Journal of the European Ceramic Society 15 (1995) 697–701

0955-2219/95/$9.50
0955-2219(95)00038-0

Mechanical Properties of Hot-Pressed 12H Ceramics

H. X. Li, W. Y. Sun & D. S. Yan

The State Key Lab. on High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P.R. China

(Received 12 January 1995; revised version received 1 February 1995; accepted 10 February 1995)

Abstract

The mechanical properties of hot-pressed 12H polytypoid phase with YAG as the sintering additive have been studied. The results showed that small amounts of YAG can greatly increase high temperature strength. At room temperature, the 12H with 2·5 wt% YAG possesses a flexural strength of 367 ± 18 MPa, but its high temperature strength can reach above 500 MPa in the temperature range from 1000 to 1300°C. The fracture mechanism has been discussed on the basis of the fracture morphology observed by SEM.

Introduction

It is well known that Sialon ceramics are a family of materials which possess high performance properties at elevated temperatures. In the Si–Al–O–N system, at compositions between β-sialon and AlN, there are six polytypoid phases (8H, 15R, 12H, 21R, 27R and $2H^{\delta}$) with wurtzite-type structures having compositions represented as M_mX_{m+1}.[1-2] These are built up by MX double layers of metal (M) and non-metal (X) atoms stacked with variants of AB and ABC sequences, as in silicon carbide and with MX_2 layers at periodic intervals to account for the different stoichiometries and structures. The crystal structures of AlN-polytypoids have been examined in detail,[3-4] but studies concerning their fabrication and mechanical properties are scarce.[5-6] Komeya[6] studied the formation and mechanical properties for 27R polytypoid and indicated that pure 27R can only be densified by 2000°C presintering and subsequent 2100°C hot-pressing; the ceramics show approximately constant strength values at room temperature to 1700°C(380–470 MPa prepared under the best conditions). This high refractoriness of the 27R polytypoid suggests that other polytypoids such as 21R, 12H and 15R would be also highly refractory. The phase relationships in the Y–Si–Al–O–N system[7] indicate that all AlN–polytypoids are compatible with β-sialon (except 8H), α-sialon (except 8H, 15R) and YAG ($3Y_2O_3{\cdot}5Al_2O_3$). This offers the possibility to incorporate polytypoid phases into α- and/or β-sialons forming composite ceramics simultaneously with YAG as the grain boundary phase. Since AlN-polytypoid phases possess fibre-like or prismatic morphology,[8] it would be interesting to document whether an *in situ* strengthening and toughening effect could be achieved in these composite ceramics. Therefore, the fabrication and mechanical properties of monolithic AlN-polytypoid ceramics prepared under the normal temperatures for nitride ceramics are worth exploration. The sinterability of sialon ceramics strongly depends on the nitrogen content in the starting compositions. In general, the more nitrides in the overall compositions, the more difficult the materials are to be densified. 12H phase contains the lowest nitrogen content among the polytypoids which are compatible with both α-sialon and β-sialon phases and therefore, it poses the greatest attraction among all AlN-polytypoid phases to be studied.

Recently, we studied monolithic 12H ceramics and α'-12H ceramics both with YAG as the sintering additive. A preceding paper[9] has described the effect of YAG on the densification and reaction sequence. The present paper reports the mechanical properties of 12H ceramics. The work on the α'-12H composite ceramics has appeared elsewhere.[10]

Experimental

As indicated in the Si–Al–O–N phase diagram, each AlN-polytypoid phase (M_mX_{m+1}) occurs along a certain line with $M:X$ equal to m:(m + 1). The nominal composition of 12H can be taken as $SiAl_5O_2N_5$. The starting materials used were Si_3N_4(LC12, Stark), AlN(1–2 μm, 1·2 wt% oxygen, (Zhuzhou Institute of Hard-Metals, China), Al_2O_3(99·99%) and Y_2O_3(99·9%). The mixed powder was ball-milled with absolute alcohol for 24 h,

dried and passed through a 120-mesh screen, and then hot-pressed at 1750°C for 1 h in a graphite-resistance furnace under 25 MPa in a flowing N_2 atmosphere. The specimens used for high temperature property determinations were heat treated at 1250°C for 24 h. The phases were identified by X-ray diffraction technique. Hardness and indentation fracture toughness were measured by using a Vickers diamond indenter under a load of 100 N. Flexural strength was tested at room temperature and high temperatures (1000–1400°C) in air by three-point bending with a 30 mm span (20 mm for high temperature test) and a cross-head speed of 0·5 mm/min. A boiling solution of $K_3Fe(CN)_6$ was used for etching the polished specimens. Both polished and fracture surfaces were observed by SEM. TEM study was also performed for revealing the grain boundary structure.

