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In situ synthesis of porous ceramics with a framework structure of aluminium borate whisker

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New porous ceramics with a framework structure of aluminium borate ($9Al_2O_3 \cdot 2B_2O_3$) whiskers, in which the whiskers are distributed uniformly and randomly, can be synthesized *in situ* by firing of a green powder compact of a mixture of aluminium hydroxide, boric acid and an additive of nickel oxide above 1100 °C. During firing, the whiskers of aluminium borate grow *in situ* in the compact, and are bonded together by sintering. The porous aluminium borate consists solely of whiskers, has a porosity of 85%–50%, which corresponds to a volume fraction of whiskers of 15%–50%, and a flexural strength of 2.2–56.1 MPa. Because the whiskers are strongly bonded to other whisker(s), the problem of whiskers scattering, that can be an inhalation hazard, is solved. The aluminium alloy matrix composite using this porous aluminium borate as reinforcement was fabricated by the squeeze-casting method. The tensile strength of the composite material with a whisker volume fraction of 20% can be improved by up to about 90% compared with the unreinforced matrix alloy at 350 °C. © *1998 Chapman & Hall*

1. Introduction

Whiskers which have a strength approximately equal to the theoretical strength of perfect crystal [1–3] have been found to be very useful as reinforcement for metal matrix composites (MMCs), which are lightweight and have excellent mechanical properties, wear resistance and thermal stability [4–12].

Ceramic whiskers, such as silicon carbide, silicon nitride and aluminium borate, were synthesized by the vapour–liquid–solid (VLS) method [13–16] and flux method [17], and they were isolated from unreacted raw material or flux. Because it is difficult to incorporate uniformly extremely fine whiskers with diameters of 0.2–1 μm and an aspect ratio of about 10–100 in molten metal, whisker-reinforced MMCs have generally been fabricated by previously formed whiskers in a preform of porous body and then infiltrating molten metal under a preset pressure into the pores of the preform [8–10, 12]. The whisker preform is conventionally prepared by dispersing whiskers and a binder in water, and filtering the aqueous dispersion medium with suction, followed by drying and calcination. Because the bonding strength between the whiskers in a preform depends on the binders and is commonly not so strong, the preform tends to be deformed or cracked in the squeeze-casting processes.

In the manufacturing processes of whiskers and preforms, there is a potential inhalation hazard from the isolated whiskers [18, 19]. Studies in animals have shown a potential carcinogenic hazard from the inhalation of fibres with lengths longer than 8 μm and diameters smaller than 0.25 μm [20, 21]. If it can be related to humans, commercially available ceramic whiskers might be a serious carcinogenic hazard.

To solve the problems of the high cost of the whiskers, potential hazards in their handling, and processing difficulties, research on the *in situ* synthesis of whisker-reinforced ceramic matrix composites, such as silicon nitride whisker/silicon nitride matrix and hollandite ($K_2Al_2Ti_6O_{16}$) whisker/tielite (Al_2TiO_5) matrix, has been carried out [22–25]. Because the melting points of metal and ceramic whisker are quite different, ceramic whisker-reinforced metal matrix composites cannot easily be fabricated by using such an *in situ* synthesis method. Tarumi [26] disclosed a process for *in situ* production of mullite whisker felt, the process having succeeded in solving the problems associated with preparation of whisker preforms as far as mullite whisker is concerned. However, this process is not easy to carry out because of the involvement of additional cost for the equipment and process control, due to the calcination in a toxic anhydrous SiF_4 atmosphere. Readey [27] prepared a porous ceramic composed of whisker-like grains of aluminium borate by firing a boric acid-stabilized aluminium acetate above 1500 °C. However, this porous ceramic is not

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suitable for metal matrix composites, because the aspect ratio of length to diameter of the whisker-like grain, which affects the properties of the composites, is lower than 10, and the porosity is lower than 50%.

A new porous ceramic (called porous aluminium borate) comprised of a framework structure of aluminium borate ($9Al_2O_3 \cdot 2B_2O_3$) whiskers has been synthesized *in situ* by firing a powder compact [28]. Porous aluminium borate, which consists solely of whiskers, is a promising reinforcement for MMCs. This paper will focus on the crystal structure, microstructure and the physical properties of this new porous ceramic, and the properties of new porous ceramics reinforced aluminium alloy matrix composite.

