

Inviscid melt-spun high-temperature alumina-magnesia fibres

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Al₂O₃–MgO (AM) fibres containing 98.16 wt % Al₂O₃ and 1.84 wt % MgO, were produced via inviscid melt spinning. By using scanning electron microscopy it was found that the as-spun AM fibres were hollow and their surfaces were very rough. The X-ray diffraction pattern of the as-spun AM fibre showed δ-Al₂O₃ as a major phase and α-Al₂O₃ as a minor phase. The DTA curve of the as-spun AM fibre showed a single endothermic peak representing the phase transformation of δ-Al₂O₃ to α-Al₂O₃. This phase transformation was readily confirmed by analysing the X-ray diffraction pattern of heat-treated AM fibres.

1. Introduction

The current ceramic fibre fabrication mainly depends on the following methods: (1) chemical vapour deposition (CVD) of ceramics on tungsten or graphite filaments [1–4], (2) pyrolysis of cured polymer fibres [5–7], (3) slurry processing of ceramic powders and organic polymer mixture [8–10], and (4) diffusion-based sol–gel processing of metal alkoxides [11–13]. These techniques, however, are costly due to the slow speed of the processes. It is obvious that melt spinning is a much faster and low-cost fibre processing method, compared to the above techniques. Rayleigh breakup, however, is a crucial problem in melt spinning of inviscid ceramic or metal melts. Inviscid melt spinning (IMS) is a noble process which can be applied to fibre production using low-viscosity melts [14–25]. The formation of a stabilizing sheath on the surface of an inviscid molten stream by introduction of a reactive gas such as propane, can prevent the Rayleigh breakup and stabilize the molten stream until solidification occurs.

The first ceramic fibre spun by this IMS process was CaO–Al₂O₃ (CA) fibre produced by Cunningham *et al.* [14]. The crystallinity of this IMS CA fibre was intensively examined by Wallenberger *et al.* [20–22]. They found that the CA fibres were vitreous up to 82 wt % Al₂O₃ as produced. Sung *et al.* [23, 24] found a non-equilibrium phase of CaO·Al₂O₃ and equilibrium phases of MgO·Al₂O₃ and α-Al₂O₃ in as-spun CaO–Al₂O₃–MgO (21 wt % CaO–74 wt % Al₂O₃–5 wt % MgO) IMS fibres. They heat treated this fibre at 1100 °C for 24 h and obtained equilibrium phases of 3CaO·5Al₂O₃, MgO·Al₂O₃, and α-Al₂O₃. Wallenberger *et al.* [21] produced Al₂O₃–ZrO₂ (65.5 wt % Al₂O₃–34.2 wt % ZrO₂–0.3 wt % CaO) fibres by IMS. Their X-ray diffraction (XRD) patterns of this fibre unexpectedly showed the formation of only a stabilized tetragonal ZrO₂(t-ZrO₂) phase.

Sung *et al.* [25] produced eutectic Al₂O₃–ZrO₂ (58.95 wt % Al₂O₃–39.02 wt % ZrO₂–2.03 wt % Y₂O₃) fibres by IMS and found the formation of t-ZrO₂, δ-Al₂O₃, and α-Al₂O₃ phases in the as-spun Al₂O₃–ZrO₂ fibres. They also found phase transformation of δ-Al₂O₃ to α-Al₂O₃ in this fibre at high temperature.

By using IMS, Al₂O₃–MgO (AM) fibres were produced for use as high-temperature reinforcements for composites. A small amount of MgO (1.84 wt %) was added to pure Al₂O₃ in order to decrease the melting temperature of Al₂O₃. The purpose of this study was to investigate the morphology of the IMS AM fibre using scanning electron microscopy (SEM) and to identify phase transformation in this fibre using XRD and differential thermal analysis (DTA).

2. Experimental procedure

The unique IMS apparatus mainly consists of three parts: (1) an induction heating unit, (2) a graphite crucible with orifice at the bottom and associated gas plate assembly, and (3) two containment chambers (furnace and intermediate chambers). In order to obtain a high temperature (~1950 °C) special care was taken for heat insulation. Fig. 1 shows an overall schematic diagram of the IMS unit [26].

