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Fabrication of Hot-Pressed Zircon Ceramics: Mechanical Properties and Microstructure

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Abstract: Zircon ceramics were fabricated by the hot-pressing process starting from synthesized sub-micron zircon powder with high purity. The effects of hot-pressing conditions on the density of the specimens were investigated. The relative density of zircon hot-pressed at 1600°C for 1 h reached 99.1%, with a flexural strength and fracture toughness of 320 ± 20 MPa and 3.0 ± 0.4 $\mathrm{MPa\cdot m^{1/2}}$, respectively. The flexural strength can be maintained up to 1000°C, followed by a slight degradation occurring at 1200°C, while the retention of room temperature strength at 1400°C was still at a level of about 70%. The fracture behaviour of zircon ceramics was studied on the basis of microstructural observations carried out by SEM, TEM and HREM, indicating that the presence of a glassy phase at some of the triple junctions was responsible for the decrease of flexural strength at high temperatures. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

It is widely known that zircon is a kind of good refractory material, which has been extensively applied in the steel industry. In recent years, more and more attention has been paid to its applications as a structural ceramic,[1-3] because highly pure zircon ceramics present many attractive properties. Zircon does not undergo any structural transformation until its dissociation at about 1700°C. It exhibits excellent chemical stability and thermal shock resistance, coupled with a very low thermal expansion coefficient (4.1×10^{-6}/°C from room temperature to 1400°C) and low heat conductivity coefficient (5.1 W/m·°C at room temperature and 3.5 W/m·°C at 1000°C). Sintered zircon with high purity can retain its bending strength up to temperatures of 1200–1400°C.[3] These properties make zircon a potential candidate as a useful structural ceramic, especially in such fields where a sudden change of temperature may occur.

Many investigations have been conducted on the preparation of ultra-fine zircon powder with high purity and the fabrication of zircon ceramics with high performance. Several methods of powder synthesis have been developed, such as sol gel processing,[4,5] wet chemical method[6] and hydrothermal method.[7] Sintered zircon was obtained by Mori and co-workers[2,3] from synthesized fine zircon powder by firing the zircon green compact at 1680°C for 4 h, which had a relative density of more than 98%.[3] Another approach to fabricate zircon ceramics is the slip casting process,[8] by which sintered zircon ceramics with a relative density of 96% could be obtained under the conditions of 1600°C/2 h. Moreover, the fabrication of a zircon matrix composite reinforced by SiC filaments and whiskers was also examined,[9,10] showing that obvious improvements in mechanical properties were achieved.

In the present paper, the hot-pressing process for the fabrication of zircon ceramics was described. The effects of hot-pressing temperature on the mechanical properties and microstructure of zircon were investigated. The fully densified zircon obtained exhibited good mechanical properties from room temperature to 1200°C. The relationship between flexural strength and temperature, which was greatly related to the microstructure and fracture behaviour of the zircon ceramics, is discussed on the basis of the microstructural observations of the specimens carried out by SEM, TEM and HREM.

2 EXPERIMENTAL PROCEDURE

2.1 Starting powder

The starting zircon powder was synthesized by a wet chemical method from $ZrOCl_2$ solution and fumed silica. The details of this process have been described elsewhere.[6,11] The TEM morphology of the synthesized powder is shown in Fig. 1, and the average primary particle size of the zircon powder was identified to be about 0.2–0.3 μm. The specific area of the starting powder measured by BET method is 5.2 m^2/g. Table 1 lists the chemical composition of the synthetic powder, demonstrating that the total impurities content was only about 0.153wt%.

2.2 Hot-pressing processing and property evaluation

The synthesized zircon powder was hot-pressed in a graphite die under a flowing inert atmosphere at 1500–1600°C for 1 h under a pressure of 25 MPa. No inorganic additive was used for densification. Specimens were cut and ground into testing bars with a size of 2.5 mm×5 mm×30 mm with a diamond wheel. The flexural strengths were measured by the three-point bending method with a span of 20 mm and a cross-head speed of 0.5 mm/min.