2. Experimental procedure

To synthesize the porous aluminium borate, aluminium hydroxide and boric acid were used. In order for the aluminium hydroxide and boric acid to react at a high temperature to grow aluminium borate whiskers, the boric acid was added in excess, and nickel oxide was also added. Aluminium hydroxide, boric acid and nickel oxide additive were finely powdered and uniformly blended. The preferred mixing molar ratio for Al_2O_3 to B_2O_3 was 9:4, and the amount of the nickel oxide added was 2 wt % based on the amount of aluminium oxide. The mixed powder was put into a die and compacted. A higher compacting pressure provides a green compact having a higher density, i.e. a lower porosity. Therefore, by adjusting the compacting pressure, a porous ceramic having a density falling in the range 0.44–1.47 g cm^{-3}, which corresponds to a porosity of about 85%–50%, can be obtained. After compacting, the green compact was removed from the die, and sintered in a furnace in air. The sintering temperature necessary to synthesize aluminium borate whiskers in the compact ranges approximately from 1100–1400 °C. The thickness and the diameter of the sintered compact were about 20 and 110 mm, respectively. After cooling, the sintered body was washed with hot water to remove residual boron oxide.

The bulk density of the sintered body was estimated from the weight and the volume, and the open porosity was measured by mercury porosimetry. The whisker volume fraction and apparent porosity were estimated from the bulk and theoretical densities. The microstructures of the sintered body were determined using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The room-temperature strength was measured using a three-point bend test with a 40 mm span at a crosshead speed of 1 mm min^{-1}. Rectangular bars (7 mm × 7 mm × 60 mm) were cut from sintered compacts corresponding to each density. The tensile surface was again normal to the compacting direction and was polished. Four to six specimens of each material were broken to obtain an average strength value.

Composite material was prepared by using the resulting porous aluminium borate as reinforcement and an aluminium alloy as a matrix. The porous aluminium borate with a porosity of 80% (or a whisker volume fraction of 20%) was preheated to 800 °C and placed in a die set at 300 °C. A molten aluminium alloy JIS AC8A(JIS H 5202) was pressed into the pores of the porous aluminium borate under a pressure of 100 MPa and cooled to solidify. The resulting composite material was removed from the die and subjected to a T6 treatment (defined in JIS H 5202). Dumb-bell specimens having a diameter of 6 mm and a length (parallel portion) of 25 mm were cut out from the composite materials to determine tensile strength, and the tensile strengths were measured at room temperature and 350 °C. Specimens (5 mm × 5 mm × 10 mm) were cut out along the pressing direction and the perpendicular direction (perpendicular to the surface of the sintered compact) to determine the coefficient of thermal expansion.

3. Results and discussion

3.1. X-ray diffraction

The crystal structures of calcined compacts and sintered compacts were characterized by the powder X-ray diffraction method, and the patterns are shown in Fig. 1. Calcination and sintering produced a number of changes in the XRD pattern. When the compact was calcined to 500 °C for 3 h, only a trace of NiO was detected, and the result indicated that the compact was amorphous (Fig. 1a). By raising the calcination temperature, the reaction between non-crystalline aluminium oxide and molten boron oxide took place, and the mixture peaks of $9Al_2O_3 \cdot 2B_2O_3$ and $2Al_2O_3 \cdot B_2O_3$ were confirmed in samples B and C, which were fired at 800 and 1000 °C for 3 h, respec-

