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Effect of grain size distribution on the strength of porous Si_3N_4 ceramics composed of elongated β-Si_3N_4 grains

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The grain size distributions (diameter and aspect ratio) of porous Si_3N_4 ceramics composed of elongated β-Si_3N_4 grains were evaluated statistically, and their effect on the pore size distribution and the flexural strength of the porous Si_3N_4 was investigated. Porous Si_3N_4 ceramics having porosities of 27 to 43% and median pore diameters of 0.56 to 0.96 μm were used as specimens. The grain diameter distribution was well correlated to the pore size distribution of the porous Si_3N_4 ceramics. We concluded that the strength of the porous Si_3N_4 ceramics increased with increasing grain length of β-Si_3N_4 as well as with decreasing porosity. *© 2001 Kluwer Academic Publishers*

1. Introduction

Ceramic materials such as Si_3N_4, ZrO_2 and Al_2O_3 have been used as a variety of engineering materials such as automotive parts and cutting tools due to their high strength and high hardness. The serious disadvantage of such ceramics is the difficulty in machining after sintering, which leads to high machining cost. To decrease such cost, various ceramics which can be machined with cemented carbide or high-speed steel tools, called machinable ceramics, have been developed. Typical machinable ceramics are mica-based glass ceramics [1–6], which are composites made of whisker-like or plate-like crystallized mica and glass matrix. The glass ceramics have machinability because cracks introduced in machining are inhibited from propagating by the crystallized grains.

Some properties are required to apply machinable ceramics to engineering use, one of which is high mechanical strength. Additionally, if they are used under high temperature, high thermal shock resistance is also necessary. However, the mechanical strength of glass ceramics is insufficient for engineering applications. The use of porous bodies is means to reduce machining cost since porous ceramics are clearly machinable ceramics. However, the strength of porous ceramics is also insufficient for engineering applications, since it decreases significantly with the increase in porosity.

We consider that there are typically four factors which determine the strength of porous ceramics: porosity, pore size, the intrinsic strength of the materials (grain and grain boundary) and microstructure. Regarding porosity, it is widely known that the strength decreases exponentially with increasing porosity. In terms of pore size, the increase in pore size decreases strength since pores in the porous bodies can be estimated as defects. The third factor is basically governed by the bonding strength between atoms constituting the materials. Ceramics such as Si_3N_4 and SiC are expected to be high-strength porous ceramics due to their strong covalent bonding between each atom. Especially, Si_3N_4 is a typical engineering ceramic having both high specific strength and high fracture toughness. It is widely known that sintered Si_3N_4 ceramics are composed of elongated β-Si_3N_4 and spherical α-Si_3N_4 grains, and their high strength is attributed to the former.

Focusing on the fact, we developed a technique for selective grain growth of β-Si_3N_4 in the fabrication of porous Si_3N_4 by the powder metallurgy [7]. The strength of porous Si_3N_4 ceramics having such microstructure was much more substantial than that of porous Si_3N_4 having another microstructures, and they were easily machined with cemented carbide drills [7]. We presume that the high strength is caused by high fracture toughness generated by the three-dimensional connection of elongated β-Si_3N_4 grains. To our knowledge, however, the effect of fracture toughness on the strength of porous ceramics has not been clarified, because the measurement of the fracture toughness of porous ceramics is difficult. Commonly, the fracture toughness of sintered Si_3N_4 ceramics increases with increasing the aspect ratio of the elongated grains. It is possible that the dimensions of the elongated grains constituting the porous Si_3N_4 are also closely related to the fracture toughness, although it is difficult to measure the fracture toughness directly. In this paper, we report the effect of the grain size (diameter and aspect ratio) of β-Si_3N_4 grains on the pore size and the strength of the porous Si_3N_4, and discuss factors governing the strength.

