Journal of the European Ceramic Society **16** (1996) 1345–1349

PII: S0955-2219(96)00079-9
0955-2219/96/$15.00

Controlling the Flaw Size and Mechanical Properties of ZTM/SiC_p Composites

Ruisong Guo, Zhengfu He, Zhengfang Yang, Qiming Yuan & Yuru Chen

Department of Materials Science and Engineering, Tianjin University, Tianjin 300072, People's Republic of China

(Received 19 December 1995; revised version received 23 March 1996; accepted 2 April 1996)

Abstract

Ultrafine mullite and zirconia powders were prepared by sol–gel and precipitation processes, then mixed homogeneously with μm-sized silicon carbide particles (SiC_p) to obtain composite powder. A dense green body with homogeneous microstructure was prepared by the pressure filtration technique. After being dried carefully, the green body was hot-pressed under different conditions to optimize its microstructure. The effect of different hot-pressing conditions on the mechanical properties was investigated and the hot-forging effect was also taken into account. It was found that the strength of the composite was greatly increased, from about 600 MPa reported to 810 MPa at room temperature and 830 MPa at 1000°C, under the conditions of moderately low hot-pressing temperature and long holding time, while the fracture toughness of the composite remained almost unchanged. From this it was shown that the control of strength-limiting processing defects was effective. Because of the homogeneous microstructure improved during forming and optimized during sintering and a combination of various strengthening mechanisms, it was possible to enhance the strength of the composite significantly. © 1996 Elsevier Science Limited

1 Introduction

Zirconia-toughened mullite (ZTM) based composites have great importance in advanced structural oxide ceramics. During the past decade investigations of fibre- or whisker-reinforced composites have been widely conducted[1–12] and the mechanical properties of the composites have also been significantly improved.[4,6,10,12] Due to the complicated preparation technique, high cost and health hazards associated with the use of whisker reinforcements, however, it appears that ZTM reinforcement by particles is more acceptable. Unfortunately, only a few reports on particle-reinforced mullite system have been published so far. Although the mechanical properties of particle-reinforced materials have not yet reached the level of fibre- or whisker-reinforced ones, strength at the level of 600 MPa and fracture toughness of 6–7 MPa $m^{1/2}$, SiC-particle reinforced ZTM has attracted much attention owing to its significant potential in mechanical properties.

Mullite ceramics obtained by the sol–gel process are a good candidate material for high-temperature applications. It has been reported that highly pure, ultrafine mullite powder can be prepared by the sol–gel process, then formed carefully to avoid flaws and sintered at a moderate temperature to prevent abnormal grain growth of mullite and to improve microstructure. According to $\sigma_f = K_{IC}/Yc^{1/2}$, although fracture toughness was not very satisfactory, a high strength was still obtained because the flaw size c decreased. In our previous work we prepared ZTM/SiC_p composites with the same composition as those in this paper and by the same processing route except for hot-pressing directly from composite powders. Although K_{IC} was very close to or even a little higher than that published, the strength never reached the level of 600 MPa, which clearly showed the flaw size in the body was considerably large. Therefore, the main reinforcement strategy of the present study was to focus on the strength-limiting flaws originating from processing defects, in collaboration with triggering of other strengthening mechanisms and improvement of microstructure of the composites.

2 Experimental Procedure

The starting materials were tetraethyl orthosilicate (TEOS), aluminium chloride, $ZrOCl_2 \cdot 8H_2O$, and μm-sized SiC particles. First, ultrafine mullite (ratio of Al_2O_3 to SiO_2 = 68 to 32) was prepared by the sol–gel process for investigations of the green body characteristics. The precursor powder was calcined at 1300°C, then shaped via different

methods. The powder was granulated, followed by pressing and/or cold-isostatic pressing. Stable, well-dispersed slurry was produced for pressure filtration (PF) forming by ball-milling for 8 h, keeping constant pH value (pH = 9) and adding a small amount of surfactant, polyacrylic acid (PAA). Density, pore size distribution, morphology and sinterability of the green body were determined.