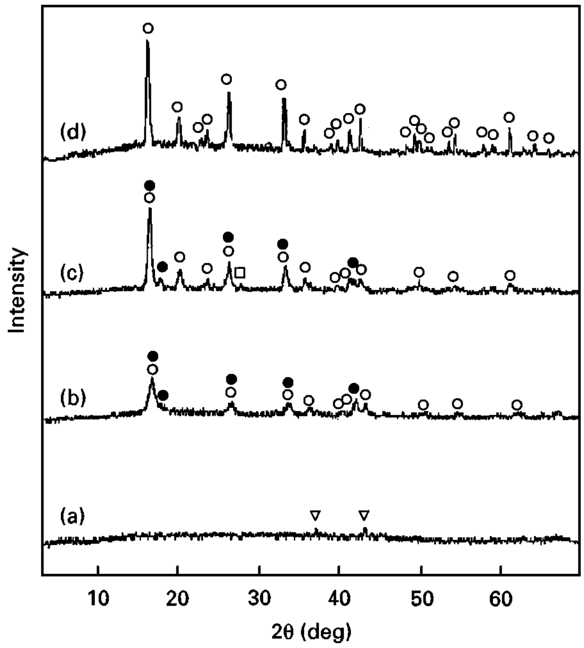

Figure 1 XRD pattern for samples fired to (a) 500 °C, (b) 800 °C, (c) 1000 °C for 3 h and (d) 1250 °C for 6 h samples A to D, respectively. In sample A, except for a trace of NiO (▽) no other phases are detected, and the result indicates this sample is amorphous. (○) $9Al_2O_3 \cdot 2B_2O_3$ and (●) $2Al_2O_3 \cdot B_2O_3$ are detected in samples B and C, but only $9Al_2O_3 \cdot 2B_2O_3$ is detected in sample D. (□) B_2O_3.

tively (Fig. 1b and c). The peaks became much stronger at higher calcination temperature, but the peaks of $9Al_2O_3 \cdot 2B_2O_3$ were overlapped by the peaks of $2Al_2O_3 \cdot B_2O_3$. In sample D, which was sintered at 1250 °C for 6 h (Fig. 1d), only $9Al_2O_3 \cdot 2B_2O_3$ was confirmed, and the crystal structure was orthorhombic. Gielisse and Foster's phase diagram [29] showed that $9Al_2O_3 \cdot 2B_2O_3$, which has a high melting point (1950 °C), was in equilibrium with a B_2O_3 liquid above 1035 °C, and $9Al_2O_3 \cdot 2B_2O_3$ and $2Al_2O_3 \cdot B_2O_3$ were solid phases in equilibrium below 1035 °C in the present Al/B molar ratio, but $9Al_2O_3 \cdot 2B_2O_3$ was stable with excess molten boron oxide during cooling. However, if the mixing ratio (Al/B) was lower than 9/6, or the resident temperature was 1035 °C or below during cooling, $2Al_2O_3 \cdot B_2O_3$ would be crystallized.

3.2. The microstructure of porous aluminium borate

The microstructure of compacts sintered from 1100–1400 °C was observed by SEM, and whiskers (needle-shaped crystals) of aluminium borate ($9Al_2O_3 \cdot 2B_2O_3$) were found in all samples. Fig. 2 shows the microstructure of compacts which were sintered at 1200–1300 °C for 6 h with a density of about 0.59 g cm^{-3}. The average diameters of the whiskers increased with increasing sintering temperature, and reached 0.3, 0.6 and 1.1 μm when sintered at 1200, 1250 and 1300 °C, respectively. The average length of whiskers also increased with increasing sintering temperature, but the length increased slightly when sintered above 1300 °C. The length of the whiskers reached 10–30 μm, and the aspect ratio of the length to diameter of whiskers was 15–50 for porous aluminium borate sintered at 1250 °C for 6 h. In the presence of excess melt of boric oxide and added nickel oxide, aluminium borate crystals, having a composition of $9Al_2O_3 \cdot 2B_2O_3$ grew into whiskers when the compact was fired above 1035 °C. The nuclei of the whiskers were nucleated uniformly throughout the compact, and the distribution of whiskers was quite random in three dimensions. Because whisker growth proceeded within a dense compact, a growing whisker came in contact with another whisker, and thus a bond was formed at the contact point, and the bond strength was enforced by subsequent whisker growth; such a structure was a characteristic feature of this framework structure. Unless nickel is added, the aluminium oxide and the boron oxide can also react at high temperature to form needle-like grains of aluminium borate ($9Al_2O_3 \cdot 2B_2O_3$), but the aspect ratio of the length to diameter is lower than 10.

