicinity of the surface of the specimens and little formation of highly anisotropic particles was observed in the interior of the specimens. One main reason for this result may be the difficulty of carrier gas penetration into the pellets under these experimental conditions. Therefore, different type of reactor was considered in an attempt to improve this result.

## 3.2. Reaction in furnace B

In order to introduce the carrier gas into the specimen pellets, a second furnace, B, as shown in Fig. 1, was designed. In this reactor the specimens were placed on the inner tube and the carrier gas flowed from the top to the bottom of the reactor in order to introduce it into the interior of the specimen. The experiments were performed for specimens with and without space-forming agents.

Experiments for specimens without space-forming agent were performed under the following conditions: $F_{gas}$ 2–19 ml min$^{-1}$; $P_{form}$ 2.94–98 MPa; $C_{AlF_3}$ 10 and 20 wt % ($C_{Al_2O_3} = 30 - C_{AlF_3}$); $T_f$ fixed at 1100 °C. In order to raise the gas permeability of the specimens, it was necessary to decrease the green density of compaction by forming under low $P_{form}$ conditions. However, the compactions prepared under such conditions broken into two and/or into pieces owing to the pressure of the carrier gas flow. On the other hand, if the compacts were prepared under high $P_{form}$ conditions, highly anisotropic shaped particles were not formed inside these specimens. The carrier gas was considered to pass through the small openings between the specimens and the tube of the reactor because the gas permeability of these compacts was too low. No appropriate conditions for the formation of highly anisotropic particles were found for the specimens without space-forming agent.

The next trial was performed for specimens mixed with polyethylene fibres as a space-forming agent. Because this agent had a very high aspect ratio, with 10 μm in diameter and 1–2 mm length, and its density was low compared with the mixed powders of $Al_2O_3$ and Y-TZP, it was quite difficult to mix them properly by a conventional mixing method. Mixtures up to only 1.5 vol % polyethylene fibres could be prepared in this case. After the whiskering treatment of the

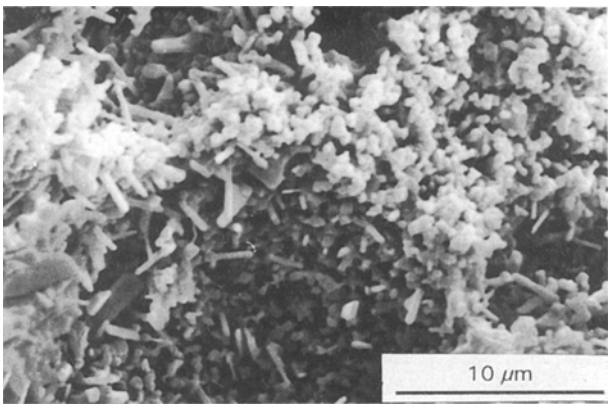


*Figure 5* Scanning electron micrograph of the inside of the specimen with organic spherical particles 30 μm in size after whisker treatment.

compacts formed at $P_{form} = 98$ MPa and firing under $F_{gas} = 4.5$ ml min$^{-1}$, whiskers 10–20 μm long and also thick platelets around 10 μm in size, were observed in the walls of pores formed by burn out of the organic fibres.

Particles were found to be obtained by mixing with organic fibres as the space-forming agent; however, this method had the disadvantage of preparing a uniform mixture of organic fibres and ceramic powders. Organic spheres were used instead of the fibres for this purpose. They were made of polymethylmethacrylate and the sizes of the spherical particles were 5, 12 and 30 μm diameter. In these cases the organic particles were able to mix up to several tens of volume per cent. Even on mixing with organic particles, no highly anisotropic particles were formed in the inside of the specimen when the size of the organic particles was small. The formation of whiskers was observed when the size of the organic particles used became larger. Fig. 5 shows a scanning electron micrograph of the inside of the specimen after the whiskering treatment. A large number of $Al_2O_3$ whiskers was found to be randomly distributed in the matrix of Y-TZP particles. The length of whiskers formed was around several micrometres, but longer sizes are required. This could be achieved by preparation under slower $F_{gas}$ conditions.

## 4. Conclusion

Preparation of preforms of Y-TZP/$Al_2O_3$ whisker was examined by an *in situ* method.

Various shapes of $Al_2O_3$ particles were formed by the *in situ* reaction with a mixture of $AlF_3$, $Al_2O_3$ and Y-TZP powders and moist nitrogen or oxygen gases at high temperature. Particle shapes were found to change following a certain trend: massive → rhombohedron → whisker → platelet as the firing temperature was increased. The $Al_2O_3$ whiskers obtained were found to elongate to ⟨1 0 0⟩ and belonged to the $A_2$ type.

To form highly anisotropic $Al_2O_3$ particles in the inside of the specimens, it was necessary to use an organic space-forming agent to increase the gas permeability of the specimen pellets to allow the carrier gas to enter the pellets. The formation of whiskers became easier when using the larger organic spherical particles instead of fibres and smaller spheres.

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## References

1. K. T. FABER and A. G. EVANS, *Acta Metall.* **31** (1983) 577.
2. S. YAMADA, S. KIMURA, E. YASUDA, Y. TANABE and Y. ASAMI, *J. Mater. Res.* **3** (1988) 538.
3. K. OKADA, N. OTSUKA, R. J. BROOK and A. J. MOULSON, *J. Am. Ceram. Soc.* **72** (1989) 2369.
4. A. MIYAMOTO, *Kogyo-Zairyo* **38** (1990)
5. T. MORI, T. ARAKAWA and S. HIGUCHI, *J. Ceram. Soc. Jpn* **96** (1988) 744.
6. W. S. COBLENZ and D. LEWIS III, *J. Am. Ceram. Soc.* **71** (1988) 1080.
7. T. SATO, H. FUJISHIRO, T. ENDO and M. SHIMADA, *J. Mater. Sci.* **22** (1987) 882.
8. M. KIMURA, T. OGATA, K. NAKAMURA and K. KOBAYASHI, *J. Ceram. Soc. Jpn* **96** (1988) 646.
9. S. RAJENDRAN, M. V. SWAIN and H. J. ROSSEL, *J. Mater. Sci.* **23** (1988) 1805.
10. R. C. DeVRIES and G. W. SEARS, *J. Chem. Phys.* **31** (1959) 1256.
11. W. W. WEBB and W. D. FORGANG, *J. Appl. Phys.* **28** (1957) 1449.
12. W. B. CAMPBELL, *Chem. Eng. Prog.* **62** (1966) 68.
13. T. HAYASHI, M. MIHOYA, I. YAMAI, H. SAITO and S. HIRANO, *J. Mater. Sci.* **22** (1987) 1305.
14. S. JAGOTA and R. RAJ, *J. Crystal Growth* **85** (1987) 527.
15. A. P. LEVITT, *Mater. Res. Stand.* **2** (1966) 64.

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