JOURNAL OF MATERIALS SCIENCE 31 (1996) 4775–4778

Fractographic analysis of vitreous calcia–alumina eutectic fibres produced by inviscid melt spinning (IMS)

YUN-MO SUNG*†
Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, WI 53706 USA
IL-MO SUNG
Propeller Shaft Division, Deok Chang Ind. Co. Ltd., Incheon, Korea

The mechanical properties of inviscid melt spun (IMS) $CaO–Al_2O_3$ (46.5 wt % CaO–53.5 wt % Al_2O_3) eutectic fibres were examined by fractographic analysis as well as four-point bending and micro-indentation. The averaged fracture strength and elastic modulus values of the IMS Calcia–Alumina (CA) fibre were determined to be 460 MPa and 99.8 GPa, respectively by using four-point bending tests. The inner mirror constant (M) was determined to be 2.39 MPa·$m^{1/2}$ by using the plot of the fracture strength (σ_f) obtained from the bending tests as a function of $r^{-1/2}$, where r is the inner mirror radius measured from scanning electron microscopy (SEM) on the fractured CA fibres. The flaw-to-mirror ratio (c/r) for the CA fibre was calculated to be 1 : 11.24. Also, the critical flaw size (c) of the CA fibre was estimated to be 2.35 μm. The averaged elastic modulus value from Knoop micro-indentation was determined to be 102.5 GPa which is in good agreement with that from the four-point bending tests.

1. Introduction

The inviscid melt spinning (IMS) technique has been successfully applied to fibre fabrication [1–12]. The development of the IMS method means that the spinning of inviscid ceramic melts has become possible. This is achieved by overcoming the Rayleigh breakup of the molten stream during spinning. This is made possible by using the pyrolysis of a hydrocarbon gas such as propane which then forms a carbon sheath on the surface of the molten stream which stabilizes the molten stream until solidification occurs. The IMS technique is a very rapid and low cost fibre fabrication method compared to other current ceramic high performance fibre fabrication methods. These other techniques include chemical vapour deposition (CVD), used to grow ceramics on tungsten and graphite filaments [13–16], the pyrolysis of cured polymer fibres [17–19], slurry processing of a ceramic powder and organic polymer mixture [20–22] and diffusion based sol–gel processing of metal alkoxides [23–25]. Ceramic fibres of $CaO–Al_2O_3$ (CA) [1–8], $BaO–TiO_2$ (BT) [9], $CaO–Al_2O_3–MgO$ (CAM) [10], $Al_2O_3–ZrO_2$ (AZ) [11] and $Al_2O_3–MgO$ (AM) [12] have been produced using the IMS process. In order to decrease the ceramic melting temperatures eutectic compositions of binary or ternary ceramic systems were used in IMS. A decreasing in the melting temperature meant that the reduction of the ceramic melts by carbon could be prevented. The as-spun eutectic CA fibre (46.5 wt % CaO–53.5 wt % Al_2O_3) was a vitreous phase whilst the other mentioned fibres were polycrystalline. In addition only the CA fibres were long ($\geqslant$30 cm) and dense, whilst the other fibres were short ($\sim$1–5 cm) and slightly porous. The CA fibres have been subjected to investigation of their microstructure, crystallization behaviour and chemical durability. It is known that due to a rapid grain growth during crystallization the mechanical properties of a CA fibre drop once it reaches the crystallization temperature of 930 °C. Thus, CA fibres can only be used for reinforcing glass–ceramic and metal matrices which can be processed and utilized at relatively low temperatures. Some glass–ceramics, such as β-spodumene containing B_2O_3 and TiO_2, can be processed at temperatures lower than 930 °C by using sintering and crystallization heat treatments [26]. Systems that have been studied to date include CA fibre reinforced cement [27], aluminium alloy [28], and

* Author to whom all correspondence should be addressed.
† *Present address*: Department of Materials Science and Engineering, Daejin University, Pochun-kun, Kyungki-do 487-800, Korea.

0022–2461

β-spodumene glass–ceramic matrix composites [29]. However, a detailed study on the mechanical properties of CA fibres has not been performed and this information is of importance to the application of CA fibres especially as a composite reinforcement, medium.