High-purity Al₂O₃ and MgO powders were well mixed using zirconia ball-milling (YTZ Zirconia-Ball Media, Tosoh USA Inc., Atlanta, GA, USA). The mixed powders (~100 g) were loaded inside the graphite crucible and heated in a vacuum atmosphere (~6.6 × 10⁻⁵ atm) by induction heating (maximum capacity 15 kW and 10 kHz). Before melting the powders at 1922 °C, both the furnace and intermediate chambers were filled with nitrogen gas at a pressure of ~3.4 atm to prevent violent gas evolution from the melt. To homogenize the melt, the temperature was

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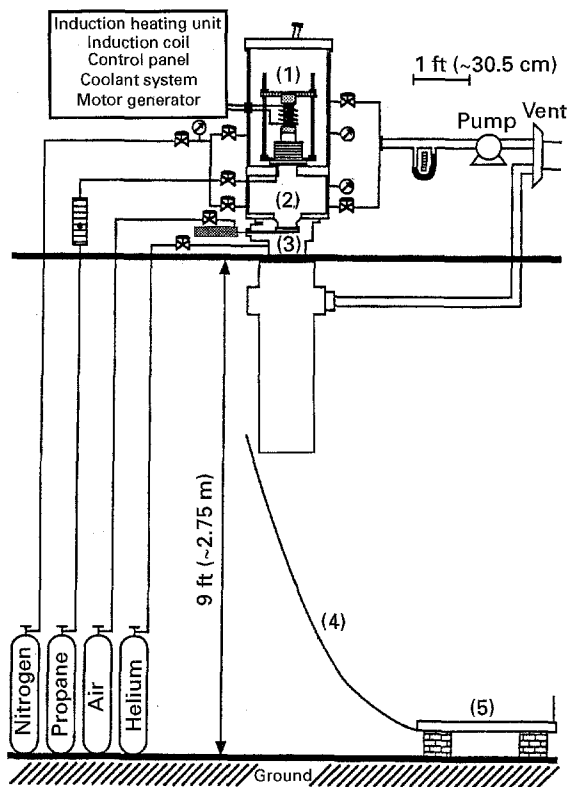
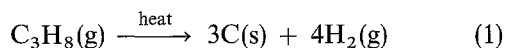


Figure 1 The overall schematic diagram of the invisid melt spinning (IMS) unit [26]. (1) Furnace chamber, (2) intermediate chamber, (3) air-actuated slide valve, (4) slide catch panel, (5) collection plate.

held at 1950 °C for 20 min. When the slide valve between intermediate and catch chamber was opened, the intermediate chamber quickly dropped to atmospheric pressure. The pressure difference between the furnace chamber and the intermediate chamber extruded the molten AM through the orifice and into intermediate chamber atmosphere. Once the molten stream was continuously flowing as droplets, the reactive gas (propane) was introduced through the gas plates. The carbon deposition on the molten stream results from pyrolysis of propane gas by the heat from the molten stream as follows



The microstructure of the as-spun AM fibre was examined using SEM (Jeol SEM 35-C, Japan). To identify crystalline phases in the as-spun AM fibres, powdered AM fibres were investigated using an XRD (Nicolet Stoe Transmission/Bragg-Brentano, Stoe Co., Germany) with a CuK_α source, 15 s time constant, 10°–70° scan range, and 0.02° step size. The resulting XRD patterns were identified using the Joint Committee on Powder Diffraction Standards (JCPDS) cards. DTA (Perkin-Elmer DTA 1700, Norwalk, CT, USA) was performed to investigate the phase transformations of this fibre. The AM fibres (~1 cm long and total weight of 100 mg) were loaded inside a platinum crucible and heated from 25 to 1400 °C at heating rate of 10 °C min⁻¹ in an air atmosphere. DTA temperatures were calibrated using pure aluminium and copper. The as-spun AM fibres

