High Temperature Characteristics of Compacts Consolidated from Rapidly Solidified Mullite Containing ZrO_2

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High purity (99.85%) and commercial purity (97.98%) conventional mullite ceramics containing 30 mass% ZrO_2 were converted to amorphous powder by rapid solidification using Plasma Centrifugal Atomization (PCA). Rapidly solidified (RS) and, for comparison, non RS powder were hot pressed into disk samples. Bending test specimens were manufactured from both RS and non RS materials in accordance with JIS R1601. The strength and plastic deformation behaviour of both materials were assessed by three point bending at elevated temperatures up to 1723 K. The transverse rupture strength (TRS) of RS materials was higher than that of non RS materials at the same temperature, regardless of mullite purity. The TRS for both materials decreased with increasing temperature, while the TRS value of high purity materials was higher than that of commercial purity materials at elevated temperature. A three point bending deflection-rate jump test was employed to assess the deflection-rate sensitivity index m' ; m' provides a measure of a material's superplasticity. The bending force was dependent on the deflection rate at elevated temperature. For the same deflection rate, the bending force of the RS high purity material was lower than that of the non RS material; this was probably attributable to the very fine microstructure of the RS material. Both RS and non RS materials exhibited an m' of approximately 0.4 between 1623 and 1723 K.

Keywords: rapid solidification, amorphous ceramic, mullite-zirconia, Plasma Centrifugal Atomization (PCA), deflection-rate sensitivity index, strain-rate sensitivity index, superplasticity

I. Introduction

Much of the research that has been performed on mullite has focused on characterizing mullite's excellent high temperature mechanical properties⁽¹⁾. However, before its high temperature properties can be fully exploited, its poor fracture toughness needs to be improved. One of the more common methods of increasing mullite's fracture toughness is by adding ZrO_2 ⁽²⁾. Although conventional powder processing techniques can be used to produce mullite - ZrO_2 ceramic material, improved homogeneity, a more finely dispersed microstructure and superior mechanical properties can be obtained from mullite - ZrO_2 ceramics produced from amorphous powder⁽³⁾⁽⁴⁾. Conditions for producing amorphous mullite - 20 mass% ZrO_2 powder by Plasma Centrifugal Atomization (PCA) have been reported elsewhere⁽⁵⁾⁽⁶⁾.

In previous work on mullite - ZrO_2 ceramics possessing a finely dispersed microstructure, high mechanical strength⁽⁷⁾ was obtained at room temperature and high ductility⁽⁸⁾ was

exhibited at elevated temperature. The possibility of these materials exhibiting superplasticity has aroused interest from the point of view of exploiting such behaviour in near net shape forming operations.

The superplastic behaviour of yttria stabilized zirconia and yttria stabilized zirconia - alumina composites has already been reviewed⁽⁹⁾. Although there is little information available on mullite - based ceramics, their superplastic behaviour has been reported⁽¹⁰⁾⁻⁽¹²⁾.

In this work, the high temperature strength and plastic deformation behaviour of mullite - 30 mass% ZrO_2 were investigated.

II. Experimental

1. Sample preparation

High purity (HP) sol-gel mullite, commercial purity (CP) synthesised mullite and unstabilized zirconia (ZrO_2) powders were used in this investigation; details are presented in Table 1.

The experimental procedure used in this work is shown schematically in Fig. 1. Mullite - 30 mass% ZrO_2 ceramic rods were produced by conventional powder processing. Both HP and CP mullite powders, mixed with 30 mass% ZrO_2 , were wet-comminuted in an alumina-lined ball mill, spray-dried and cold isostatically pressed at 100 MPa to form a rod shape. The green compacts were machined, sintered at 1848 K (CP mullite) and 1903 K (HP mullite) and ground to produce rods, 20 mm in diameter and 200 mm in length.

By using PCA, the sintered rods were rapidly solidified (RS) to obtain amorphous ceramic powder. A schematic drawing of the plasma centrifugal atomizer used in this investigation is shown in Fig. 2. The sintered rod, placed in the centre of the atomizer, was rotated at high speed. The top end of the rotating rod was heated by a plasma torch to melt the ceramic material. As the ceramic melted, the molten material was atomized into fine droplets by the

centrifugal force exerted on the rod. The droplets were rapidly solidified on a quenching substrate surrounding the rod. A full description of the process conditions can be found in earlier work⁽⁶⁾.