Testing bars of dimensions 5 mm×2.5 mm×30 mm were prepared for single edge notched beam (SENB) fracture toughness measurements. The SENB specimens were fractured by the three-point bending method at a cross-head speed of 0.05 mm/min with a span of 20 mm. The notches used were 0.25 mm wide and 2.5 mm deep. Vickers hardness indentation tests were carried out on the polished surface with a load of 98 N. Bulk density of specimens was measured by the Archimedes' method, and relative densities of the specimens were calculated by using 4.67 g/cm^3 as the theoretical density.

The morphologies of the fracture surfaces of hot-pressed zircon specimens were observed by scanning electron microscopy (EPMA-8705, Electron probe microanalyser, Shimadzu). The microstructural features, especially the morphologies of grain boundaries, were examined by using transmission electron microscopy (JEM-200CX, JEOL, Japan) and high resolution electron microscopy (JEM-400CX, JEOL, Japan).

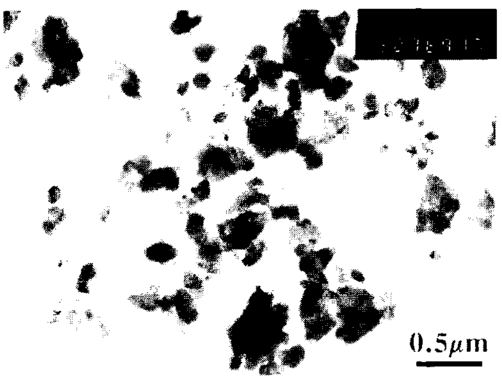

Fig. 1. TEM morphology of starting zircon powder.

Table 1. Chemical composition of synthetic zircon powder

Composition	ZrO_2	SiO_2	HfO_2	Al_2O_3	Fe_2O_3	MgO
Content (wt%)	67.22	30.85	1.39	0.11	0.029	0.014

3 RESULTS AND DISCUSSION

3.1 Relative density

Figure 2 shows the relationship between the relative density of the specimens and the hot-pressing temperature when the holding time and pressure were 1 h and 25 MPa, respectively. It can be seen that at a temperature of 1500°C, the relative density of the specimen was still below 90%, indicating the densification of zircon powder was very poor. However, it increased rapidly to 98–99% as the temperature was raised to 1550–1600°C, reaching the highest value of 99.1% at 1600°C. This densification temperature is lower than the temperature of 1680°C at which Mori *et al.* obtained their sintered zircon ceramics with 98% relative density by pressureless sintering.[3] It could be attributed to

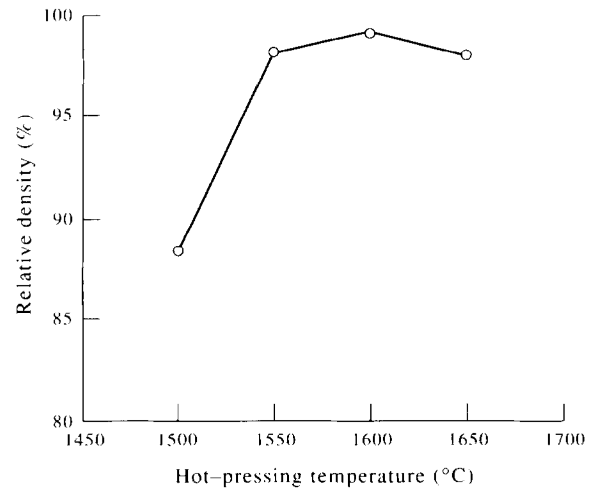

Fig. 2. The relationship between the relative density of the zircon specimens and the hot-pressing temperature.

the external pressure which prompted and accelerated the process of densification. At the same time, the occurrence of extensive grain growth and secondary recrystallization were restrained effectively, resulting in the optimization of the microstructure and the mechanical properties of the zircon material obtained. From the result of Fig. 2, it may be argued that 1600°C/1 h is a favourable condition for the densification of the present zircon powder by the hot-pressing process.