Secondly, ultrafine mullite (same composition as above) and zirconia powders were prepared by sol–gel and precipitation processes, respectively. After being calcined at 1000°C, mullite powder was mixed homogeneously with commercial SiC_p and $Zr(OH)_4$ slurry, precipitated from $ZrOCl_2 \cdot 8H_2O$ by adjusting the pH value to 8·5, by a coating–coprecipitation method. This composite powder was calcined again at low temperature (600°C). The average grain size of mullite and zirconia was about 15 nm by transmission electron microscopy (TEM) observation. SiC powder was milled before mixing and its average grain size was about 1–3 μm. The composition of the composite powder was 40% mullite / 25% ZrO_2 / 35% SiC (by volume). The green disc body was obtained by PF of composite slurry which was prepared by the same way as mentioned above. After being dried carefully, the green body, whose diameter was a few millimetres smaller than that of graphite die, was hot-press(HP)ed under different conditions in an Ar atmosphere. The HPing pressure was 36 MPa.

The HPed bodies were ground and cut into bars with cross-section of 2·5 × 5 mm, then polished. The strength was measured by three-point bending with spans of 20 and 30 mm for room-temperature strength and high-temperature strength, respectively. The fracture toughness was determined by the single-edge notched beam method at room temperature. Every strength value reported was the average of at least five samples and every fracture toughness value was obtained from at least three bars. The microstructural morphology of the sample surface and fractured surface was observed by scanning electron microscopy (SEM) and TEM.

3 Results and Discussion

3.1 Characteristics of green body and control of flaw size

Studies of the dry- and wet-forming techniques and the compact characteristics of highly pure, ultrafine mullite obtained by the sol–gel process, which had been calcined at 1300°C and had an average grain size of 50 nm, have been performed previously by the present authors.[7] It can be seen from Table 1 that the green compact density by the PF route is 8% higher than that by dry-forming. The PF compact reached 46% theoretical density (TD), but it was only 38% TD for the dry-forming one. Microstructural observation revealed that the PF compact was much more homogeneous than the dry-forming one. The fracture surface of the PF compact was homogeneous, fine and smooth. There were no large agglomerates left in the body, as these had been crushed by ball-milling. Static- and stereo-stabilizing mechanisms had operated very well while preparing the slurry. Therefore the particles were well dispersed and stable in the suspension. Moreover, the pore size distribution of the green body was much narrower by PF than by dry-forming. Its main peak located at about 100–120 Å, which corresponds exactly to the size of the tetrahedron pore formed by four primary particles (diameter 50 nm) according to the close-packing principle. No pores larger than 600 Å existed. After sintering at 1590°C for 4 h in air, the density difference between the two bodies was considerably large. The PF compact density was 19% higher than the other, reaching 95% TD, which could undoubtedly be attributed to microstructural improvement and the elimination of large pores from the green body. It is very difficult to eliminate the flaws related to dry-forming during sintering. So it is clear from the above that the compact, whose density was not high enough, could also be well sintered provided it was homogeneous enough and the pores in the body were fine and well distributed.

Based on the results and discussion above, the PF route was employed as a primary strategy to realize elimination of processing defects and therefore improvement of microstructure. Then the body was sintered by the HPing route under different conditions as a second measure to finely adjust and optimize the microstructure. In the meanwhile, the hot-forging effect was taken into account to achieve flaw-free materials. Comparison of the surface morphology of two kinds of samples, i.e. those HPed from a disc body by PF and those obtained directly from composite powder at the same conditions, showed that the former was homogeneous and dense. No large agglomerates remained. Its room-temperature strength reached 720 MPa, although no large K_{IC} difference existed between both materials, which resulted obviously

Table 1. Density of green body formed by different routes and sintered body

Forming method	*Green body*		*Sintered body*	
	ρ(g cm^{-3})	ρ/ρ_{th} (%)	ρ(g cm^{-3})	ρ/ρ_{th} (%)
Dry-forming	1·21–1·24	37·7–38·6	2·29–2·44	71·3–76·0
PF	1·47	45·9	3·06	95·3

Sintered at 1590°C for 4 h in air; ρ_{th} = 3·21 g cm^{-3}.

from the effective control of processing defects and the improvement of microstructure.

3.2 Effect of different HPing conditions on composite mechanical properties

Four different HPing conditions (nos 1–4) were chosen to investigate the mechanical properties of the composites. Condition no. 5 was used as a comparison with nos 2 and 4. The mechanical properties of the composites are summarized in Table 2. It can be seen that there is no great difference in fracture toughness among the samples. The strength of sample 1 was the lowest, which can be attributed to low HPing temperature although it had the longest holding time. When the composite was sintered at such a low temperature, its microstructure (grain growth and grain bonding, etc.) had not been optimized. Increasing the HPing temperature to 1575°C increased the strength to the maximum value of 730 MPa because of improvement of the microstructure. But the strength of sample 4 (HPed at 1600°C) decreased and its K_{IC} value was also the lowest, which was related to its short holding time. As the holding time at 1600°C increased (Sample 5), strength and K_{IC} were enhanced. In addition, the strength of samples 2 and 5, tested at 1000°C, decreased only slightly and was still over 650 MPa. It is well known that the zirconia transformation toughening mechanism almost fails at this temperature. It was considered, in that case, that apart from SiC particle reinforcement, effective control of flaws was also an important factor for enhancing the strength of the composite. Strength at 1200°C decreased significantly, which was related to impurities introduced into the composite by the SiC powder.

