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Mechanical properties of alkoxy-derived cordierite ceramics

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Mechanical properties of cordierite ceramics prepared by the controlled hydrolysis and following polycondensation of aluminium, magnesium and silicon alkoxides were investigated in great detail. Flexural strengths of μ- and α-cordierite ceramics are about 60 and 100 MPa, respectively. The flexural strengths of these ceramics are mainly influenced by cracks arising from thermal mismatch between μ- and α-cordierite precipitated during sintering. High fracture toughness of α-cordierite ceramics prepared by this method is ascribed to the fine microstructure of the ceramics. The high-temperature flexural strength of α-cordierite ceramics is little reduced below 1000° C because of high purity of the ceramics.

1. Introduction

Recently, wet chemical techniques such as the sol–gel method have attracted attention in the preparation of ceramic powders [1, 2] and bodies [3] which have a high purity and homogeneity, resulting in a high performance. Usually, metal alkoxides are used as raw materials in the sol–gel method but the difference in the hydrolysis rate between the alkoxides frequently causes inhomogeneity in the resultant ceramic powders in the case of the sol–gel method using metal alkoxides [4–7]. It has been demonstrated that the partial hydrolysis method was effective to prepare pure and homogeneous cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$), ceramics [8] having a low thermal expansion coefficient [9, 10] and a low dielectric constant (about 5 at 1 MHz) [11]. It is well known that cordierite ceramics have been used as catalyst carriers for exhaust gas control in automobiles and also are promising as integral circuit substrates having a low dielectric constant [12] and a superior heat conductivity compared with forsterite, steatite or glass ceramics, but it has not been possible to sinter pure and dense cordierite ceramics without using any sintering aid [13]. Using sintering aids results in inferior properties of the resultant ceramics. In the previous paper [14], pure and dense cordierite ceramics were obtained by sintering the pure and homogeneous cordierite powder compacts prepared by partial hydrolysis of alkoxides [8] without using any sintering aid. In this paper, the mechanical properties of the alkoxy-derived pure and dense cordierite ceramics are investigated and discussed in great detail.

2. Experimental procedure

Pure and homogeneous alkoxy-derived powder having a cordierite composition as described elsewhere [8] was calcined at 800° C for 12 h and then uniaxially pressed at 40 MPa followed by isostatic pressing at 300 MPa. The green compact of 55 mm × 15 mm × 4 mm was dried at 100° C for 24 h and sintered in an electric furnace. Pressureless sintering was carried out at temperatures ranging from 900 to 1450° C. The sintering schedule was described elsewhere [14]. Flexural strength was measured by the four-point bending test with a rectangular specimen of 3 mm × 4 mm × 40 mm. Young's modulus of the sintered cordierite was estimated by the Knoop indentation method [15] at a load of 19.6 N using the following equation

$$\begin{aligned} b'/a' &\simeq b'/a \\ &= b/a - \alpha H/E \end{aligned}$$

where b/a is the ratio of the diagonal dimensions, b'/a' is the ratio of the residual Knoop indentation impression after loading, α is a coefficient ($\alpha = 0.45$), H is Vickers hardness and E is Young's modulus. Fracture toughness was evaluated by the indentation microfracture method [16] at loads ranging from 9.8 to 49 N using the following equation

$$K_{IC}/Ha^{1/2} = 0.203\,(c/a)^{-3/2}$$

where K_{IC} is fracture toughness, H is the Vickers hardness, a is the half-diagonal of the Vickers indent and c is the radius of the surface crack. Fracture surfaces of sintered compacts after the bending tests were observed using a scanning electron microscope (SEM).