TABLE I Phase identification of invisid melt spun Al_2O_3 -MgO fibres

	Crystalline phases	
	δ - Al_2O_3	α - Al_2O_3
d_1 (nm)	0.1396	0.2083
$2\theta_1$ (deg)	66.98	43.40
d_2 (nm)	0.1986	0.2552
$2\theta_2$ (deg)	45.64	35.14
d_3 (nm)	0.2460	0.1601
$2\theta_3$ (deg)	36.49	57.52
d_4 (nm)	0.1407	0.3479
$2\theta_4$ (deg)	66.39	25.58
d_5 (nm)	0.2279	0.1374
$2\theta_5$ (deg)	39.51	68.20
d_6 (nm)	0.1953	0.2379
$2\theta_6$ (deg)	46.46	37.78
d_7 (nm)	0.2728	0.1740
$2\theta_7$ (deg)	32.80	52.55
d_8 (nm)	0.2601	0.1404
$2\theta_8$ (deg)	34.45	66.55

were heated from 25 to 1297 °C at heating rate of 10 °C min⁻¹ inside a horizontal furnace (DT-31-HT, Deltech Inc., Denver, CO) in an air atmosphere and then quenched into distilled water. The heat-treated AM fibres were ground and phase analysed by XRD. Table I shows a list of XRD peak positions of δ - Al_2O_3 and α - Al_2O_3 in decreasing order of intensities, as given in the JCPDS cards.

3. Results and discussion

During IMS the AM molten streams became partially stabilized within a few seconds or less. The AM fibres were approximately 200 μm diameter and 2 cm long as produced via IMS. The surface of the fibres was black due to carbon deposition. Obvious cavity and surface porosity was observed in SEM of the as-spun AM fibre as shown in Fig. 2. The cavity inside the fibre is most likely caused by shrinkage during solidification and the porosity at the surface of the fibre by possible gas evolution during cooling.

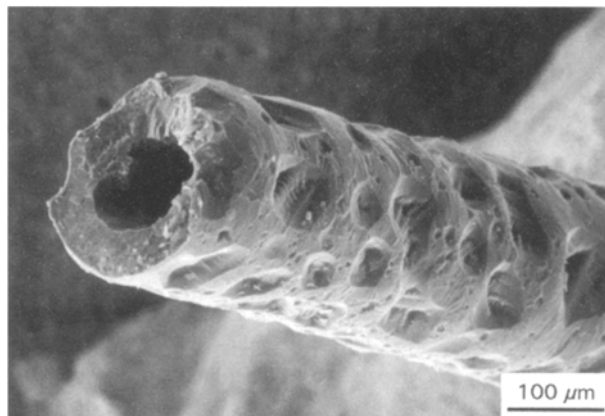


Figure 2 Scanning electron micrograph of as-spun Al_2O_3 -MgO fibre produced by invisid melt spinning.

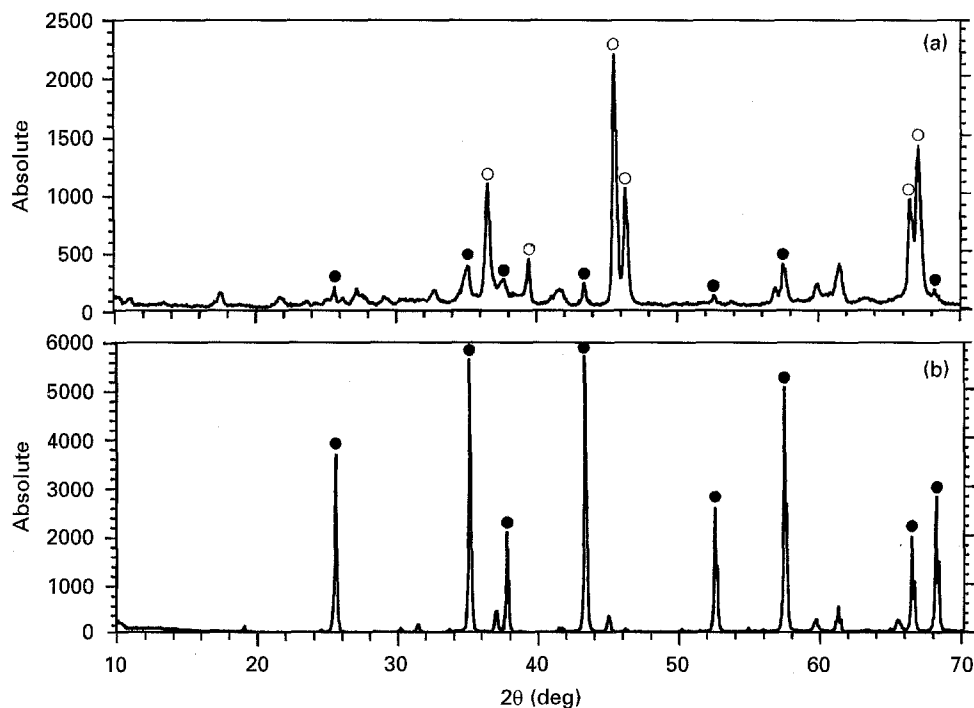
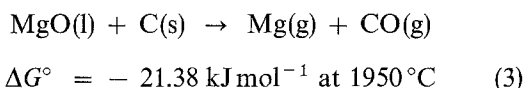
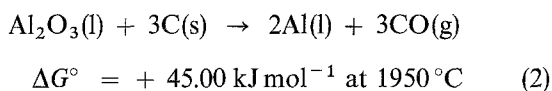