2. Experimental procedure

A powder mixture of α-Si_3N_4 (SN-E10, Ube Co. Ltd, Tokyo Japan) and a small amount of Er_2O_3 (Shin-etsu Kagaku Co. Ltd, Tokyo Japan) sintering aid was used

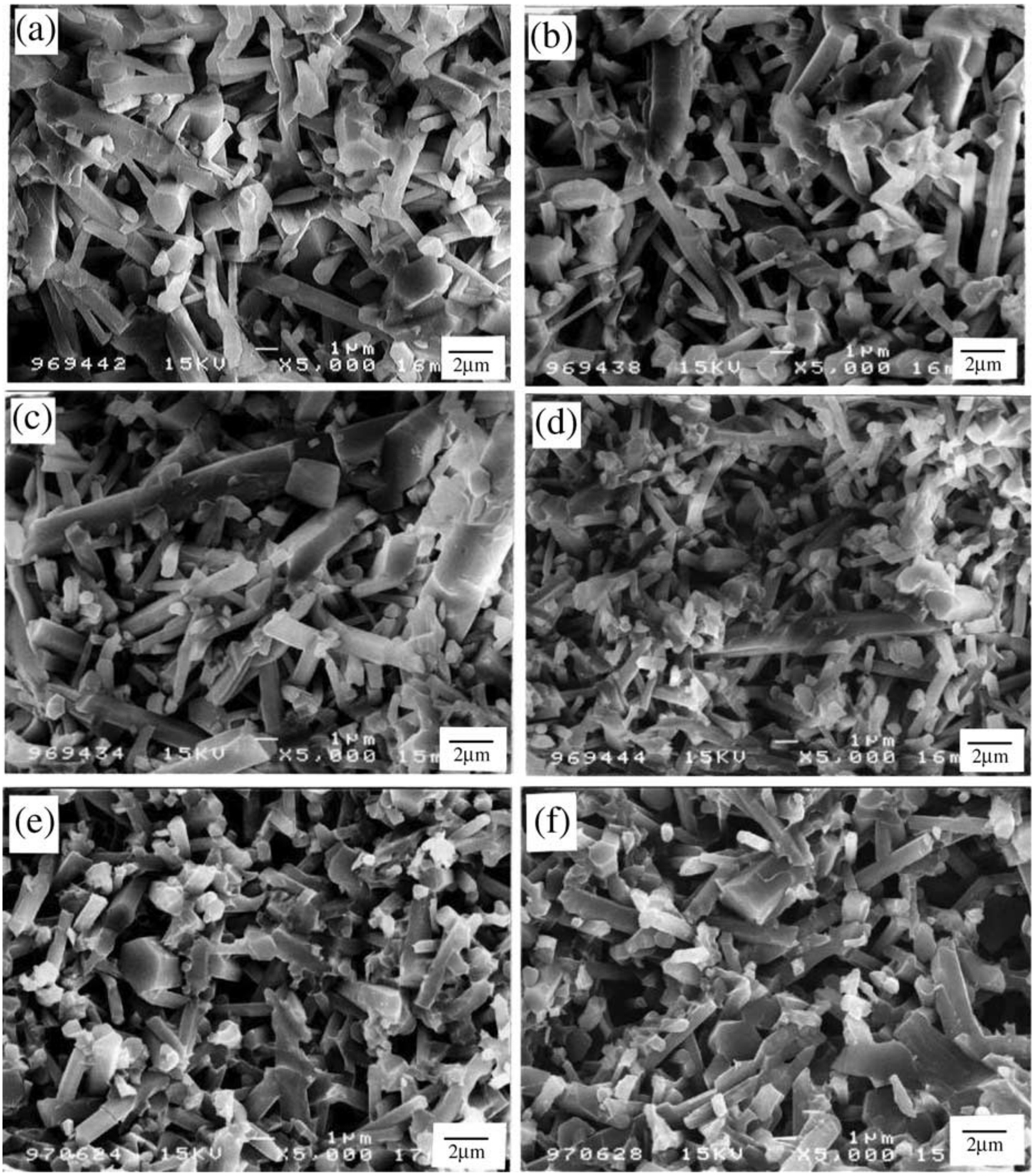

Figure 1 SEM micrographs of porous Si_3N_4 having porosities and flexural strengths of (a) 43.1%, 307 MPa, (b) 39.0%, 359 MPa, (c) 35.3%, 449 MPa, (d) 28.7%, 475 MPa, (e) 30.3%, 366 MPa and (f) 33.7%, 323 MPa.

as the starting powder. It was pressed to the dimensions of 45 mm square and 5 mm thick. The resulting powder compact was sintered various conditions. Thus, 6 kinds of porous Si_3N_4 specimens having porosities of about 27 to 43% were obtained. Where, porosity was calculated using a theoretical density of 3330 kg/m^3.