3. Results and discussion

3.1. Flexural strength

The results of the four-point bending tests are shown in Fig. 1. The compact sintered at 1300° C for 2 h, whose crystalline phase identified by X-ray diffraction was α-cordierite [14], shows the highest value of flexural strength of about 100 MPa. On the other hand, it was impossible to evaluate the flexural strength of the compact sintered at 1100° C because of the significant cracking ascribed to the difference in the thermal expansion coefficient between μ- and α-cordierite in the compact, i.e. cordierite ceramics

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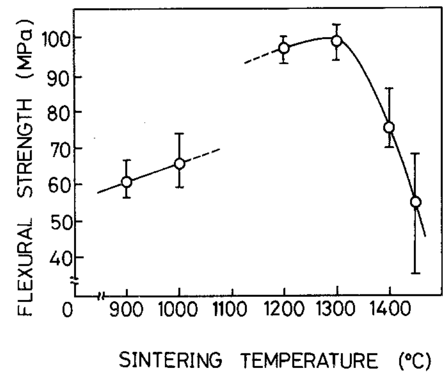


Figure 1 Flexural strengths of cordierite ceramics.

have an average thermal expansion coefficient of about $1.8 \times 10^{-6} {}^\circ C^{-1}$ which is calculated by the following equation

$$\alpha = (2\alpha_a + \alpha_c)/3$$

where α is an average thermal expansion coefficient, α_a is a linear thermal expansion coefficient along the *a*-axis and α_c is a linear thermal expansion coefficient along the *c*-axis. On the other hand, the thermal expansion coefficient of cordierite glass is about $3.8 \times 10^{-6} {}^\circ C^{-1}$ [19] and that of μ-cordierite, which has metastable β-quartz-like structure, is larger compared with α-cordierite. Therefore, sintering the