Results and Discussion

1 The effect of YAG on mechanical properties

Table 1 shows the starting compositions and their phase compositions present after hot-pressing and further heat treatment. The room temperature mechanical properties — Vickers hardness, indentation fracture toughness and the flexural strength are shown in Figs 1–3 respectively, and high temperature flexural strength is shown in Fig. 4.

At room temperature, as shown in Figs 1–3, when YAG is below 5 wt%, the flexural strength

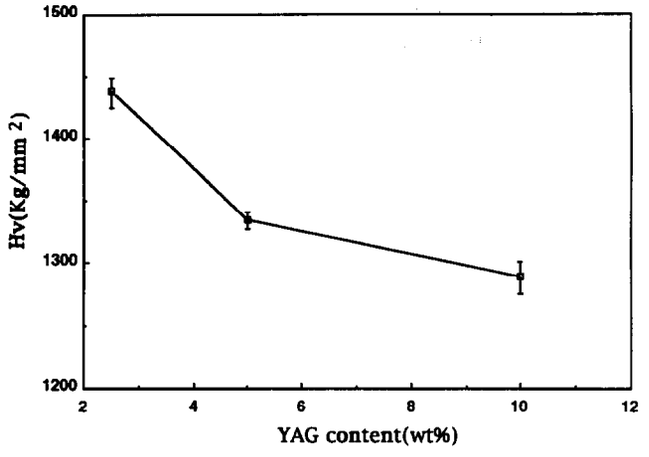

Fig. 1. Hardness of 12H compositions with different contents of YAG addition.

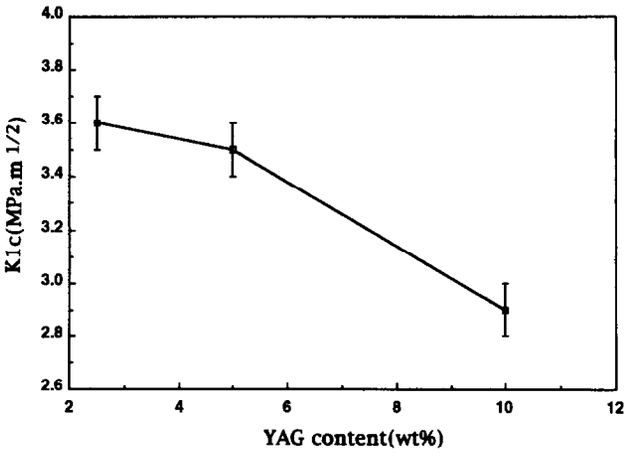

Fig. 2. Indentation fracture toughness of 12H compositions with different contents of YAG addition.

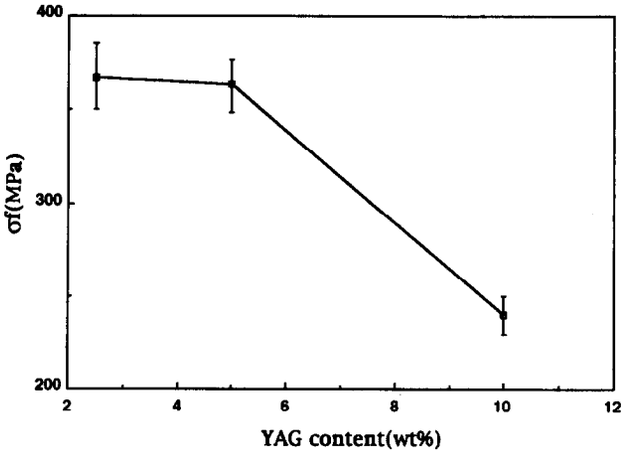

Fig. 3. Flexural strength of 12H compositions with different contents of YAG addition.