The resulting RS powder was ball-milled for 96 h and hot pressed at 30 MPa into disk samples at 1723 K (CP mullite) and 1773 K (HP mullite). For comparison, the same procedure was performed with non RS powder. Bending test specimens ($3 \times 4 \times 38$ mm) were machined from the hot pressed samples.

2. Bending test

The strength and the plastic deformation behaviour of both RS and non RS materials were assessed by three point bending at elevated temperatures up to 1723 K. Tests were performed on a Shimadzu computer-controlled fatigue test machine, Model EHF-ED50kN, equipped with a mullite bending jig and a high temperature furnace. Transverse rupture strength was measured in accordance with JIS R1601.

To investigate plastic deformation behaviour, bend tests⁽¹³⁾ were chosen over tensile tests because bend test specimens were easier to machine. Having decided to adopt bend tests, the deflection-rate jump (DRJ) test⁽¹⁴⁾ was selected in preference to constant deflection-rate bend tests; DRJ tests yield more information per specimen (Fig. 3) and therefore the number of test specimens can be reduced. The plastic deformation behaviour was assessed by measuring the deflection-rate sensitivity index m' corresponding to strain-rate sensitivity index m , which provides a measure of

Fig. 1 Experimental procedure.

Fig. 2 Schematic diagram of the plasma centrifugal atomizer (PCA).

Table 1 Chemical compositions of starting powders.

	mass%									
	SiO_2	Al_2O_3	ZrO_2	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	others
CP mullite	26.53	71.46	-	0.80	0.09	0.17	0.19	0.17	0.30	0.29
HP mullite	28.05	71.80	-	-	0.10	-	-	-	0.01	0.04
zirconia	0.045	-	99.76	0.035	0.16	-	-	-	-	-

a material's superplasticity. m' and m are defined by the following equations:

$$m' = \delta \ln P / \delta \ln \dot{v} \quad (1. a)$$

$$m = \delta \ln \sigma / \delta \ln \dot{\epsilon} \quad (1. b)$$

where P and $\dot{v}$ are bending force and deflection-rate, respectively. P corresponds to a stress, σ and $\dot{v}$ to a strain-rate, $\dot{\epsilon}$.

Fig. 3 Schematic diagram showing the response of bending force after an abrupt change in bending rate.

III. Results

1. Microstructure

Figure 4 shows SEM micrographs of RS and non RS mullite - 30mass% ZrO₂ after chemical and thermal etching; dark areas are mullite and the lighter areas are zirconia. These micrographs confirmed that RS materials had much finer microstructures than non RS materials. RS material had a characteristic microstructure, termed nanostructure⁽¹⁵⁾, showing fine t-ZrO₂ particles in the mullite grains and at the grain boundaries; this nanostructure cannot be obtained by sintering non RS powder. Average grain sizes determined by the linear intercept method are listed in Table 2. The grain size of the HP material was less than half that of the CP material despite being hot pressed at 50 K higher than the CP material. Both HP- and CP-RS materials exhibited a finer grain size than their respective non RS materials.

Table 2 Average grain sizes of the specimens.

	Grain size, $d / \mu\text{m}$			
	CP mullite - 30Z		HP mullite - 30Z	
	Hot-pressed at 1723 K		Hot-pressed at 1773 K	
Procedure	mullite	zirconia	mullite	zirconia
RS	0.92	0.54	0.38	0.30
Non RS	1.22	0.65	0.71	0.57

Fig. 4 SEM micrographs of thermally and chemically etched RS and non RS, commercial purity (CP) and high purity (HP) mullite - 30 mass% ZrO₂ samples.