There was a small decrease of relative density when the hot-pressing temperature continued to increase to 1650°C, which may have been caused by the slight decomposition of $ZrSiO_4$ as shown by the following reaction:

$$ZrSiO_4 = ZrO_2 + SiO_2 \qquad (1)$$

with a volume expansion percentage of about 20%. Normally, the starting decomposition temperature of zircon is about 1675°C according to the ZrO_2–SiO_2 phase diagram. The existence of some impurities in the starting powder (Al_2O_3, TiO_2, etc.) could have lowered the decomposition temperature conspicuously. Comparing the SEM micrographs shown in Fig. 3, it could be seen that the microstructural feature of the fracture surface of a specimen hot-pressed at 1650°C [Fig. 3(B)] was different from that of a specimen fabricated at 1600°C [Fig. 3(A)]. There existed several circular particles on the fracture surface [Fig. 3(B)], which might be ZrO_2 particles formed by reaction (1). However, the amount of zircon decomposition under 1650°C was too limited to be detected by the X-ray diffraction (XRD) method.

3.2 Mechanical properties

The data of flexural strength of fabricated zircon samples are presented in Fig. 4. σ_f increased significantly from 150 MPa for the specimens hot-pressed at 1500°C to 320 MPa for those fabricated at 1600°C, which fits well with the change of relative densities. When the hot-pressing temperature was further increased to 1650°C, a slight decrease of σ_f occurred, correlated with the decline of the relative density due to the decomposition of zircon as indicated in the previous section. The mechanical properties of zircon fabricated from commercial zircon sand powder with 93% purity were also determined in order to compare with the mechanical properties of specimens from synthesized powder. Because of its higher impurity content, a much lower hot-pressing temperature (1500°C) was adopted to prevent it from decomposition during hot-pressing. The flexural strength of the specimens with relative density of 98.9% was 250 ± 24 MPa, which was about 20% lower than the value from synthesized powder. Table 2 lists the fracture toughness and Vickers hardness of hot-pressed zircon specimens. The highest values of K_{IC} and Vickers hardness were $3.0 \pm 0.4\,MPa{\cdot}m^{1/2}$ and 10.6 GPa, respectively, for the specimens hot-pressed at 1600°C for 1 h with synthesized powder.

The flexural strengths of hot-pressed zircon specimens fabricated from synthetic zircon powder (SP) and commercial zircon powder (CP) were measured at 1000°C, 1200°C and 1400°C, respectively. Figure 5 shows the dependence of the flexural strengths of two kinds of zircon ceramics on the testing temperatures. As for zircon SP, its flexural strength can be maintained up to 1000°C, followed by a slight decrease when the temperature is increased to 1200°C. At 1400°C, the σ_f still had a value of 214 ± 44 MPa, retaining about 70% of its room temperature strength. But the flexural strength of zircon CP decreased drastically when the temperature exceeded 1000°C. At 1200°C, the σ_f of zircon CP was 110 ± 10 MPa, which was lower than 50% of its flexural strength at room temperature.

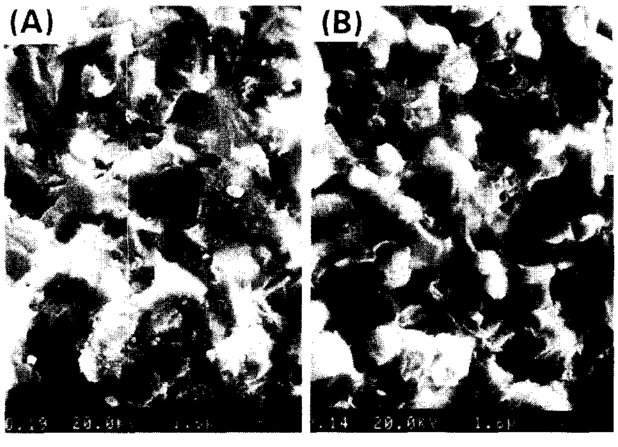

Fig. 3. SEM micrograph of the fracture surface of zircon hot-pressed at (A) 1600°C and (B) 1650°C.

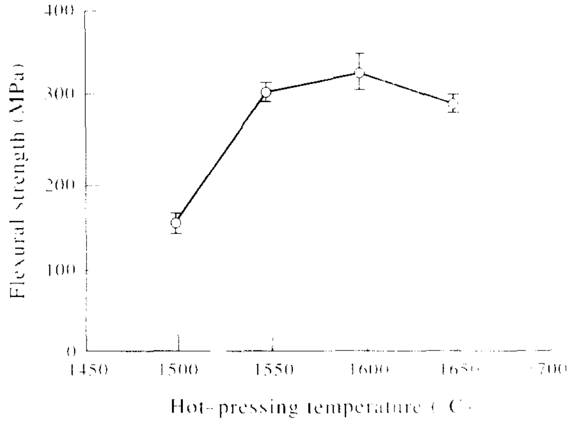

Fig. 4. Dependence of the flexural strength of zircon on the hot-pressing temperature.