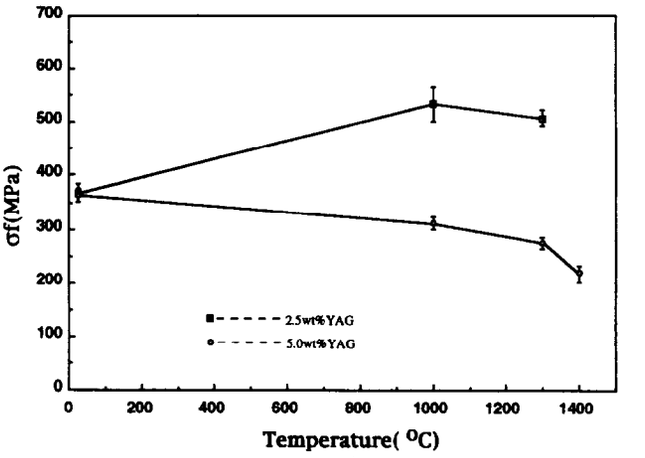

Fig. 4. Flexural strength of 12H with different YAG content versus temperature.

Table 1. The compositions and phases present after hot-pressed at 1750°C for 1 h

Specimens	*Starting compositions*				*Phase compositions*	
	Si_3N_4	*AlN*	Al_2O_3	Y_2O_3	*Before H. T.*	*After H. T.*
12H–2·5 YAG	17·2	57·6	23·8	1·5	12Hvs;YAGvw	12Hvs;YAGw
12H–5 YAG	16·8	56·2	24·2	2·9	12Hvs;YAGw	12Hvs;YAGmw
12H–10 YAG	15·9	53·2	25·2	5·7	12Hvs;YAGm; 15Rw	12Hvs;YAGm; 15Rw

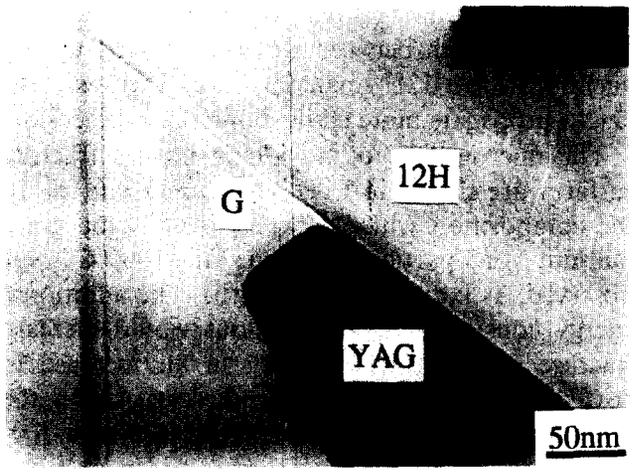

Fig. 5. HREM micrograph of 12H (2·5 wt% YAG) showing YAG and glassy phase at triple grain junction.

and fracture toughness are not sensitive to YAG content and the Vickers hardness decreases with the amount of YAG, but with further increase of YAG, all these mechanical properties become poorer. At high temperatures, as shown in Fig. 4, the effect of YAG on the flexural strength becomes more complex. The flexural strength of 12 H with 2·5 wt% YAG is much higher at high temperatures than at room temperature with an increment of 45 and 37% at 1000 and 1300°C respectively. However, when 5 wt% of YAG is added, the flexural strength decreases gradually with temperature rise.

The grain boundary phases in the 12H materials are YAG and glassy phase as revealed by TEM and X-ray diffraction technique. YAG as a sintering additive in 12H ceramics is more easily crystallized out than in β-sialon where YAG can only be obtained through post heat treatment. Fig. 5 is a TEM grain boundary micrograph of as fired 12H with 2·5 wt% YAG showing YAG with glassy phase existing at the triple grain junction. The microstructures of the compositions with different YAG contents are shown in Fig. 6. With increasing YAG, the content of grain boundary phase composed of both the glassy phase and YAG (white contrast) increases, and the grain size becomes smaller. The grain size change might be the result of having more nucleation sites being developed because of more liquid phase present during hot pressing. Clearly, the variation in the microstructure should be reflected in the mechanical properties. It has been known that the grain size has an obvious effect on the work of fracture in ceramic materials with non-equiaxed grains. The fracture energy can be improved through increasing the grain size.[11,12] Therefore, the higher fracture toughness of 12H materials with smaller amount of YAG addition can be attributed to the smaller quantity of grain boundary phase and to the relatively large grain size. The decreasing hardness in the compositions with higher YAG content can be envisaged by similar reasoning. In the composition with 10 wt% YAG, as indicated in Table 1, there still exists a small amount of 15R(an AlN-polytypoid containing less nitrogen than 12H) which is a transitional phase in the formation of 12H.[9] Whether the small amount of 15R has some effect on the mechanical properties is not clear, but it probably has slightly worse mechanical properties than 12H because of the lower N content in the composition.