2. Strength

The transverse rupture strength of CP mullite - 30 mass% ZrO_2 , at temperatures up to 1473 K, is shown in Fig. 5. RS material exhibited a higher TRS than the non RS material throughout the temperature range under test. TRS values obtained at room temperature show a high degree of scatter. The strength appeared to remain fairly constant up to 1073 K after which the strength decreased at an approximately constant rate. At 1473 K the TRS of CP mullite - 30 mass% ZrO_2 exhibited only 10% of its room temperature value. HP mullite - 30 mass% ZrO_2 possessed a superior TRS value at elevated temperature compared to CP mullite - 30 mass% ZrO_2 although their room temperature values were similar.

3. Plastic deformation

Figure 6 shows the bending force as a function of deflection rate between 1623 K and 1723 K for both RS and non-RS HP mullite - 30 mass% ZrO_2 . Each bending force/deflection rate line was generated from data obtained from one specimen. The bending force was dependent on the deflection rate and decreased with increasing temperature. At the same deflection rate, the bending force of the RS material was lower than that of the non-RS material. The gradient of the straight lines obtained in Fig. 6 correspond to the bending deflection-rate sensitivity index, m' , which was approximately 0.4 in all cases. To permit comparison between materials, the deflection-rate axis and the bending-force axis shown in Fig. 6 were converted to an outer fiber strain-rate ($\dot{\epsilon}_s$) axis and an outer fiber stress (σ_s) axis, using an equation described by Motohashi *et al.*⁽¹³⁾:

$$\dot{\epsilon}_s = 4(1 + m') y_t \dot{v} / l^2 m' \quad (2)$$

$$\sigma_s = (2 + m') l P / 2 w t^2 \quad (3)$$

where l is the span distance and y_t is the distance from the neutral plane to the specimen surface, w and t are the width and thickness of specimen, respectively. A representative value of 0.4 was assigned to m' for this conversion.

Figure 7 shows the response of the RS and non-RS CP mullite - 30 mass% ZrO_2 to deflection rate jump testing. In this figure, the same data 'tick' indicates that the data was obtained from the same specimen. The m' values

Fig. 5 Transverse rupture strength of commercial purity (CP) and high purity (HP) mullite - 30 mass% ZrO_2 samples as a function of temperature.

Fig. 6 Bending force of (a) RS and (b) non RS high purity (HP) mullite - 30 mass% ZrO_2 samples as a function of deflection rate.

Fig. 7 Bending force of (a) RS and (b) non RS commercial purity (CP) mullite - 30 mass% ZrO_2 samples as a function of deflection rate.

increased with increasing temperature, similar to the results for Y-TZP obtained by Motohashi *et al.*⁽¹³⁾. Although the results obtained for RS and non RS materials were similar, the m' values for non RS mullite - 30 mass% ZrO_2 showed a greater dependency on temperature.

Comparing Figs. 6 and 7, it is apparent that the bending force at a given deflection rate is significantly higher for the HP materials compared to the CP materials.

Arrhenius plots of deflection rate against inverse temperature are given in Fig. 8. The apparent activation energies, Q , for the onset of plastic flow in RS HP and non RS HP materials were calculated as 890 and 780 kJ/mol respectively.

Fig. 8 Arrhenius plots showing the activation energy of HP and CP mullite - 30 mass% ZrO₂.

IV. Discussion

1. Effect of microstructure on the high temperature strength

Consolidated compacts hot-pressed from RS powder can exhibit improved homogeneity, a more finely dispersed microstructure and superior mechanical properties. Improvements in room temperature mechanical properties of RS CP mullite-20 mass% ZrO₂ were reported in a previous paper⁽⁷⁾. This was probably attributable to the very fine microstructure. The improvements obtained in TRS for RS mullite - 30 mass% ZrO₂ in this work can be explained similarly, by the fine microstructure obtained via the rapid solidification procedure. The strength decrease with increasing temperature is due to the mullite matrix strength itself decreasing with temperature and the progressive transformation of t-ZrO₂ into m-ZrO₂. Claussen⁽¹⁶⁾ showed that the stability of t-ZrO₂ increased with decreasing grain size. Therefore the t-ZrO₂ present in the very fine microstructure of the RS material might be expected to exhibit greater stability compared with the t-ZrO₂ present in the non RS material. By increasing the stability of t-ZrO₂, the material's strengthening mechanism can be maintained to higher temperatures. Clearly, the material's mechanical properties are greatly affected by grain size.