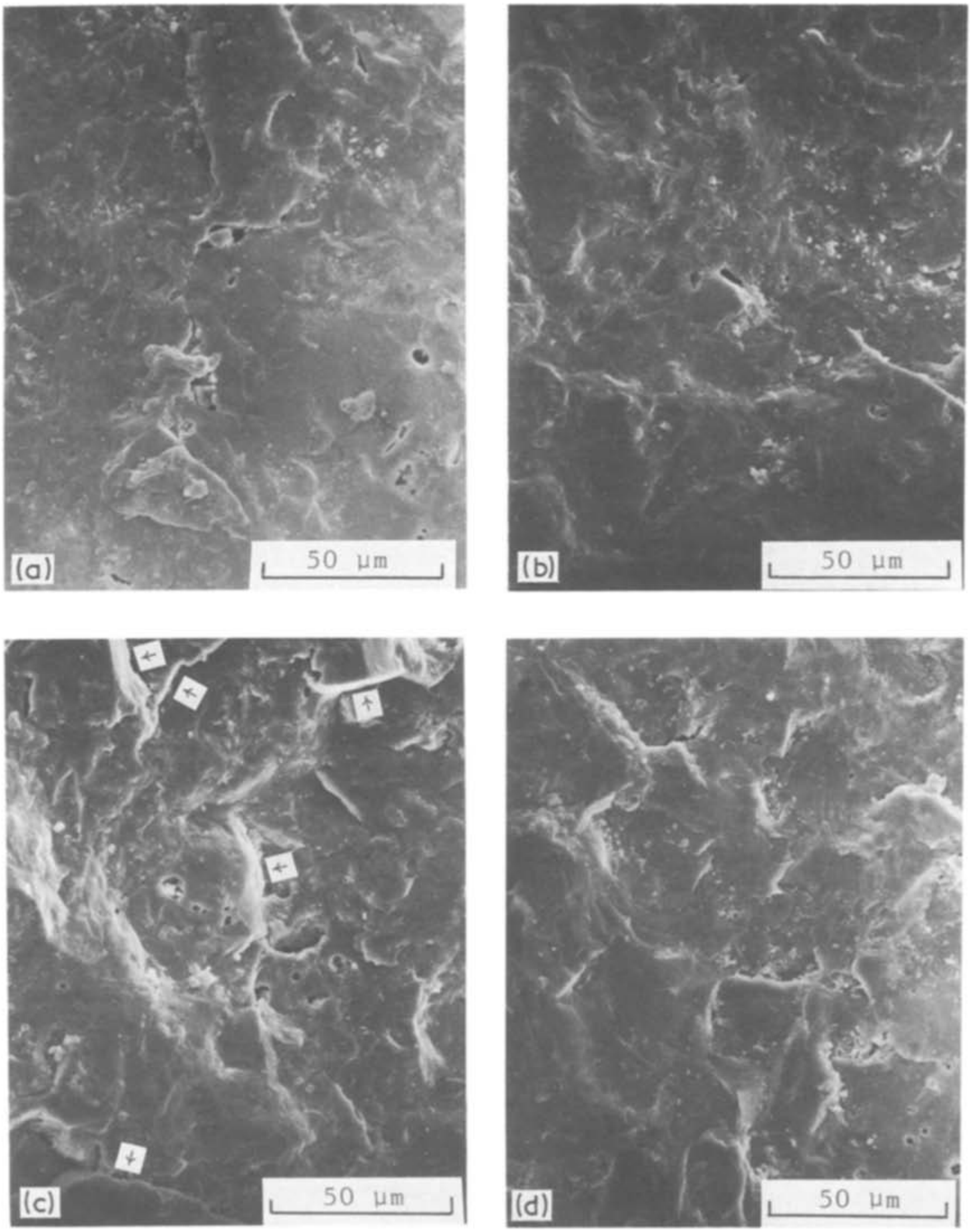
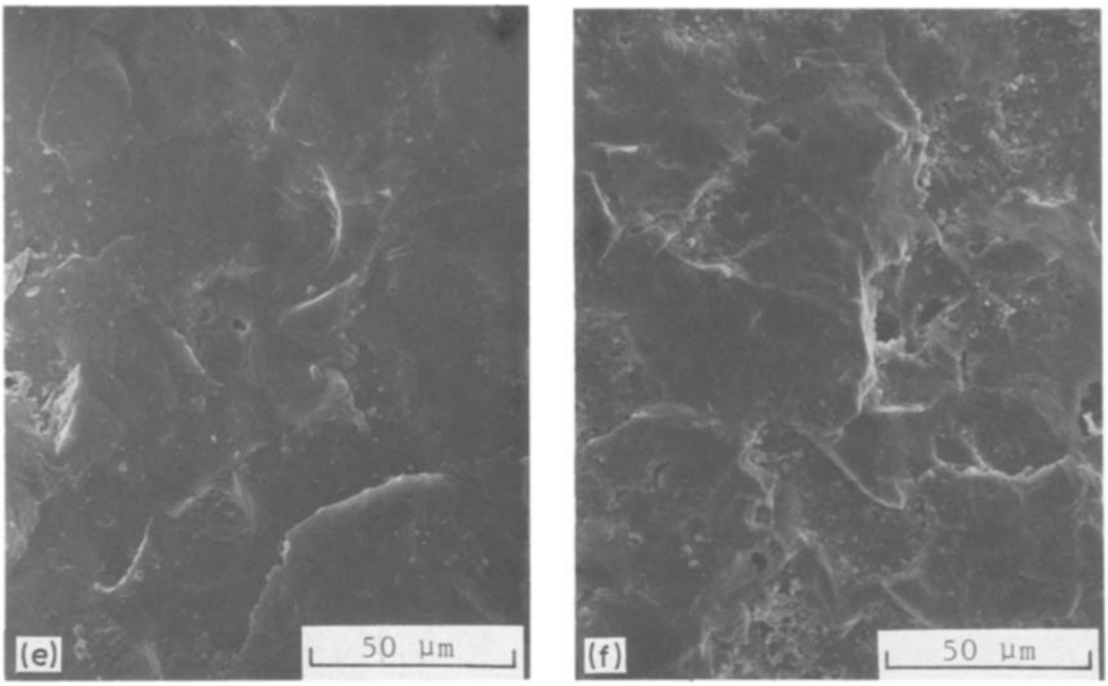


Figure 2 SEM images of the fractured surfaces of cordierite ceramics sintered at (a) 900° C, (b) 1000° C, (c) 1100° C, (d) 1200° C, (e) 1300° C, (f) 1400° C, (g) 1450° C.