X-ray diffraction was performed for phase identification. The specimens were subjected to measurements of flexural strength (3-point bending strength), in which $3 \times 4 \times 40$ mm test pieces were employed. Ten numbers of test pieces per a kind of specimen were measured and their average strengths were calculated. After the bending test, the microstructure of the fracture surfaces of specimens was observed with a scanning electron microscope (SEM). Pore size distribution was measured by mercury porosimetric analysis.

Measurement of the grain size distribution of elongated β-Si_3N_4 grains was carried out referring to a method reported by Nagaoka *et al.* [8]. Specimens after the bending test were crushed roughly, then soaked in 5% aqueous solution of hydrofluoric acid (HF) at 90°C for 10 hr to dissolve grain boundary phases between the Si_3N_4 grains. The resulting suspensions of the grains were washed with fresh water, then small amounts of suspensions were dropped on the surface of a slide glass. After drying, the grains were observed with the SEM. The diameter and length of 200 pieces of grains were measured based on the SEM micrographs.

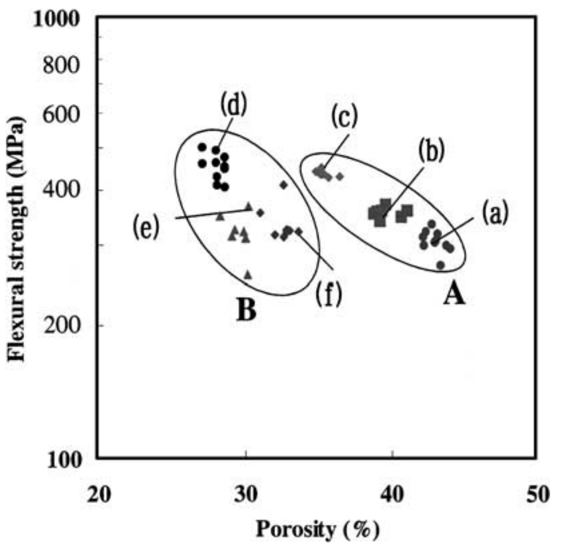

Figure 2 Semi-logarithm plots of the flexural strength of the porous Si_3N_4 as a function of porosity.

TABLE I Grain sizes of β-Si_3N_4 grains analyzed statistically

		Diameter (μm)		Length (μm)		Aspect ratio	
No.	Porosity (%)	Ave.	S. D.	Ave.	S. D.	Ave.	S. D.
a	43.1	1.41	0.53	12.60	5.44	9.31	3.15
b	39.0	1.35	0.52	10.39	4.45	7.93	2.57
c	35.3	1.31	0.60	10.23	4.88	8.08	2.45
d	28.7	0.91	0.34	7.49	2.95	8.50	2.47
e	30.3	1.35	0.52	7.82	3.76	7.47	2.21
f	33.7	0.93	0.28	6.03	2.27	6.73	2.33

Ave: Average, S. D.: Standard deviation.

3. Results and discussion

X-ray diffraction showed that all the specimens consisted of β-Si_3N_4 and Si-Er-O-N oxides as grain boundary phases. Fig. 1 shows typical SEM micrographs of the fracture surfaces of specimens. We can see that all the specimens are composed of elongated β-Si_3N_4 grains connected randomly in three dimensions. We cannot find significant difference in grain size among their specimens from these micrographs. Apparent fracture origins such as extraordinarily large pores were not confirmed in the fracture surfaces of all the specimens after the bending test.

The strength of porous ceramics is exhibited as a function of porosity by [9]

$$\sigma = \sigma_0 \exp(-\beta p) \tag{1}$$

where, σ_0 is strength at porosity of 0, β is a structural factor and p is porosity. The strength decreases exponentially with the increase in porosity.

Fig. 2 shows the semi-logarithm plots of the flexural strength of six kinds of specimens. Labels (a) to (f) are referred to the specimens in Fig. 1. The strength of the porous Si_3N_4 ceramics does not always increase with decreasing porosity. The strength of specimen (a) is almost the same as that of specimen (f) although specimen (a) has much higher porosity. Similar relation is seen between specimen (c) and (d), and between (b) and (e).