2. Effect of microstructure on the deformation behaviour at high temperature

The high temperature flow of ceramic materials can be expressed by

$$\dot{\epsilon} = A (\sigma^n / d^p) \exp(-Q / RT) \quad (4)$$

where

$\dot{\epsilon}$ - strain-rate	n - stress exponent
A - constant	p - grain-size exponent
σ - deformation stress	Q - activation energy
d - grain size	R - gas constant
T - temperature (K)	

n is equal to $(1/m)$, where m is a strain-rate sensitivity index. Motohashi *et al.* reported that in the bending system, the bending force P , the deflection-rate $\dot{v}$ and the deflection-rate sensitivity index m' correspond respectively to σ , $\dot{\epsilon}$ and m in the tensile system. They showed that m' was at least 95% of m . The results given in Fig. 6 show that $\ln(\text{bending force})$ is directly proportional to $\ln(\text{deflection rate})$. In bending deformation systems specimens are subjected to both tension and compression. As strain rates are not uniform throughout the material, strictly m' can not be used in valid analyses of superplastic behaviour. However, m' is recognized as an important factor for relating the deflection rate to the bending force. Although an m value exceeding approximately 0.5 is generally regarded as the lower limit for superplasticity⁽⁹⁾, Motohashi reported an m' value of 0.4 for the superplastic material Y-TZP. From this, the values of m' obtained in the present work, approximately 0.4 for the HP materials, indicate the possibility of superplastic behaviour.

Fig. 9 Deflection rate as a function of grain size.

The grain size exponent, p , is described by equation 5:

$$p = -\partial \ln \dot{v} / \partial \ln d \quad (5)$$

Data obtained from this work was substituted into equation 5 to generate a plot of $\ln(\dot{v})$ against $\ln(d)$ (Fig. 9). These

initial results given in Fig. 9 indicate that p is approximately 3. Although further work is necessary for confirmation, this value compares well to that reported by Yoon and Chen for mullite-TZP composites; they calculated p to lie between 2 and 3 which they suggested was indicative of a superplastic material.

In addition to the grain size, the grain boundary condition also exerts a profound influence over the plastic behaviour of ceramic materials. It is generally accepted that much of the superplastic behaviour reported for ceramic materials can be attributed to a glassy phase existing between grain boundaries. Ashizuka *et al.*⁽¹⁷⁾ detected a glassy phase between grain boundary triple points in 72 mass% Al_2O_3 mullite but not in 74 mass% Al_2O_3 mullite; in later work⁽¹⁸⁾ they obtained similar results for mullite - ZrO_2 materials. Differences observed in plastic behaviour can be directly attributed to the amount of amorphous phase present.

The results given in Fig. 6 indicate that there was little variation of m' with temperature. This was thought to be due to an insufficient amount of grain boundary glassy phase being present in the HP materials. The slight differences in m' between RS and non RS materials are thought to be due to differences in grain size (Table 2). In Fig. 7 however, the differences in grain size of the CP materials are less than for HP materials (Table 2) yet the dependence of m' on temperature is far greater. In this case the presence of a grain boundary glassy phase is thought to be largely responsible for these observations.

It appears that the difference in deformation behaviour between RS and non RS materials can be explained in terms of the grain size effect for HP material and the volume of grain boundary glassy phase for CP material. Further work is necessary to provide microstructural evidence to support these findings.

2. Activation energy, Q

Yoon *et al.* reported similar values of Q , between 500 and 800 kJ/mol, to those obtained in this work. Q was observed to increase as the percentage of mullite increased because the Q of mullite was higher than Y-TZP. The differences in Q between RS and non RS materials might be due to the grain size. Wakai *et al.*⁽¹⁹⁾ reported that the value of Q decreased with increasing grain size which was thought to be due to a difference in diffusion mechanisms operating during plastic flow.

On the other hand, values for Q obtained for the CP material were quite low, approximately half of that obtained for HP material. This might suggest that plastic flow may occur between the glassy phase and grain boundaries as has been reported previously⁽²⁰⁾.