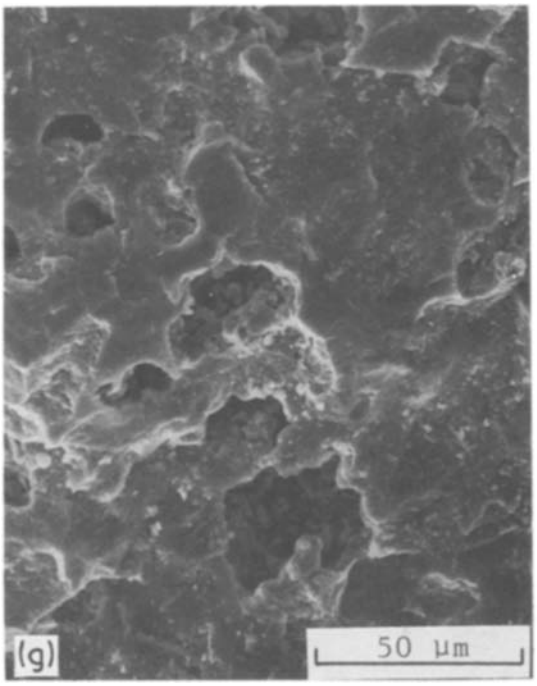


Figure 2 Continued.

powder compact at 1100° C results in the precipitation of μ-cordierite followed by the μ to α transformation, and then the mismatch of thermal expansion coefficients between μ- and α-cordierite in the sintered compact causes the stress leading to cracking. In addition, the flexural strengths of the compacts sintered above 1400° C decrease because of the micro-cracking due to the increased pressure in pores. This is confirmed by observations of the fracture surfaces of the compacts sintered at 1100, 1400 and 1450° C, indicating the existence of micro-cracks and expanded pores (Fig. 2). As the compacts sintered below 1000° C show dense fracture surfaces, the lower flexural strength of about 60 MPa may be due to the difference in the phases of the compacts. Fig. 2 also suggests that the micro-cracks arising from mismatch of thermal expansion coefficients are healed as sintering temperature increases. Fig. 3 shows X-ray diffraction patterns of the powder calcined at 980° C for 2 and 160 h, indicating the absence of α-cordierite below 1000° C. Therefore, flexural strength of μ-cordierite ceramics is estimated to be about 60 MPa and that of α-cordierite ceramics to be about 100 MPa.

3.2. Hardness, Young's modulus and fracture toughness

In contrast with the flexural strength, Vickers hardness of the sintered compacts is almost constant below 1300° C (Fig. 4). This result indicates that consolidation of the compacts is completed above 900° C and is not influenced by the crystalline phase. Young's modulus of the compacts sintered below 1300° C is also independent of crystalline phase (Fig. 5). These results suggest that the compacts sintered below

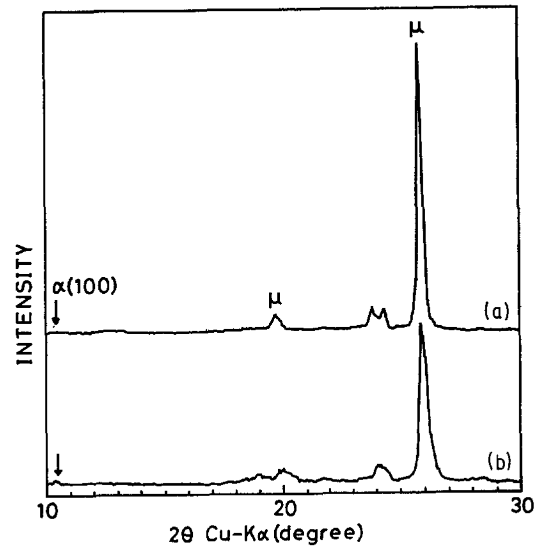


Figure 3 X-ray diffraction patterns of the cordierite powders. (a) Calcined at 980° C for 2 h, (b) calcined at 980° C for 160 h.

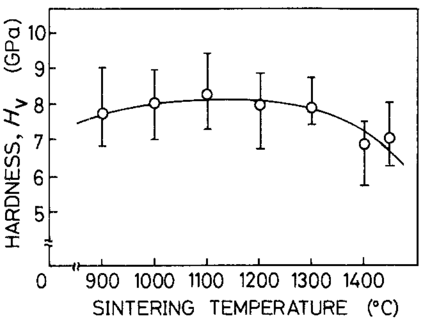


Figure 4 Vickers hardness of cordierite ceramics.