Important factors affecting the strength of porous ceramics are porosity, pore size, and grain size. Figs 3 and 4 show the grain diameter distributions of specimens (a) to (f) with pore size distributions (solid lines) and the aspect ratio distributions. Parameters V and r in left vertical axis show pore volume and pore diameter, respectively. The data analyzed statistically is summarized in Table I. Although differences in grain diameter (0.9 to 1.4 μm) and aspect ratio (6.73 to 9.31) of all the specimens are small, there is a significant difference in grain length (6.03 to 12.60 μm). For instance, the grain length of specimen (a) is almost twice as long as that of specimen (f). The statistically data of Table I permits us to classify the specimens into two groups; specimens (a) to (c) having longer β-Si_3N_4 grains belong to group A and specimens (d) to (f) having shorter β-Si_3N_4 grains belong to group B.

From Fig. 3, we can see the relation between the grain diameter and the pore size of specimens. The median pore diameter of the specimens were 0.56 to 0.96 μm and it is well correlated to the grain diameter. As porosity decreases, the grain diameter distribution shifts approximately to the small, resulting in the decrease of large pores and the increase of small pores, especially, of less than 0.5 μm size. Decreasing large pores as well as porosity should seriously increase the strength of porous Si_3N_4 ceramics. However, the strength does not always increase with the decrease in porosity and pore size. For example, the pore size of specimen (f) is smaller than that of specimen (c), despite close porosities of these specimens.

On the other hand, the effect of closed-pores on strength must also be considered since pore size measured using mercury porosimetry is for open-pores. Fig. 5 shows the relation between the overall porosity and the closed-porosity of specimens (a) to (f). At overall porosities above 30%, there is no closed-pores, and the closed-porosity increases with decreasing overall porosity. Maximum closed-porosity was about 7%. It is predicted that increasing closed-porosity led to higher strength. However, the strength does not depend on the closed-porosity. Therefore, the effect of pore size on strength is small in the present work.

We consider a important factor determing the strength to be the grain length of β-Si_3N_4; the difference in strength between group A and B is caused by differences in grain length.

In densified Si_3N_4 ceramics, increasing the major axis of the elongated β-Si_3N_4 grains increases fracture toughness [10–13] due to crack deflection [14] in fracture. Becher *et al.* [15] reported that increasing volume fraction of whiskers having larger diameter increased fracture toughness regarding the toughening mechanism of whisker-reinforced ceramic matrix composites. Nagaoka *et al.* [8] reported that elongated grains having aspect ratios of more than 4 contributed significantly to the increase in K_{IC} in sintered Si_3N_4 ceramics.

The Griffith's theory [16] shows that the strength of ceramics is a function of fracture toughness (K_{IC}), as follows.