Fig. 3 shows the microstructures of compacts sintered at 1250 °C for 6 h with bulk densities of about 1.16 and 1.51 g cm^{-3} (whisker volume fraction of about 40% and 50%), and indicates that the size of the whiskers did not change when compacted to higher density, but the size of pores decreased with increasing bulk density of porous aluminium borate.

3.3. Physical properties

After reaction at high temperatures, the sintered compact was allowed to cool to provide a porous ceramic

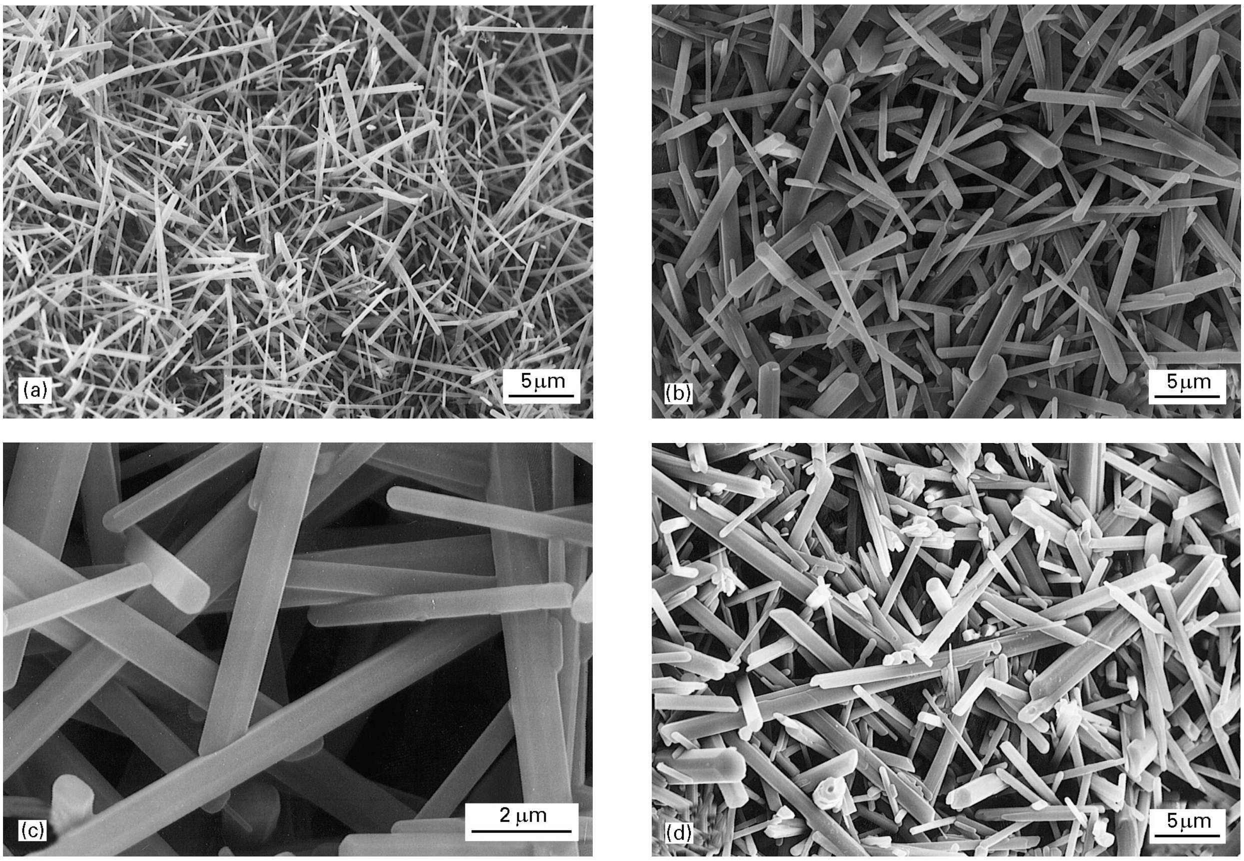

Figure 2 Scanning electron micrographs of compacts sintered at (a) 1200 °C, (b, c) 1250 °C, (d) 1300 °C for 6 h (samples A–D, respectively).