Table 2. Fracture toughness and Vickers hardness of hot-pressed zircon specimens

Starting powder	Commercial	Synthesized	Synthesized	Synthesized
Hot-pressing temperature	1500°C	1550°C	1600°C	1650°C
K_{1C} (MPa·m$^{1/2}$)	2.5±0.2	2.5±0.2	3.0±0.4	2.2±0.1
Vickers hardness (GPa)	10.0	9.3	10.6	6.2

3.3 Microstructural characterization

The typical microstructures of zircon SP and CP are displayed in Fig. 6. It was observed that zircon SP consists of equiaxed grains whose sizes are mainly in the range of 1–2 μm [Fig. 6(A)]. No glassy phase was found either at the two-grain boundary or at the triple-grain junction. However, the grains of zircon CP were much coarser than those of zircon SP, which could explain why the mechanical properties of zircon SP were superior to those of zircon CP. Moreover, Fig. 6(B) revealed that there remained a considerable amount of glassy phase at the three-grain junction. The drastic decrease of flexural strength of zircon CP at high temperatures is apparently attributed to the existence of this glassy phase, which resulted from the oxide impurities in the starting commercial zircon powder.

In order to probe the reason for strength degradation at high temperatures, grain boundary features of hot-pressed zircon SP were observed by high resolution electron microscopy (HREM). Figure 7 shows that the boundary between two zircon grains is essentially free from glassy phase, the fringes of grains I and II meet each other at the grain boundary, showing numerous steps. However, two kinds of microstructural feature of triple junctions were observed, which have quite different TEM morphologies.[11] In most cases, the three-grain junction was clear, without any glassy phase in it. Furthermore, another sort of triple junction was scarcely observed, with glassy phase among three adjacent zircon grains, which is shown in Fig. 8. The HREM micrograph in Fig. 8(B) shows that the size of the glassy phase was approximately

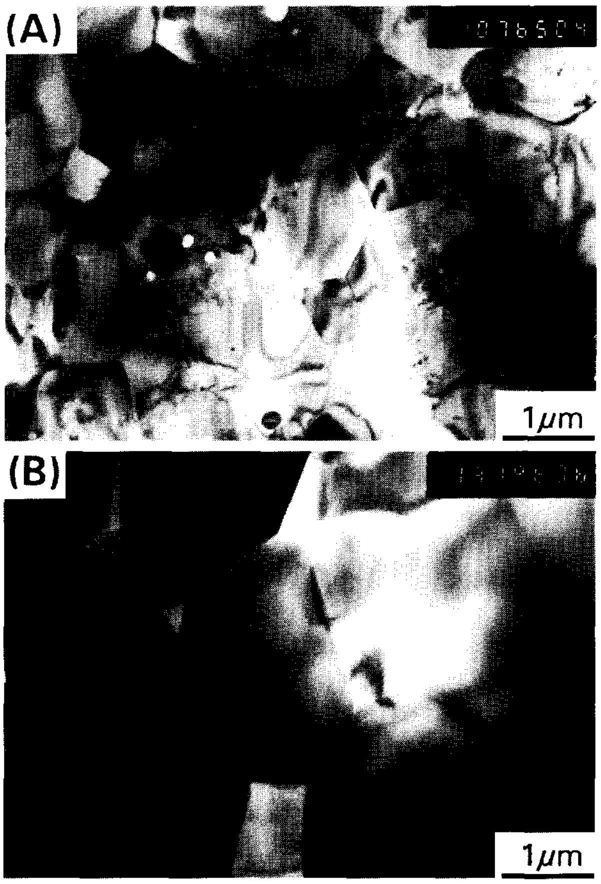

Fig. 6. TEM micrograph of (A) zircon SP and (B) zircon CP.