1300° C are fully densified and the difference in the densities with sintering temperatures may probably be ascribed to the amount of glassy phase, μ- and α-cordierite. Typical values of mechanical properties of cordierite and cordierite glass are listed in Table I. In this work, the fracture toughness of compacts depends upon sintering temperature or crystalline phases (Fig. 6). Above 1100° C, the fracture toughness is about 2.8 MPa m$^{1/2}$ which is higher than that listed in Table I. The fracture toughness and strength of materials are represented by the following equations [20]

$$K_{IC} = (2\gamma_s E)^{1/2}$$

$$\sigma = (2\gamma_s E/\pi C)^{1/2}$$

where γ_s is the surface energy, E is Young's modulus, and C is the flaw size. However, Young's modulus of the compacts sintered above 1200° C is about 90 MPa and is near the value of cordierite glass. This indicates the presence of a small amount of residual glassy phase and pores and is confirmed by scanning electron microscopy, transmission electron microscopy [8] and the measurement of densities of the sintered compacts [14]. Therefore, higher values of fracture toughness of the compacts sintered above 1200° C may probably be ascribed to higher values of surface energy due to the fine micro-structure.

Fig. 7 shows a high magnification SEM image of the polished and chemically etched surface of a compact sintered at 1300° C for 2 h including small pores, indicating the fine micro-structure. The grain size is as large as 0.5 μm. However, exaggerated grain growth due to large agglomerates may occur in the compacts during sintering, leading to lower flexural strength. This problem may be settled by a granulation of the powder before sintering. Lower values of flexural strengths compared with cordierite ceramics listed in Table I are due to lower Young's modulus and larger flaw size originating from unhealed cracks arising from thermal mismatch between μ- and α-cordierite. These cracks are healed by the prolonged heating of compacts, resulting in higher flexural strength of the compact (flexural strength of the compact sintered at 1300° C for 12 h is about 120 MPa). The fracture toughness of compacts sintered below 1000° C is higher (about 2 MPa m$^{1/2}$) compared with cordierite glass listed in Table I (0.9 MPa m$^{1/2}$). This indicates the fracture toughness of μ-cordierite is higher than that of cordierite glass. A lower value of fracture toughness at 1450° C may be ascribed to the expanded pores in the compact.

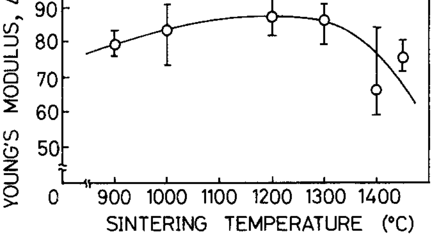


Figure 5 Young's modulus of cordierite ceramics.

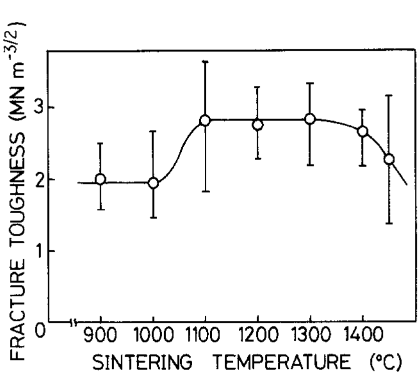


Figure 6 Fracture toughness of cordierite ceramics.

3.3. High-temperature flexural strength

As shown in Fig. 8, flexural strengths of sintered compacts do not decrease significantly at elevated temperatures. Below 1000° C, flexural strengths decrease only slightly. This indicates the yield point of the cordierite ceramics prepared in this method is beyond 1000° C. Above 1000° C, the compact sintered at 1300° C for 2 h maintains a high flexural strength above 70 MPa, which is due to the small amount of glassy phase and high purity of the ceramics derived from using no sintering aid. These superior mechanical properties of the cordierite ceramics are promising for application to a heat exchanger in a gas turbine engine.