$$\sigma = (1/Y)(K_{IC}/c^{0.5}) \tag{2}$$

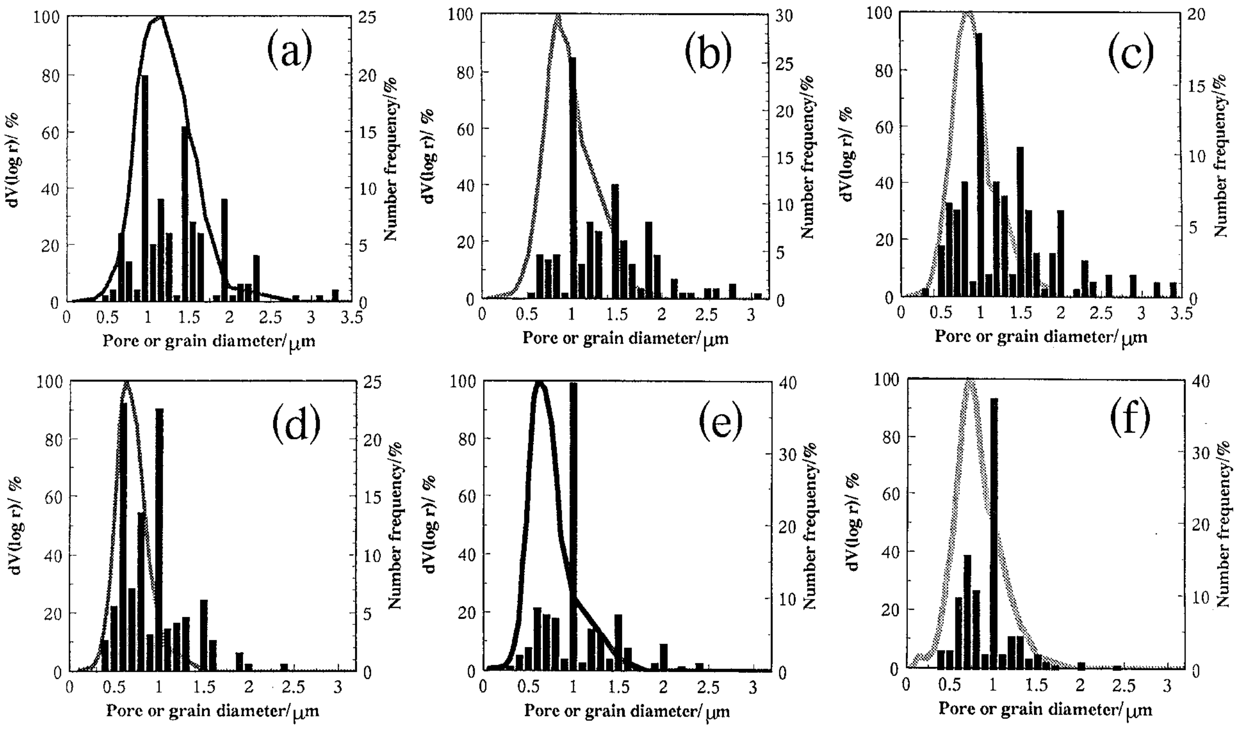

Figure 3 Grain diameter distributions (histograms) and pore size distributions (solid line) of specimens (a) to (f).