To control the flaw size and to hinder grain growth, it was inadvisable to choose a high HPing temperature. The mechanical properties of the composites HPed at 1550°C for different holding times are shown in Fig. 1. The room-temperature strength exceeded 600 MPa for all the samples and the K_{IC} values were similar. As holding time increased to 80 min, the strength also increased to maximum 810 MPa, and the strength at 1000°C reached 836 MPa. This revealed that the major source for strength improvement was microstructural factors. It is proposed that the processing defects are limited to minimum extent after being sintered at appropriate conditions if the green body is homogeneous and no large pores remained in it. Meanwhile, the microstructural factors, e.g. ZrO_2 transformation strengthening and toughening mechanism, are also optimized. Under a comparable condition, the transformable ZrO_2 content of this composite was highest. As the holding time was increased continuously, the strength of the composite decreased but it was still above 720 MPa,

Table 2. Mechanical properties of composites HPed under different conditions

No.	*HPing conditions*		*Strength (MPa)*			K_{IC} *(MPa m$^{1/2}$)*
	Temperature (°C)	*Time (min)*	*RT*	*1000°C*	*1200°C*	
1	1525	80	599			5·9
2	1550	60	686	653	490	5·5
3	1575	40	730			5·7
4	1600	25	689			5·2
5	1600	60	720	657	485	6·0

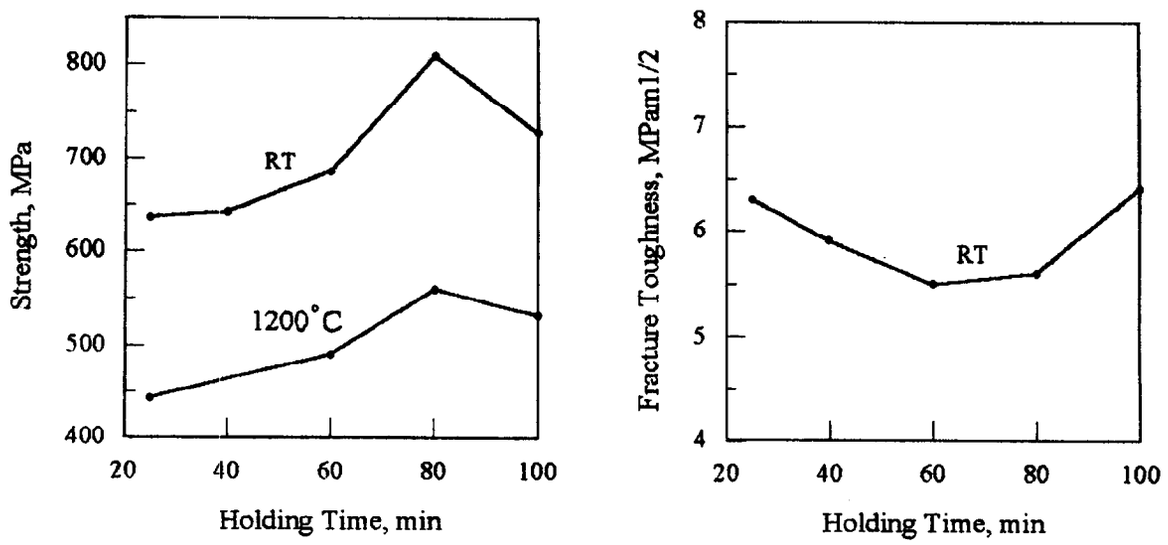

Fig. 1. Mechanical properties versus holding time (HPing temperature 1550°C).