4. Conclusions

Mechanical properties of the cordierite ceramics prepared from metal alkoxides were examined. Flexural strengths of the ceramics depend upon the crystalline phases in the ceramics, cracks arising from thermal mismatch between μ- and α-cordierite and pores due to increased pressure in the channels near the melting point of cordierite. Higher fracture

TABLE I Properties of cordierite and cordierite glass

Property	Cordierite	Cordierite glass
Bending strength (MPa)	245 [21]	100 [22]
Fracture toughness (MPa m$^{1/2}$)	2.3 [21]	0.9 [23]
Vickers hardness (GPa)	8.2 [24]	6.6 [25]
Young's modulus (GPa)	139 [24]	96 [22]

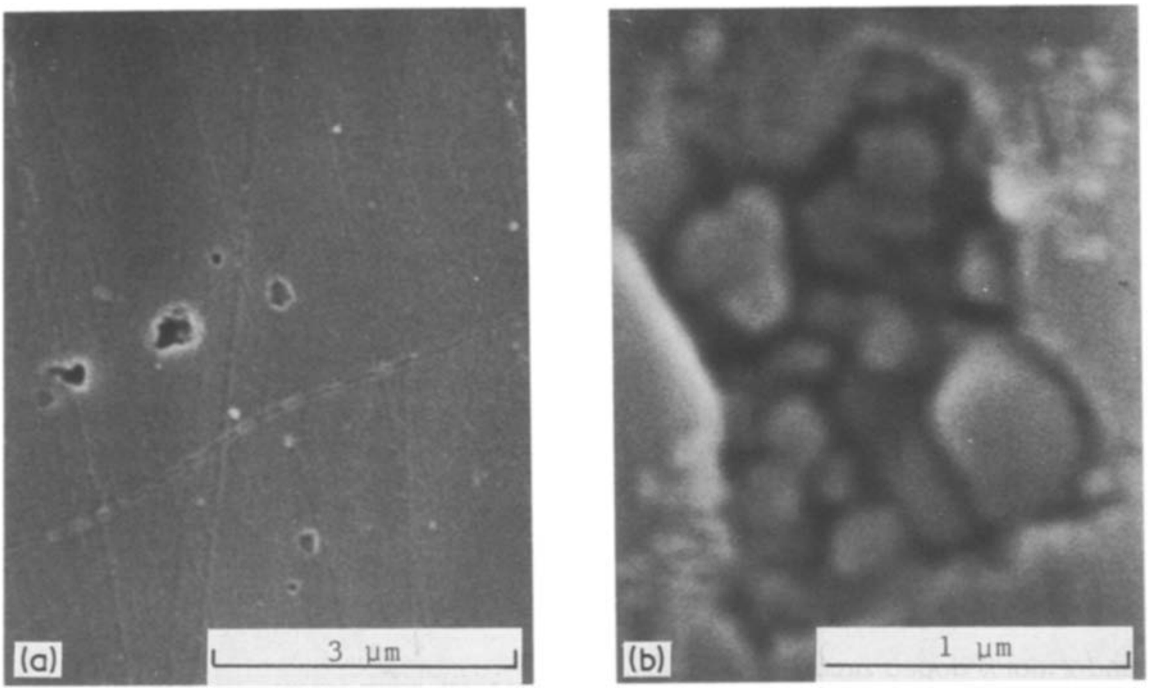


Figure 7 High-magnification SEM images of the polished and chemically etched surface of α-cordierite ceramics sintered at 1300° C for 2 h.

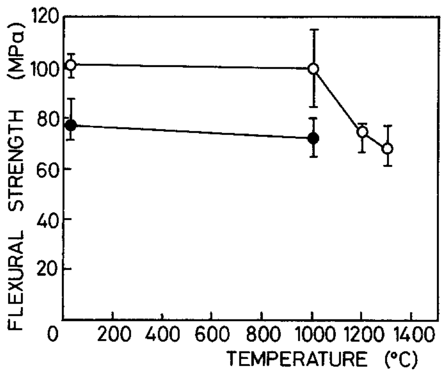


Figure 8 High-temperature flexural strengths of α-cordierite ceramics.

toughness of the ceramics is ascribed to their fine microstructure. Sintering the compacts without additives results in superior high-temperature strengths of the ceramics.

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