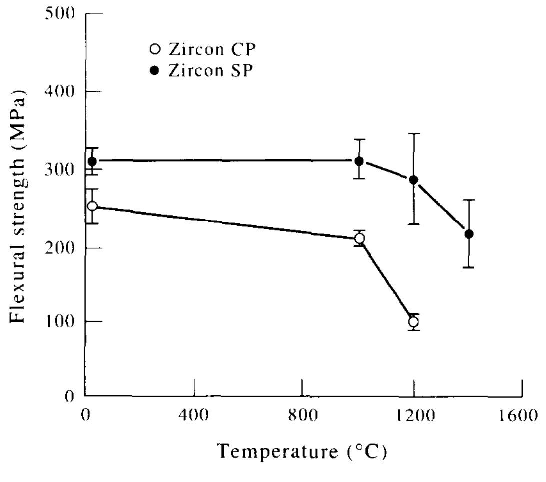

Fig. 5. Dependence of the flexural strength of zircon on temperature.

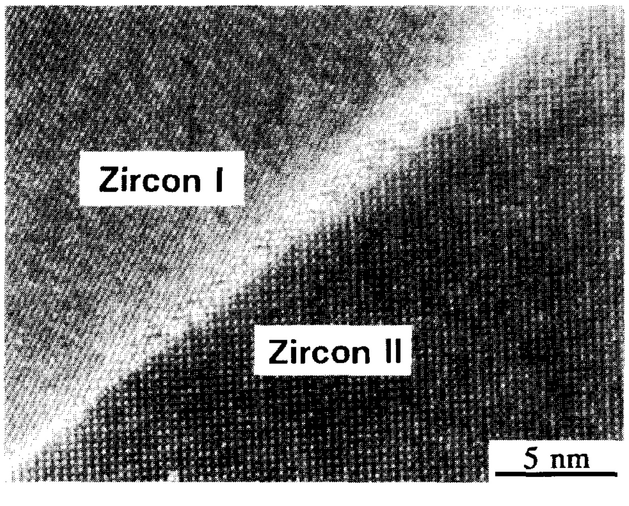

Fig. 7. HREM image of a two-grain boundary without any glassy phase.

10–15 nm. It can be inferred that the glassy phase originated from the trace impurities in the synthesized zircon powder, whose chemical composition was listed in Table 1.

4 DISCUSSION

The fracture surfaces of hot-pressed zircon SP specimens tested at different testing temperatures (R.T., 1000°C, 1200°C and 1400°C) were observed by scanning electron microscopy (SEM). From the cleavage steps shown in Fig. 9(A) and (B), it is evident that the mode of zircon fracture at both room temperature and 1000°C was transgranular. However, the SEM micrograph of the fracture surface tested at 1200°C [Fig. 9(C)] shows some triple junctions on the fracture surface, which are indicated by arrows, although the fracture mode at 1200°C is still mainly transgranular. At a temperature of 1400°C, the SEM micrograph of the fracture surface [Fig. 9(D)] shows the contour of zircon grains, demonstrating that an intergranular fracture mode has become predominant at 1400°C.

Considering the results of TEM and SEM observations, it can be deduced that the glassy phase at some of the triple junctions plays an important role in influencing the fracture behaviour of zircon ceramics. Under the conditions of temperatures lower than 1000°C, the combining strength of adjacent zircon grains was very high, the crack had to penetrate through the zircon grains in the course of crack growth, so the fracture mode of zircon SP was transgranular. When the testing temperature reached 1200°C, the glassy phase at triple junctions began to soften and its strength decreased simultaneously, resulting in the occurrence of "debonding" of zircon grains near the glassy triple junctions under the conditions of the fracture test [Fig. 9(C)]. At a temperature of 1400°C, the strength of the glassy phase at some triple junctions has dropped to such an extent that the initiation of a crack at the glassy triple junctions and the growth of the crack by grain boundary sliding would occur easily when an external force acted on the specimen during fracture. Thereby, the crack was prone to propagate along the grain boundary due to grain boundary sliding instead of through the zircon grain at low temperatures (below 1000°C) because the strength of the zircon grain was higher than that of the grain boundary. The schematic diagram of this mechanism is illustrated in Fig. 10. At this time, the glassy phase at triple junctions began to show its significance, as it weakens the grain boundaries and causes grain boundary sliding. As a result, the fracture