The central focus of this study is on the fractographic analysis of the CA fibre. The analysis of fracture strength, elastic modulus, and fracture toughness of the CA fibre was also performed. Four-point bending, Knoop and Vickers micro-indentation tests and also scanning electron microscopy (SEM) have been used in this study.

2. Experimental procedure

The detail procedure of CA fibre fabrication is described in previous papers [1–12]. The as-spun CA fibres were straight and approximately 30 cm in length and 200–300 μm in diameter. Fracture strength and elastic modulus values of the CA fibres were determined by four-point bending tests. Since the diameter of the CA fibres were large in scale, a single fibre could be handled very easily. The inner and outer span distances for the bending jig were 11.61 and 23.22 mm, respectively. The lowest crosshead speed of 0.254 mm per min was used for the bending tests. All the fractured samples were labeled for further fractographic analysis.

Scanning electron microscopy (SEM: Jeol 35-C, Japan) was applied to the fracture surface analysis of the CA fibres which were used for the bending tests. The inner mirror radius which is the distance from the fracture origin to the mirror-mist boundary (r), was measured from the samples. Specimens with asymmetric mirror were excluded in the measurements.

Vickers and Knoop micro-indentation tests were used to obtain the fracture toughness and elastic modulus of the CA fibre. The CA fibres were cut into 15 mm lengths using a razor blade and the faces were polished using SiC papers (grit #600). Five fibres were vertically embedded in an epoxy mount using a clip. The top and bottom surfaces of the sample mounts were polished using the SiC paper (t) and alumina powders (1.00 and 0.05 μm). During the polishing special care was taken to maintain the top and bottom surfaces parallel. After the polishing the CA fibres were exposed at both the top and bottom surfaces of each mount. For both the Vickers and Knoop micro-indentation tests the applied load was 2.7 N.

3. Results and discussion

From the straight lines observed for the deflection data in the four-point bending tests the averaged elastic modulus value was determined to be 99.8 GPa. The fracture strength values also obtained from the bending tests ranged from 365–512 MPa and the averaged value was determined to be 465 MPa. The fracture surfaces of the CA fibres were examined by SEM. Fig. 1 shows a typical fracture surface of an IMS CA fibre. The flat and smooth 'mirror' is bounded by the

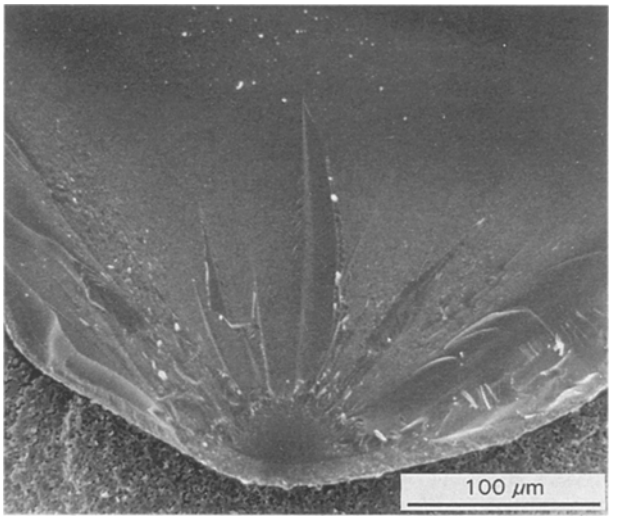

Figure 1 Scanning electron micrograph (SEM) of typical fracture surface of the inviscid melt spun (IMS) $CaO–Al_2O_3$ (CA) eutectic fibre.

region containing small radial ridges known as 'mist'. The mist is bounded in turn by 'hackle' containing larger radial ridges, which is bounded by macroscopic crack branching. The inner mirror radius (r) of each fractured CA fibre was measured. The fracture strength (σ_f) values are plotted as a function of $r^{-1/2}$ in Fig. 2 in which the line represents the least square fit to the data. All the data points can be expressed using the empirical relation [30–37]:

$$M = \sigma_f r^{1/2} \quad (1)$$

where σ_f is the fracture strength, M is the inner mirror constant, and r is the inner mirror radius. From the slope of the line in Fig. 2 the inner mirror constant of the CA fibre (M) was determined to be 2.39 $MPa \cdot m^{1/2}$. This value is close to that of silica glass (~2.33 $MPa \cdot m^{1/2}$) and higher than those of borosilicate glass (~1.87 $MPa \cdot m^{1/2}$), aluminosilicate glass (~2.14 $MPa \cdot m^{1/2}$), and soda-lime glass (~1.92 $MPa \cdot m^{1/2}$) [33].