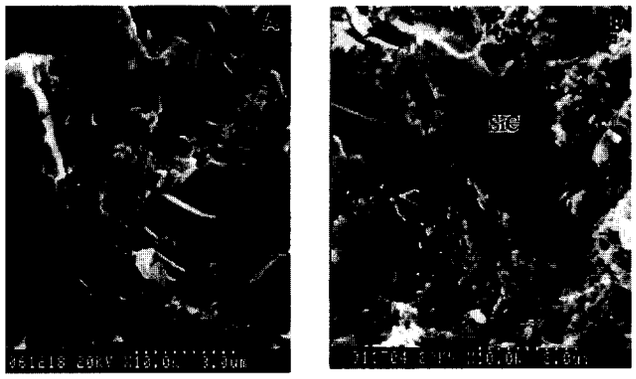

Fig. 2. SEM micrographs of fracture surface of ZTM/SiC_p composites HPed from a disc body by PF.

which is higher than that for a holding time of 60 min. The strength at 1200°C followed the same trend except for a downwards shift in value by about 200 MPa. It was consequently revealed that if the material was hot-pressed at moderately low temperature and for moderately long holding time, improved microstructure and excellent properties could be achieved.

3.3 Hot-forging

It has been reported that hot-forging is a good way to obtain flaw-free material. In this paper this strategy was also taken into account. The diameter of the green disc was a few millimetres smaller than that of the graphite die. During HPing, the disc not only suffered a vertical pressure resulting in decreasing thickness, but also was squeezed to expand in diameter to the size of the graphite die. Agglomerates were broken down and grain sliding and rearrangement occurred. Obviously it is very advantageous for pores to be eliminated before complete densification, giving rise to a flaw-free material.

3.4 Microstructure observation and strengthening mechanism

The mechanical properties of the ZTM/SiC_p composites produced in this work have been much improved compared with our previous results, the strength reaching 810 MPa at room temperature and 836 MPa at 1000°C. It is strongly suggested that elimination of processing defects and optimization of microstructure are of vital importance for strengthening the composite. Microstructural investigations of the fracture surface revealed features that correlated with the strength data. It can be seen from Fig. 2 that the fracture surface of the composite HPed from a PF disc body was very rough. Holes are visible in the fracture surface caused by particle pull-out and transgranular fracture across SiC particles has occurred, which all contributed greatly to improving strength. In addition, stress-induced transformation toughening of ZrO_2 and microstress fields around ZrO_2 particles produced by ZrO_2 transformation, ZrO_2 and SiC particle reinforcement[3] all contribute to strengthening of the composite. When a propagating crack in a fine matrix encountered a μm-sized SiC particle embedded in the matrix, it would be impeded severely by the particle, causing crack deflection, crack bridging and consequently significant enhancement of the fracture energy. Figure 3(a) shows the deflection of a crack by SiC and ZrO_2 particles. Figure 3(b) shows the main crack bridged by a t-ZrO_2 particle and demonstrates that a microstress field existed at boundaries between ZrO_2 and mullite. It also reveals that the main crack stopped by cutting and transformation of t-ZrO_2 during propagation [Fig. 3(c)]. The crack could propagate across SiC_p [Fig. 2(b)] when the energy needed for crack deflection was too high.