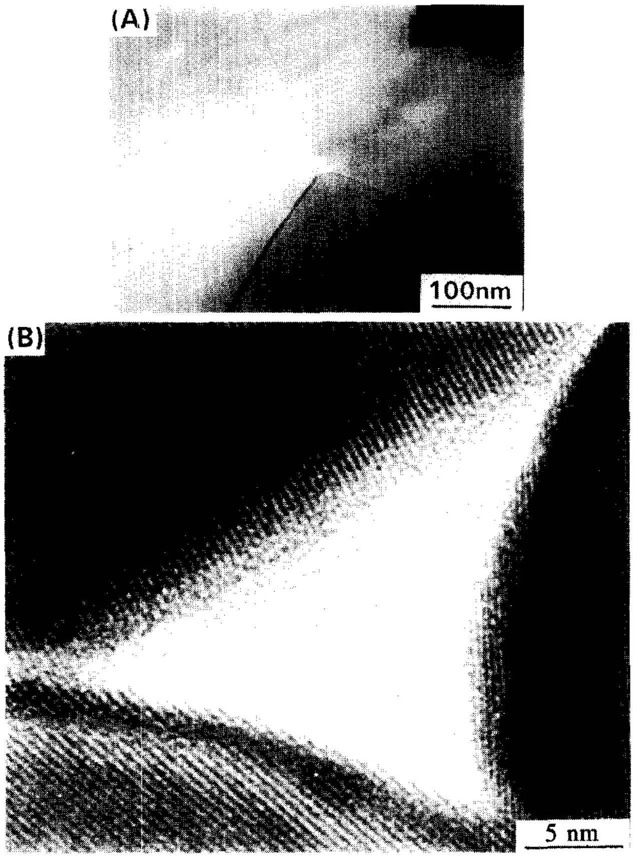

Fig. 8. (A) TEM morphology of three-grain junctions with glassy phase in zircon SP and (B) HREM image of (A).

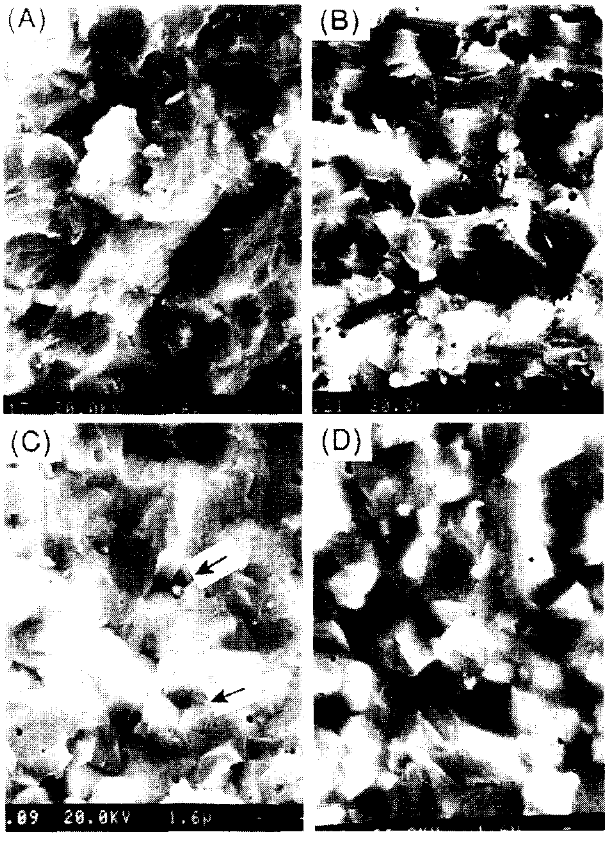

Fig. 9. SEM micrographs of the fracture surface of zircon SP specimens tested at (A) room temperature, (B) 1000°C, (C) 1200°C and (D) 1400°C.