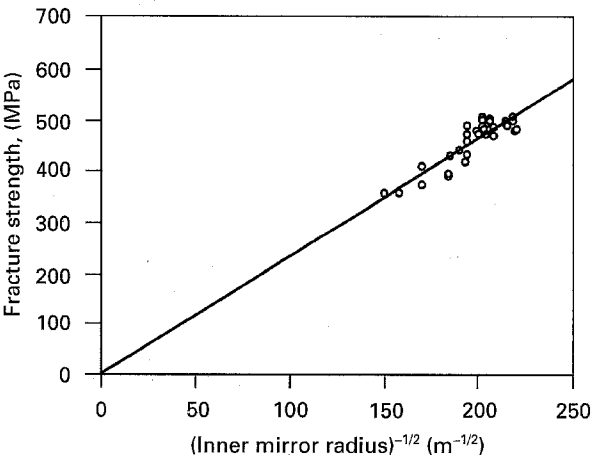

Figure 2 Plot of fracture strength (σ_f) of the IMS CA fibre obtained from four-point bending as a function of $r^{-1/2}$, where r is the inner mirror radius measured from SEM, micrographs.

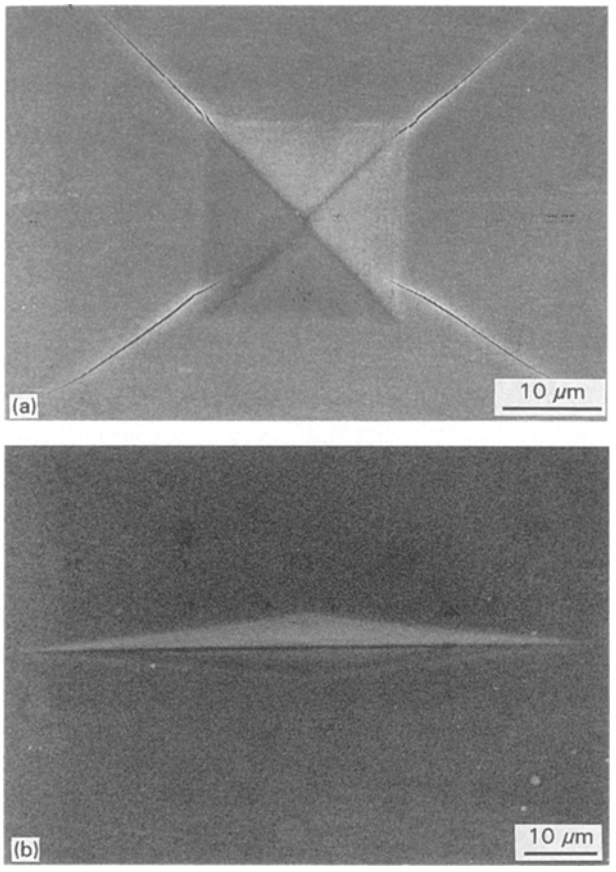

Figure 3 Scanning electron micrographs (SEM) of typical (a) Vickers and (b) Knoop micro-indents on the polished IMS CA fibre. Fibres were vertically mounted in epoxy resin.

Fig. 3 (a and b) shows SEM micrographs of the typical Vickers and Knoop micro-indents on the polished CA fibre. From Vickers micro-indentation the averaged fracture toughness value (K_{IC}) of the CA fibre was determined to be 0.9 MPa·m$^{1/2}$. This value is close to that of aluminosilicate glass (~0.91 MPa m$^{1/2}$) and slightly higher than that of soda-lime glass (~0.75 MPa m$^{1/2}$).