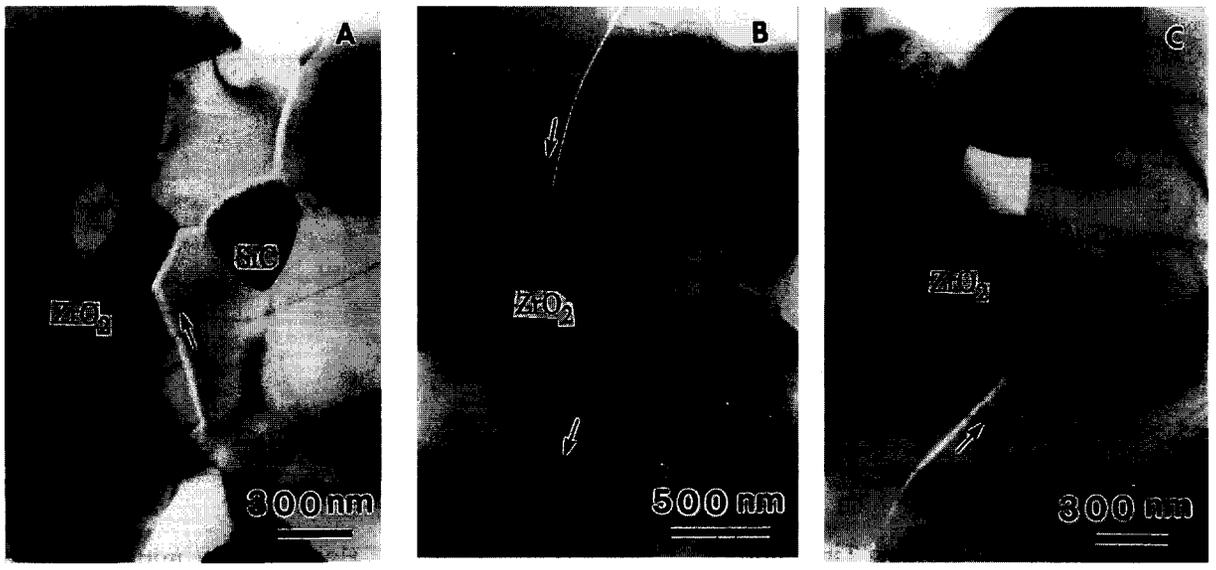

Fig. 3. TEM micrographs of ZTM/SiC_p composites showing crack deflection, bridging and stopping.

Fig. 4. Dislocations in mullite.

Dislocations were often found to exist in mullite grains. Figure 4(a) shows dislocations pinned by second phase particles. These pinned dislocations would need more energy to remove them because the resistance of dislocation sliding was increased. Extremely high dislocation density was observed in mullite after high-temperature strength determination, which explains the much improved high-temperature strength. Dislocations climbed at high temperature and twined with each other forming a network, which greatly decreased the mobility of dislocations. These dislocations would strongly hinder the propagation of cracks, and therefore improve the strength of the composite.

4 Summary

Strength-limiting flaws originating from processing defects could be effectively eliminated and the microstructural homogeneity of ZTM/SiC$_p$ composite could be greatly improved by the pressure filtration route. This material could further be optimized under HPing conditions of moderately low temperature and long holding time. As a result of various strengthening mechanisms, the strength of the composite at room temperature and at 1000°C increased significantly while the fracture toughness remained almost unchanged.

References

1. Yang, Z F., Xu, H. Y., Tan, J. Q., *et al.*, Mechanical properties of mullite-based composites. *J. Chinese Ceram. Soc.*, **17**[5] (1989) 467–471.
2. Xu, M. X., Cui, F., Jin, Z. G., *et al.*, Study on preparation of ultra-fine mullite powder. *J. Chinese Ceram. Soc.*, **19**[1] (1991) 80–85.
3. Liu, Q., Chen, Y. R., Yuan, Q. M., *et al.*, Mechanism of strengthening and toughening by zirconia in mullite–zirconia composite. *J. Chinese Ceram. Soc.*, **20**[4] (1992) 353–359.
4. Becher, P. F. & Tiegs, T. N., Toughening behavior involving multiple mechanisms: whisker reinforcement and zirconia toughening. *J. Am. Ceram. Soc.*, **70**[9] (1987) 651–654.
5. Huang, X. X., Hong, J. S. & Guo, J. K., SiC particle and Y-TZP reinforced mullite matrix composites. In *Proc. 4th Int. Symp. on Ceramic Materials and Components for Engines*, eds R. Carlsson, T. Johansson & L. Kahlman. Elsevier Applied Science, New York, 1992, pp. 795–799.
6. Nakano, K., *et al.*, in *Extended Abstracts of Annual Meeting*, The Ceramic Society of Japan, Tokyo, 1989, p. 311 (2E36).
7. Guo, R. S., Yang, Z. F., Yuan, Q. M., *et al.*, Preparation of ultrafine mullite powder and characteristics of its compact. *J. Chinese Ceram. Soc.*, **22**[3] (1994) 299–303.
8. Somiya, S. & Hirata, Y., Mullite powder technology and applications in Japan. *Am. Ceram. Soc. Bull.*, **70**[10] (1991) 1624–1632.
9. Okada, K., Otsuka, N. & Somiya, S., Review of mullite synthesis routes in Japan. *Am. Ceram. Soc. Bull.*, **70**[10] (1991) 1663–1640.
10. Zhou, G., The optimization study of preparing process of mullite-based composites. Master thesis, Tianjin University, China, 1991.
11. Guo, R. S., He, Z. F., Yang, Z. F., *et al.*, Controlling of flaw size and strength of ZTM/SiC$_p$ composites. *J. Chinese Ceram. Soc.*, **23**[1] (1995) 92–96.
12. Schneider, H., Okada, K. & Pask, J., *Mullite and Mullite Ceramics*. John Wiley & Sons, Chichester, 1994.