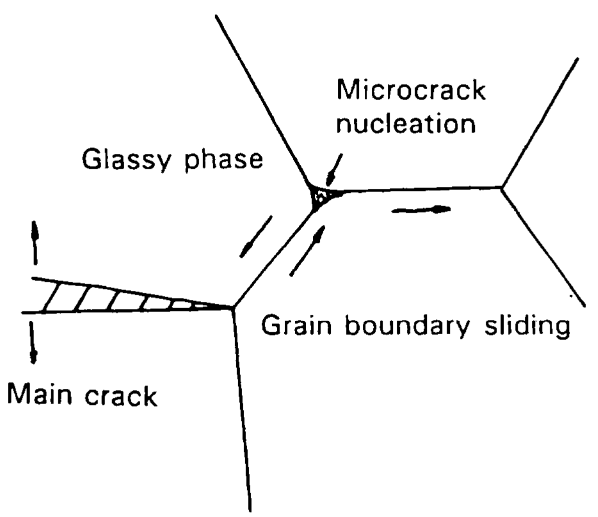

Fig. 10. Schematic diagram for the crack propagation in zircon SP at elevated temperatures.

mode of zircon transformed from transgranular at low temperatures to intergranular at elevated temperatures, which corresponded to the reduction of the flexural strength of zircon specimens at temperatures above 1200°C.

5 CONCLUSIONS

The following conclusions can be drawn from the work detailed above:

1. Fully densified zircon ceramics were fabricated by the hot-pressing process, under conditions of 1600°C/1 h with a pressure of 25 MPa by using synthesized sub-micron zircon powder. The flexural strength and fracture toughness of the zircon specimen with a relative density of 99.1% were 320 ± 20 MPa and 3.0 ± 0.4 MPa·m$^{1/2}$, respectively.
2. The flexural strength of the zircon ceramics hot-pressed from synthetic powder can be retained up to 1000°C, however, it began to decrease slowly when the temperature exceeded 1200°C. In the meanwhile, the fracture mode of zircon transformed gradually from transgranular to intergranular. Based on the SEM and HREM observations, it was proposed that the presence of a glassy phase at some of the triple junctions would initiate grain boundary sliding between zircon grains at high temperatures, which was responsible for the decrease of the flexural strength of zircon SP at high temperatures.

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REFERENCES

1. SINGH, R. N., SiC fibre-reinforced zircon composites. *Am. Ceram. Soc. Bull.*, **70**(1) (1991) 55–56.
2. MORI, T., YAMAMURA, H., KOBAYASHI, H. & MITAMURA, T., Preparation of high-purity $ZrSiO_4$ using sol–gel processing and mechanical properties of the sintered body. *J. Am. Ceram. Soc.*, **75**(9) (1990) 2420–2426.
3. MORI, T., HOSHINO, H., YAMAMURA, H., KOBAYASHI, H. & MITAMURA, T., Mechanical properties of high purity sintered $ZrSiO_4$. *J. Ceram. Soc. Jpn*, **98**(9) (1990) 1017–1022.
4. HAAKER, R. F. & EWING, R. C., Solution-gelation method for preparing polycrystalline zircon. *Commun. Am. Ceram. Soc.*, **64** (1981) C-149.
5. KOBAYASHI, H., TAKANO, T., MORI, T., YAMAMURA, H. & MITAMURA, T., Preparation of $ZrSiO_4$ powders by sol–gel process: influence of starting materials and seeding. *J. Ceram. Soc. Jpn*, **98**(6) (1990) 567–572.
6. SHI, Y., HUANG, X. X. & YAN, D. S., Preparation and characterization of highly pure, fine zircon powder. *J. Europ. Ceram. Soc.*, **13**(2) (1994) 113–119.
7. ELESWARAPU, C. S., DINESH, K. A., HERBERT, A. M., CHRISTOPHER, W. S. & RUSTUM, R., Thermal expansion of compounds of zircon structure. *J. Am. Ceram. Soc.*, **73**(5) (1990) 1246–1252.
8. MORENO, R., MOYA, J. S. & REQUENA, J., Slip casting of zircon by using an organic surfactant. *Ceram. Int.*, **17** (1991) 37–40.
9. SINGH, R. N., High-temperature mechanical properties of uniaxially reinforced zircon–silicon carbide composites. *J. Am. Ceram. Soc.*, **73**(8) (1990) 2399–2406.
10. KONDIH, I., TANAKA, T. & TAMARI, N., Sintering of zircon–silicon carbide whisker composites and their mechanical properties. *J. Ceram. Soc. Jpn*, **101**(3) (1993) 369–372.
11. SHI, Y., HUANG, X. X. & YAN, D. S., TEM and HREM characterization of hot-pressed zircon ceramics. *Mater. Lett.*, **23** (1995) 247–252.