The big difference in high temperature flexural strength caused by the amount of YAG must have some indication in their fracture morphology. In general, the glassy phase adversely affects high temperature mechanical properties more severely than at room temperature. But for the composition with 2·5 wt% YAG, the material behaves diff-

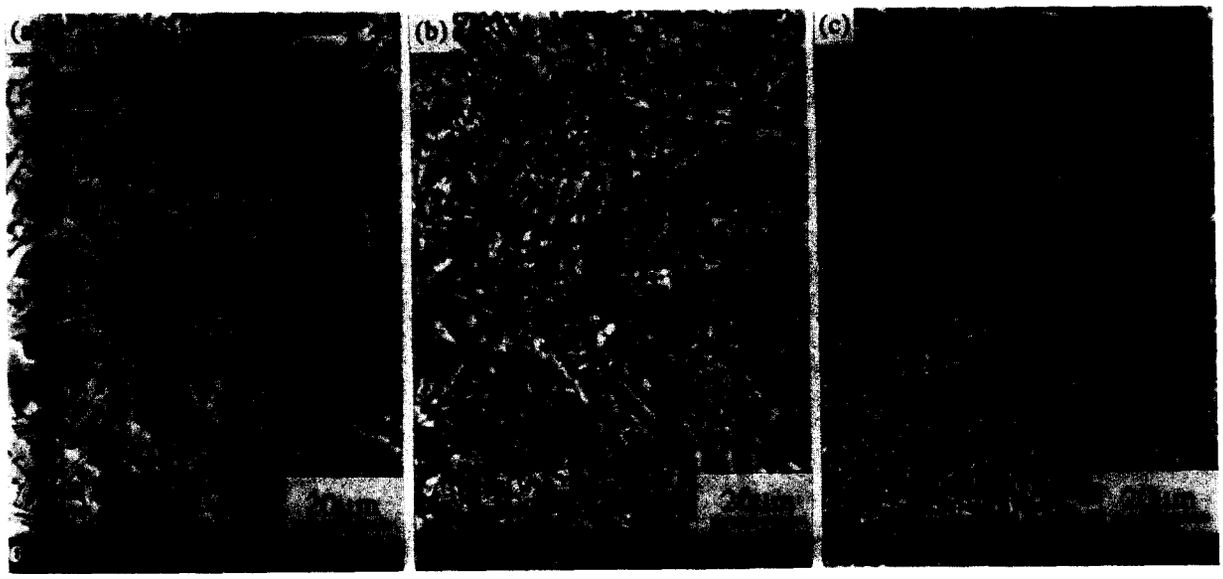

Fig. 6. SEM micrographs of 12H densified with (a) 2·5; (b) 5·0 and (c) 10 wt% YAG.

erently. There must be some strengthening mechanism occurring at high temperatures and this may be found through observing the fracture morphology.

2 The characteristics of fracture morphology

The micrograph of the fracture surface at room temperature for the composition with 2·5 wt% is shown in Fig. 7(a). As observed, 12H materials fractured in a transgranular mode. Some cracks propagated within the 12H grains with a stepwise fracture surface. The transgranular fractural mode is thought to be associated with the interlocking arrangement of 12H grains and their relatively poor strength. The step-like morphology is apparently related to the crystal structure of 12H. The hexagonal AlN-polytypoid phases prefer to grow along the a-dimension, and the width of the grains corresponds to the c-dimension, along which the MX and MX_2 layers stack up. Therefore, the strength of 12H grains varies with their orientation and is weaker along their width due to the poor cleavage strength between structural layers. Consequently, when 12H materials are fractured, the cracks propagate more easily along the c-dimension.