V. Conclusions

Strength and plastic deformation behaviour of compacts possessing a fine microstructure hot-pressed from rapidly solidified (RS) mullite powder containing 30 mass% ZrO_2 were investigated at the elevated temperature up to 1723 K.

Differences between high purity (HP) and commercial purity (CP) materials were discussed. The main results are as follows:

- (1) RS material showed higher transverse rupture strength (TRS) than non RS materials throughout the range of temperature under test regardless of mullite purity.
- (2) The TRS of both RS and non RS materials decreased with increasing temperature.
- (3) The bending force was dependent on the deflection rate. Both RS and non RS materials exhibited a deflection sensitivity index, m' , of approximately 0.4 between 1623 and 1723 K.
- (4) For the same deflection rate in HP material, the bending force of the RS material was lower than that of the non RS material at elevated temperature; this was probably attributable to the very fine microstructure.
- (5) Apparent activation energies for the onset of plastic flow in HP material obtained from an Arrhenius plot were approximately 890 kJ/mol for the RS and 780 kJ/mol for the non RS HP material. Both values were higher than those for CP materials.

REFERENCES

- (1) P. C. Dokko, J. A. Pask and K. S. Mazdiyani: *J. Am. Ceram. Soc.*, **60**(1977), 150.
- (2) N. Claussen and J. Jahn: *J. Am. Ceram. Soc.*, **63**(1980), 228.
- (3) M. Yoshimura, Y. Hanaue and S. Somiya: *Mullite and Mullite Matrix Composites*, *Ceram. Trans.* **6**(1990), 449.
- (4) P. Pilate and F. Cambier: *Br. Ceram. Proc.*, **45**(1990), 71.
- (5) H. Ito, K. Morino, Y. Yamasaki, K. Takagai and T. Ando: *Advanced Materials '93, I/A*, *Trans. Mat. Res. Soc. Japan*, **14A**(1994), 487.
- (6) H. Ito, Y. Yamasaki, S. Matsuo, K. Takagai, K. Morino and H. Kuroki: *J. High Temp. Soc. Japan*, **21**(1995), 192.
- (7) H. Ito, Y. Yamasaki, S. Matsuo, K. Takagai, K. Morino and H. Kuroki: *J. Japan Inst. Metals*, **60**(1996), 169.
- (8) H. Ito *et al.*: in preparation.
- (9) T. G. Langdon: *Bull. Japan Inst. Metals*, **30**(1991), 1001.
- (10) C. K. Yoon and I-Wei Chen: *J. Am. Ceram. Soc.*, **73**(1990), 1555.
- (11) C. K. Yoon and I-Wei Chen: *Mullite and Mullite Matrix Composites*, *Ceram. Trans.*, **6**(1990), 567.
- (12) T. Nagano, H. Kato and F. Wakai: *J. Mater. Sci.*, **27**(1992), 3375.
- (13) Y. Motohashi, K. Watanabe, M. Ohmori and M. Kubota: *Trans. Japan Soc. Mech. Engrs.*, **56A**(1990), 156.
- (14) Y. Motohashi and K. Watanabe: *Trans. Japan Soc. Mech. Engrs.*, **58A**(1992), 1438.
- (15) K. Niihara: *J. Japan Ceram. Soc.*, **99**(1991), 974.
- (16) N. Claussen and M. Ruhle: *Advances in Ceramics, Vol. 3*, *Am. Ceram. Soc.*, (1981), 137.
- (17) M. Ashizuka, T. Honda and Y. Kubota: *J. Japan Ceram. Soc.*, **99**(1991), 292.
- (18) M. Ashizuka, T. Honda and Y. Kubota: *J. Japan Ceram. Soc.*, **99**(1991), 357.
- (19) F. Wakai, Y. Kodama and T. Nagano: *Japan J. Appl. Phys. Series 2, Lattice Defects in Ceramics*, (1989), 57.
- (20) M. Gust, G. Goo, J. Wolfenstine and M. L. McCartney: *J. Am. Ceram. Soc.*, **76**(1993), 1681.