The prediction of critical flaw size is of importance to the application of glasses. The general expression commonly used to calculate critical flaw size, c, is [33, 34]:

$$c = (Y^2/2)(2E\gamma_c/\sigma_f^2) = (Y^2/2)(K_{IC}^2/\sigma_f^2) \quad (2)$$

where σ_f is the fracture strength, E is the elastic modulus, γ_c is the critical fracture energy, and Y is a constant which depends on the flaw geometry. Equation 2 can be rewritten for σ_f as:

$$\sigma_f = YK_{IC}/(2c)^{1/2} \quad (3)$$

By substituting Equation 3 into Equation 1 the following relationship can be obtained [34]:

$$M = YK_{IC}/(2c/r)^{1/2} \quad (4)$$

By using the mirror constant (M) of 2.39 MPa·m$^{1/2}$ and a fracture toughness (K_{IC}) of 0.90 MPa·m$^{1/2}$ and assuming Y is equal to 1.12, corresponding to a penny shaped (semi-circular) flaw, the flaw-to-mirror size ratio (c:r) of the CA fibre was determined to be 1:11.24. According to the measurements of Mecholsky *et al.* [33] the flaw-to-mirror size ratios for most glasses range from 1:10 to 1:12.5. Krohn and Hasselman [36] have calculated this ratio for soda-lime glass and found it to be 1:10. Thus, the flaw-to-mirror size ratio for the CA fibre seems to be reasonable. Substituting the values of K_{IC} (0.9 MPa·m$^{1/2}$), σ_f (465 MPa), and Y (1.12) in Equation 2, the critical flaw size of the CA fibre was calculated to be 2.35 μm. From the SEM observation the averaged inner mirror radius was ~26.5 μm. Thus, from the flaw-to-mirror ratio of 1:11.24 the critical flaw size of the CA fibre was again estimated to be 2.36 μm.

The averaged Vickers micro-hardness value of the CA fibre was determined as 7.1 GPa which is higher than that of aluminosilicate glass (~6.6 GPa) and soda-lime glass (~5.6 GPa). From Knoop micro-indentation tests the average elastic modulus of the CA fibre was determined to be 102.5 GPa which is very close to the 99.8 GPa obtained from the four-point bending tests. Table I lists the mechanical properties of the CA fibres obtained in the present study.

4. Conclusions

The averaged fracture strength of an IMS CA fibre was determined to be 460 MPa from four-point bending tests. The fracture strength (σ_f) values from bending tests were plotted as a function of $r^{-1/2}$, where r is the inner mirror radius whose values were measured from SEM micrographs of the fractured CA fibres. From this plot the inner mirror constant (M) was determined to be 2.52 MPa·m$^{1/2}$. From Vickers micro-indentation tests, an averaged value for the fracture toughness (K_{IC}) of the CA fibre was determined to be 0.9 MPa·m$^{1/2}$. In addition the flaw-to-mirror ratio (c/r) of the CA fibre was calculated to be 1:11.24. Also, the critical flaw size (c) of the CA fibre was estimated to be 2.35 μm. The averaged Vickers micro-hardness value was determined to be 7.1 GPa for the CA fibre. The averaged elastic modulus values of the CA fibre from the four-point bending and Knoop micro-indentation tests were determined to be 99.8 and 102.5 GPa, respectively.

TABLE I Summary of averaged mechanical properties of the inviscid melt spun (IMS) CaO–Al_2O_3 eutectic fibre

Vickers hardness, H_v (GPa)	Elastic modulus, E (GPa)	Fracture strength, σ_f (MPa)	Fracture toughness, K_{IC} (MPa·m$^{1/2}$)	Inner mirror constant, M (MPa·m$^{1/2}$)	Critical flaw size, c (μm)	Flaw-to-mirror ratio, c:r
~7.1	~100	~645	~0.90	~2.39	~2.35	~1:11.24