The micrographs of high temperature fracture surfaces are shown in Figs 7 (b–c) and 8 (a–c). In the composition with 2·5 wt% YAG, some grain pull-out or partial pull-out at 1000°C was observed, as indicated in Fig. 7(b). The additional energy consumed by the pull-out would increase fracture energy thus resulting in an increase in flexural strength. At 1300°C, microcracks on the fracture surface were observed, as shown in Fig. 7(c). The formation of microcracks also provides an additional contribution to the energy dissipation, thus improving the strength. Therefore, in the composition with less YAG content, the possible mechanism for the increment of high temperature strength are thought to be grain pull-out and the formation of microcracks. However, when

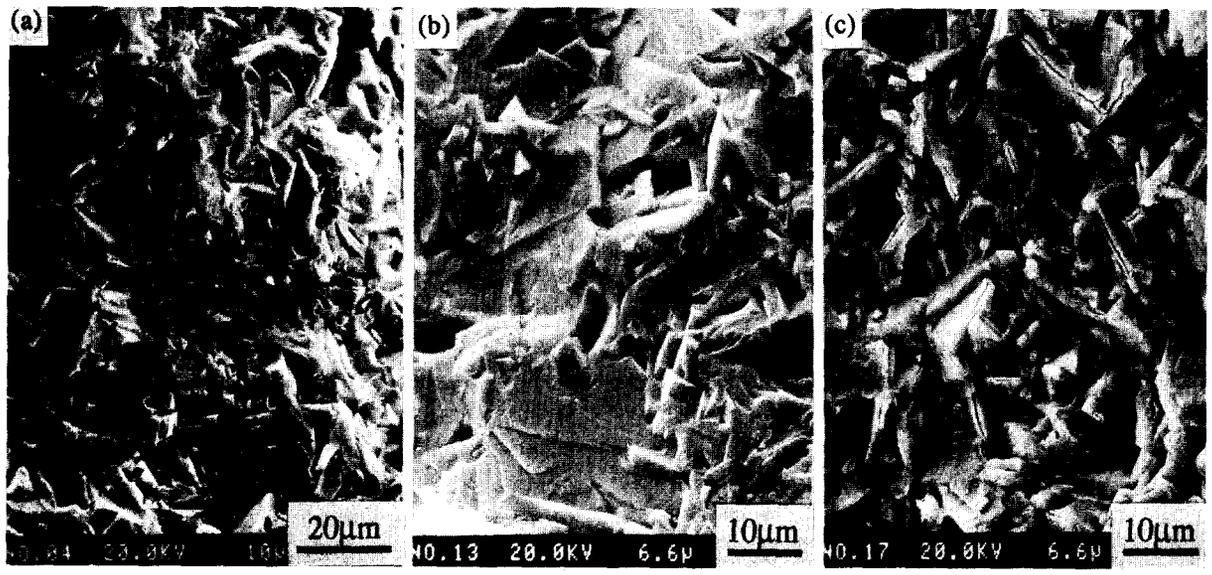

Fig. 7. Micrographs of fracture surface of 12H with 2·5 wt% at (a) room temperature, (b) 1000°C and (c) 1300°C.