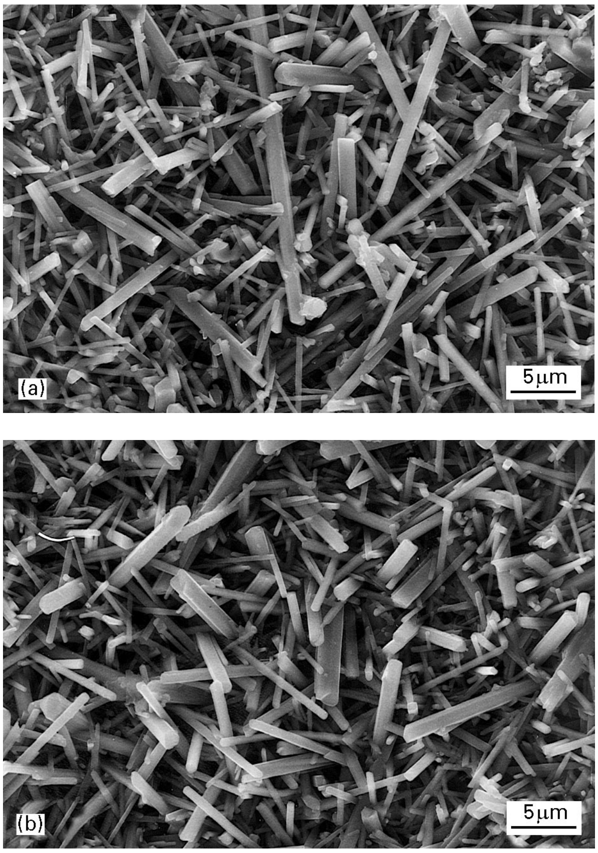

Figure 3 Scanning electron micrographs of sintered compacts with a density of (a) 1.16 g cm^{-3} and (b) 1.51 g cm^{-3}.

composed of aluminium borate whiskers only. The resulting porous aluminium borate had substantially the same geometry as the green compact before firing. The shrinkage due to structural change was about 10% at most. In this method, by adjusting the density of the green compact from 0.34–1.27 g cm^{-3} and sintering the green compacts at 1250 °C for 6 h, porous aluminium borate with a density in the range 0.47–1.51 g cm^{-3}, which corresponds to porosity of about 84.3%–48.6%, was obtained. The density for green compacts, and bulk density, whisker volume fraction, apparent porosity and open porosity for sintered compacts, are shown in Table I. The whisker volume fraction and the apparent porosity were calculated from the theoretical density (2.93 g cm^{-3}) of aluminium borate [30] and the bulk density of sintered compacts, and the open porosity was measured by the mercury porosimetry method. Because the apparent porosity is almost equal to the open porosity, all of the pores existing in the porous aluminium borate are open pores, indicating that the aluminium borate is very suitable for metal matrix composites.

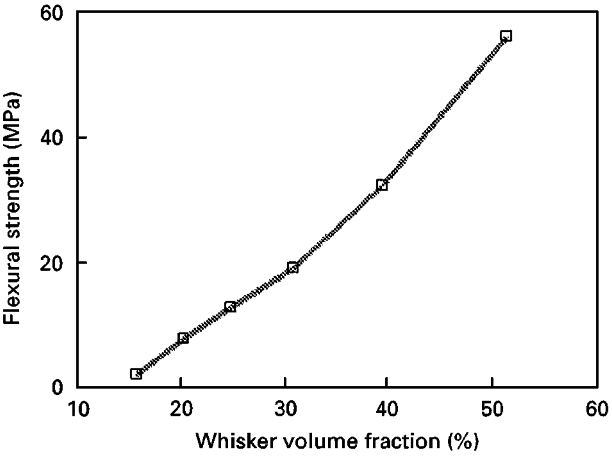

Figure 4 Flexural strengths of porous aluminium borate for different whisker volume fractions.