References

1. R. E. CUNNINGHAM, L. F. RAKESTRAW and S. A. DUNN, in "Spinning Wire From Molten Metal" AIChE Symposium Series, Vol. **74**, edited by J. W. Mottern and W. J. Privott (American Institute of Chemical Engineers, NY, 1978) p. 20.
2. B. S. MITCHELL, K. Y. YON, S. A. DUNN and J. A. KOUTSKY, *Mater. Lett.* **10** (1990) 71.
3. F. T. WALLENBERGER, N. E. WESTON and S. A. DUNN, *J. Non-Cryst. Solids* **24** (1990) 116.
4. F. T. WALLENBERGER, *Ceram. Bull.* **69** (1990) 1646.
5. F. T. WALLENBERGER, N. E. WESTON and S. A. DUNN, *J. Mater. Res.* **5** (1990) 2682.
6. *Idem, SAMPE Quart.* **21** (1990) 30.
7. F. T. WALLENBERGER, N. E. WESTON, K. MOTZFELT and D. G. SWARTZFAGER, *J. Amer. Ceram. Soc.* **75** (1992) 629.
8. Y.-M. SUNG, S. A. DUNN and J. A. KOUTSKY, *Ceram. Inter.* **21** (1995) 169.
9. B. S. MITCHELL, K. Y. YON, S. A. DUNN and J. A. KOUTSKY, *Chem. Engng Comm.* **106** (1991) 87.
10. Y.-M. SUNG, S. A. DUNN and J. A. KOUTSKY, *Ceram. Inter.* **20** (1994) 337.
11. Y.-M. SUNG, J. A. KOUTSKY, and S. A. DUNN, *J. Mater. Sci.* **30** (1995) 5995.
12. Y.-M. SUNG and S. A. DUNN, *J. Mater. Sci.* in press.
13. J. O. CARLSSON, in "Encyclopedia of Materials Science and Engineering" edited by M. B. Bever (Pergamon Press, Oxford, 1986) p. 4406.
14. P. MARTINEAN, M. LAHAYE, R. PAILLER, R. NALSAN, M. COUZI and F. CRUEGE, *J. Mater. Sci.* **19** (1984) 2371.
15. S. R. NUTT and F. E. WAWNER, *ibid.* **20** (1985) 1953.
16. J. A. DICARLO, *ibid.* **21** (1986) 217.
17. S. YAJIMA, Y. HASEGAWA, J. HAYASI and M. IMURA, *ibid.* **13** (1978) 2569.
18. Y. HASEGAWA, *ibid.* **24** (1989) 1177.
19. K. OKAMURA, M. SATO, T. MATSUZAWA, T. SEGUCHI and S. KAWANISHI, *Ceramic Engng Sci. Proc.* **9** (1988) 909.
20. J. D. BIRCHALL, in "Encyclopedia of Materials Science and Engineering" edited by M. B. Bever (Pergamon Press, Oxford, 1986) p. 2333.
21. J. D. BIRCHALL, J. A. BRADBURY and J. DINWOODIE, in "Handbook of Composites" edited by W. Watt and B. V. Perov (North-Holland, Amsterdam, 1985).
22. S. NOURBAKHSH, F. L. LIANG and H. MARGOLIN, *J. Mater. Sci. Lett.* **8** (1989) 1252.
23. K. R. VENKATACHARI, L. T. MOETI, M. D. SACKS and J. H. SIMMONS, *Ceram. Engng Sci. Proc.* **11** (1990) 1512.
24. D. D. JOHNSON, A. R. HOLTZ and M. F. GRETHER, *ibid.* **8** (1987) 744.
25. T. NISHIO and Y. FUJIKA, *J. Ceram. Soc. Jpn, Int.* **99** (1991) 638.
26. Y.-M. SUNG, S. A. DUNN and J. A. KOUTSKY, *J. Eur. Ceram. Soc.* **14** (1994) 455.
27. K.-Y. YON, B. S. MITCHELL, S. A. DUNN and J. A. KOUTSKY, *Cement & Concrete Composites* **15** (1993) 165.
28. Y.-M. SUNG, K.-Y. YON, S. A. DUNN and J. A. KOUTSKY, *J. Mater. Sci.* **29** (1994) 5583.
29. Y.-M. SUNG, in preparation.
30. W. C. LEVENGOOD, *J. Appl. Phys.* **29** (1958) 820.
31. E. B. SHAND, *J. Amer. Ceram. Soc.* **42** (1959) 474.
32. J. W. JOHSON and D. G. HOLLOWAY, *Phil. Mag.* **14** (1966) 731.
33. J. J. MECHOLSKY, R. W. RICE and S. W. FREIMAN, *J. Amer. Ceram. Soc.* **57** (1974) 440.
34. J. J. MECHOLSKY, S. W. FREIMAN, and R. W. RICE, *J. Mater. Sci.* **11** (1976) 1310.
35. J. J. MECHOLSKY and M. G. DREXHAGE, *J. Amer. Ceram. Soc.* **63** (1980) 347.
36. D. A. KROHN and D. P. H. HASSELMAN, *Ibid* **54** (1971) 411.
37. S. R . CHOI, *Phys. & Chem. Glass.* **32** (1991) 79.

Received 10 October 1995
and accepted 13 February 1996