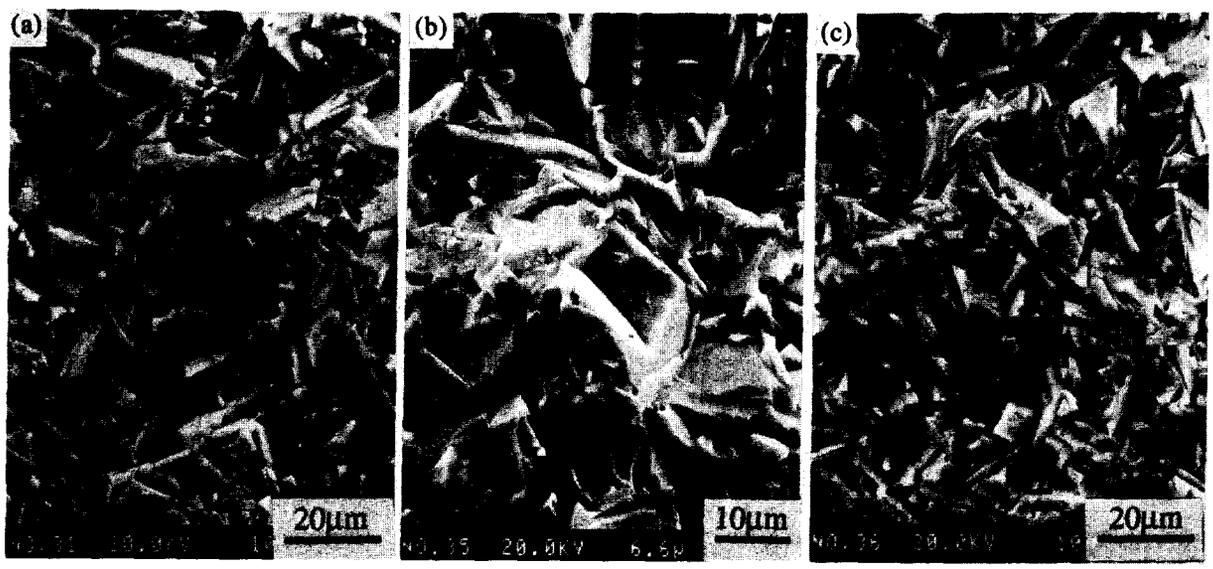

Fig. 8. Micrographs of fracture surface of 12H with 5·0 wt% YAG at (a)1000°C, (b) 1300°C and (c) 1400°C.

more YAG was added, no grain pull-out was observed and the grain boundaries appear to be less sharply defined, as shown in Fig. 8(a–c). The formation of this morphology can be attributed to more glassy phase present at the grain boundaries. Therefore, high temperature mechanical properties are more sensitive to the amount of YAG in the microstructure and better mechanical properties can be obtained through careful control of the grain boundary phases.

Conclusion

YAG as the sintering additive for 12H ceramics plays a decisive role in determining the mechanical properties of the material, especially at high temperatures. The composition with a small amount of YAG (about 2·5 wt%), gives a substantially higher flexural strength at temperatures between 1000 and 1300°C than its room temperature strength. Grain pull-out at 1000°C and microcracks formed in the 12H grains at 1300°C as manifested on the fracture surfaces are supposedly the main mechanisms for the strengthening effect at low additive level of YAG.

Acknowledgements

This work has received financial support from the National Natural Science Foundation of China, Contract No. 59132031. The authors would also like to thank Prof. T. R. Lai for helpful discussions.

References

1. Jack, K. H., Nitrogen ceramics. *J. Brit. Ceram. Soc.*, **72** (1973) 376–86.
2. Gauckler, L. J., Lukas, H. L. & Petzow, G., Contribution to the phase diagram Si_3N_4–SiO_2–AlN–Al_2O_3. *J. Am. Ceram. Soc.*, **58** (1975) 346–7.
3. Thompson, D. P., Korgue, P. & Hendry, A., The structural characterization of sialon polytypoids. In *Progress in Nitrogen Ceramics*, ed. F. L. Riley, Martinus Nijhoff, The Hague, The Netherlands, 1983, pp. 61–74.
4. Bando, Y., Mitomo, M., Kitami, Y. & Izumi, F., Structure and composition analysis of silicon aluminium oxynitride polytypes by combined use of structure imaging and microanalysis. *J. Microscopy*, **142** (1986) 235–46.
5. Cannard, P. J., Ekström, & Tilly, R. J. D., The formation of phases in the AlN-rich corner of the Si–Al–O–N system. *J. Euro. Ceram. Soc.*, **8** (1991) 375–82.
6. Komeya, K. & Tsuse, A., Formation of AlN polytype ceramics and some of their properties. *Yogyo-kyokai-Shi*, **89** (1981) 615–20.
7. Sun, W. Y., Tien, T. Y. & Yan, D. S., Subsolidus phase relationships in part of the system Si,Al,Y/N,O: the system Si_3N_4–AlN–YN–Al_2O_3–Y_2O_3. *J. Am. Ceram. Soc.*, **74** (1991) 2753–8.
8. Tendeloo, G. V., Faber, K. T. & Thomas, G., Characterization of AlN ceramics containing long-period polytypes. *J. Mater. Sci.*, **18** (1983) 525–32.
9. Li, H. X., Sun, W. Y. & Yan, D. S., Fabrication of 12H AlN-polytypoid ceramics. *Eur. J. Solid State Inorg. Chem.*, (in press).
10. Li, H. X., Sun, W. Y., Yan, D. S. & Tien, T. Y., Fabrication and mechanical properties of α'-sialon-12H multiphase ceramics, In *Proc. 5th Int. Sym. on Ceramic Materials & Components for Engines*, 1994, Shanghai, China, (in press).
11. Lange, F. F., Relation between strength, fracture energy and microstructure of hot-pressed Si_3N_4. *J. Am. Ceram. Soc.*, **56** (1973) 518–22.
12. Rice, R. W., Freiman, S. W. & Becher, P. F., Grain-size depend of fracture energy in ceramics: I, experiment. *J. Am. Ceram. Soc.*, **64** (1981) 345–50.