The bending test was used to evaluate the load–deformation behaviour and mechanical properties of the porous aluminium borate and to relate the effect of the whisker volume fraction to the properties of the porous aluminium borate. Porous aluminium borate with a whisker volume fraction from 15%–50% were tested. The load–deformation diagrams of all samples showed a linear behaviour, and porous aluminium borate failed in a brittle manner. Fig. 4 shows the flexural strength for porous aluminium borate. Each point in Fig. 4 represents the average flexural strength. Strength increased with increasing whisker volume fraction, and ranged from 2.2–56.1 MPa for a whisker volume fraction of 15.7%–51.4%.

Without the addition of NiO, porous aluminium borate with a bulk density of 0.59 g cm^{-3} could also be obtained, but the strength was only 1.2 MPa. As can be seen from Fig. 4, the strength of the new porous aluminium borate, with the same bulk density, was 7.9 MPa. The result indicated that the addition of NiO not only accelerated the growth of the whiskers, but also enhanced the bonding strength between the whiskers. The porous aluminium borate exhibits a very high bonding strength between the whiskers, and would never cause any inhalation hazard.

3.4. The mechanical properties of porous aluminium borate–reinforced aluminium alloy matrix composite

Porous aluminium borate with a whisker volume fraction of 20% reinforced AC8A matrix composite (called new MMC) was prepared by squeeze casting.

TABLE I Sintering behaviours and the porosity of new porous ceramics

Density of green compact (g cm^{-3})	0.34	0.45	0.57	0.78	0.99	1.27
Bulk density of sintered compact (g cm^{-3})	0.47	0.60	0.73	0.93	1.16	1.51
Whisker volume fraction (%)[a]	15.7	20.2	24.8	31.7	39.7	51.4
Apparent porosity (%)[a]	84.3	79.8	75.2	68.3	60.3	48.6
Open porosity (%)[b]	84.2	80.5	75.5	69.4	61.0	48.6

[a] Calculated from the theoretical density and the bulk density of sintered compact.

[b] Measured by mercury porosimetry.

On observing the macrostructure of the new MMC, no deformation nor cracks were found, and whiskers were distributed uniformly in the matrix. The average tensile strengths of the new MMC and the AC8A alloy were measured, respectively, as 315 and 285 MPa, at room temperature, and as 162 and 85 MPa at 350 °C. The tensile strengths of the composite material were improved by up to about 10% and 90% compared with the unreinforced matrix alloy at room temperature and 350 °C, and the improvement was more pronounced at elevate temperature. This seems to be because of the higher strength and excellent thermal stability possessed by the porous aluminium borate *per se*.

The thermal expansion coefficients of new MMC and AC8A alloy have been measured using thermomechanical analysis (TMA) in the temperature range between room temperature and 600 °C. The TMA measurements reveal that the AC8A alloy was softened when heated to 555 °C, but no softening point was found in the new MMC until 600 °C. For the new MMC and AC8A alloy, the thermal expansion coefficients of the pressing direction were 17.2, 21.3, and the thermal expansion coefficients of the perpendicular direction were 17.2, 21.2×10^{-6} °C^{-1} in the 25–300 °C range, respectively. The new MMC shows a relatively smaller thermal expansion coefficient than AC8A alloy, and also no directional difference of the thermal expansion coefficient was found. The new MMC, which has high strength, low coefficient of thermal expansion and perfect isotropy, is very suitable for automotive components.

4. Conclusion

A porous ceramic, composed of aluminium borate whiskers, has been obtained through a simple process comprising compacting a mixture of inexpensive raw materials and sintering the green compact, in which the aluminium borate whiskers are distributed uniformly and randomly, and the individual whiskers are strongly bonded to each other at one or more sites. All the problems associated with the conventional process which arise from scattering of whiskers causing an inhalation hazard and uneven distribution or orientation of whiskers, are solved. Because the product density can be controlled simply by adjusting the green density of the compact or the compact pressure, it is easy to obtain the product density in accordance with the end use. The MMC using the porous aluminium borate as reinforcement has a high strength and low thermal expansion coefficient and by controlling the whisker volume fraction of the composite the physical properties such as strength, coefficient of thermal expansion and wear resistance, can also be varied to suit the specific application. *In situ* synthesized porous ceramics with a framework structure of aluminium borate whiskers, must be a promising material for application as a reinforcement for composites, a structural material for high temperature use, a heat insulating material, or a filter medium.

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