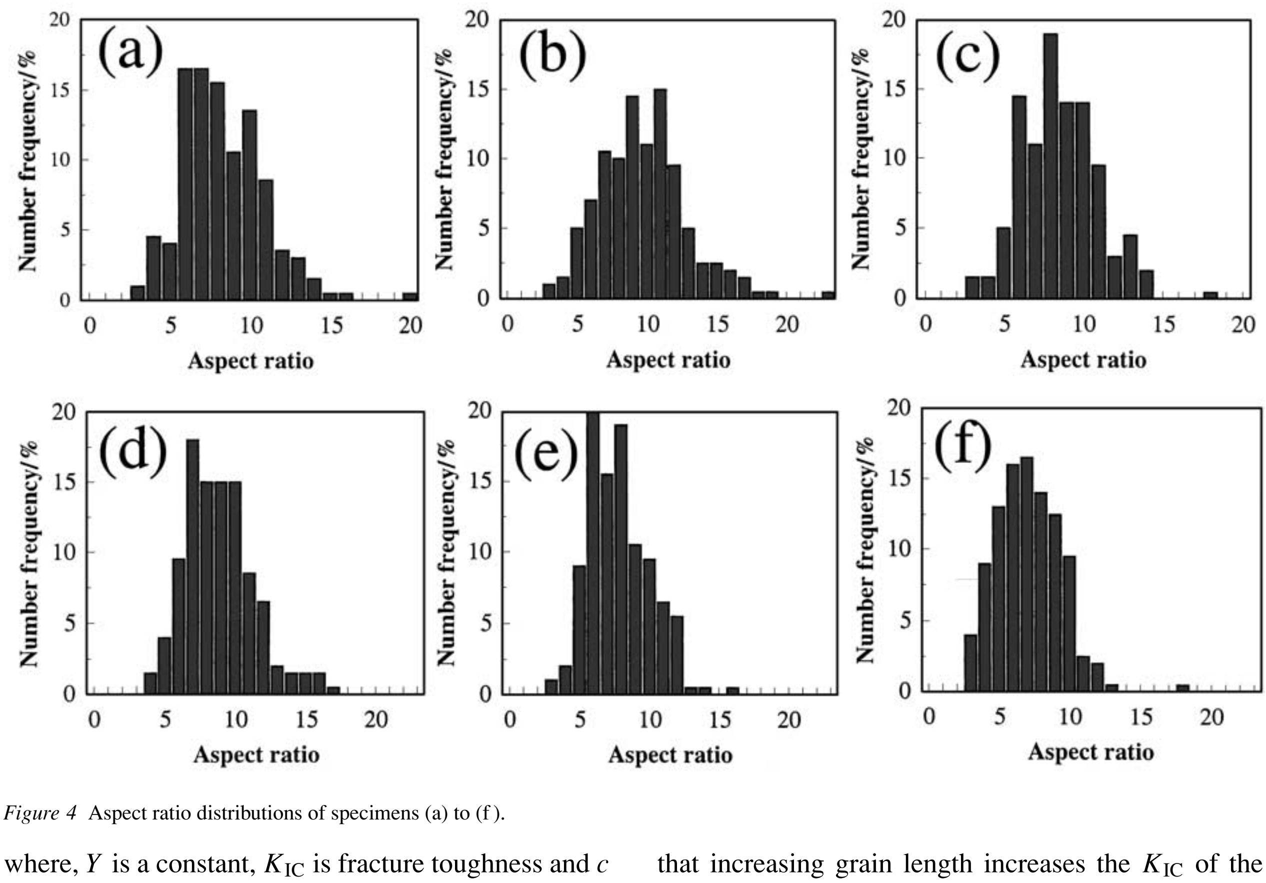

Figure 4 Aspect ratio distributions of specimens (a) to (f).

where, Y is a constant, K_{IC} is fracture toughness and c is crack length. In general, the size of defects such as pores, impurities and the secondary phase composed of unreacted sintering aids are used as the c value.

As shown in Fig. 3, there is no significant difference in maximum pore diameter, which affects c value, among the specimens (a) to (f). Accordingly, it is possible that K_{IC} is a factor affecting the strength of the porous Si_3N_4 ceramics although the above theory is not always applied to highly porous ceramics. We consider that increasing grain length increases the K_{IC} of the porous Si_3N_4 ceramics.

On the other hand, the strength of specimen (e) is almost equals to that of specimen (f), considering error in strength. Moreover, it is much smaller than that of specimen (d) despite close porosities of these specimens in Group B with small grain length. Although the reason for this phenomena has not been clarified, it is possibly caused by difference in grain diameter of the specimens; the grain diameter of specimen (e) is larger than

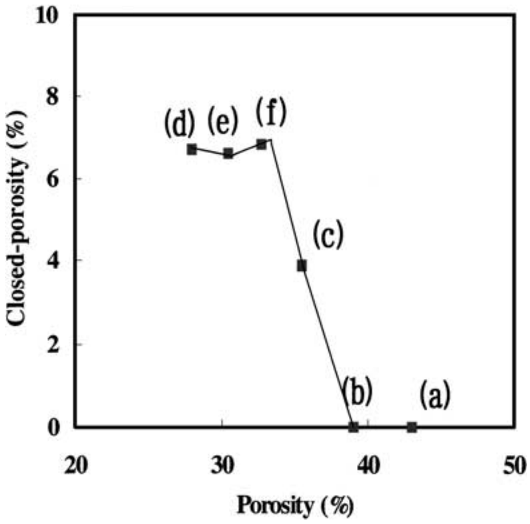

Figure 5 Relation between the overall porosity and the closed-porosity of specimen (a) to (f).

that of specimens (d) and (f). Because specimens (d) to (f) have almost the same aspect ratio, the larger grain diameter of specimen (e) shows it is coarse-grained. Such coarse grains possibly decrease strength.

As demonstrated above, the most important factor determing the strength of the porous Si_3N_4 ceramics is the grain length rather than the grain diameter. At current stage, we have not measured the K_{IC} of the porous Si_3N_4 ceramics. Further research is required to clarify the effect of grain size on the fracture toughness of highly porous ceramics.

4. Conclusions

Porous Si_3N_4 ceramics composed of elongated β-Si_3N_4 grains, and having porosities of 27 to 43%, were fabricated, and the effect of their grain size (diameter and aspect ratio) distribution on the pore size distribution and the flexural strength was investigated. We can conclude as follows.

1. Beta-Si_3N_4 grains have grain diameters of 0.9 to 1.4 μm, grain lengths of 6.0 to 12.6 μm, and aspect ratios of 6.7 to 9.3.
2. The porous Si_3N_4 ceramics have open-pores of diameters ranging from 0.1 to 2.8 μm. The grain diameter distribution of the elongated grains correlated well to the pore size distribution of the porous Si_3N_4 ceramics.
3. The strength of the porous Si_3N_4 ceramics does not always increase with the decreasing porosity and depends on the grain length of β-Si_3N_4; longer grain leads to higher strength.

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