Figure 3 (a) The X-ray diffraction (XRD) pattern of as-spun Al_2O_3 -MgO fibre showing crystalline phase formation of (○) δ - Al_2O_3 and (●) α - Al_2O_3 ; (b) XRD pattern of Al_2O_3 -MgO fibre heat-treated from 25 to 1297 °C at heating rate of 10 °C min⁻¹ and water-quenched at 1280 °C showing crystalline phase formation of (●) α - Al_2O_3 .

Thermodynamic stability of a mixture of molten Al_2O_3 and MgO against reduction by carbon at 1950 °C was examined as follows



The positive free energy value of Equation 2 implies that Al_2O_3 would not be reduced to aluminium at 1950 °C. The negative free energy value of Equation 3 means that MgO would be reduced to magnesium and CO gas would evolve. The surface porosity might result from the violent magnesium and/or CO gas evolution during IMS.

XRD was performed to examine crystalline phases in the AM fibre. Fig. 3a shows XRD patterns of the as-spun AM fibres. Identification of phases in the fibre can be accomplished through comparison of XRD peak locations and intensities with those of standards in Table I. High-intensity peaks from δ - Al_2O_3 and low-intensity peaks from α - Al_2O_3 are identified. The peak positions for δ - Al_2O_3 , listed in decreasing order of intensity, are 0.1395, 0.1988, 0.2450, 0.1959, 0.1406 and 0.2280 nm. This result corresponds well with the data in Table I. The peak positions for α - Al_2O_3 , listed in decreasing order of intensity, are 0.2060, 0.2550, 0.1604, 0.3480, 0.1376, 0.1743, 0.238 and 0.1406 nm. All of the peak positions are in good agreement with the data in Table I.

To investigate a possible phase transformation in this as-spun AM fibre, DTA was performed. The DTA curve in Fig. 4 shows one endothermic peak ranging from 1185 to 1297 °C at heating rate of 10 °C min⁻¹.

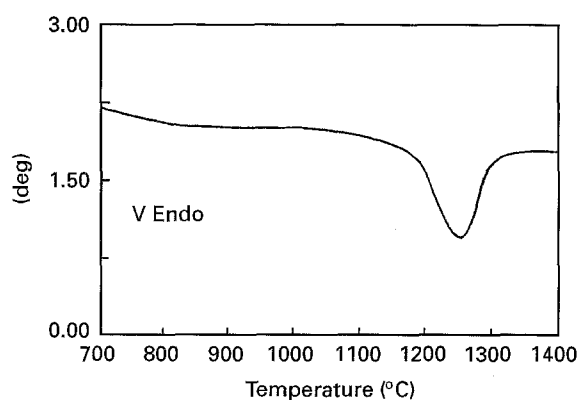


Figure 4 The differential thermal analysis curve of as-spun Al_2O_3 -MgO fibre at heating rate of 10 °C min⁻¹.

The peak temperature was 1250 °C. No exothermic peak representing crystallization of amorphous phase in the as-spun AM fibre was detected from this DTA curve. This implies that the as-spun AM fibres are almost fully crystallized as-prepared.

To identify the phase transformation, the as-spun AM fibres were heated from 25 to 1297 °C at heating rate of 10 °C min⁻¹ inside a furnace and quenched into water at 1297 °C. The heat-treated AM fibres were ground and phase analysed using XRD. Obviously, the peak intensities of α - Al_2O_3 increased and δ - Al_2O_3 peaks disappeared as shown in Fig. 3b. Therefore, it can be concluded that the endothermic peak in the DTA curve corresponds to the phase transformation of δ - Al_2O_3 to α - Al_2O_3 .

4. Conclusion

SEM of IMS Al_2O_3 -MgO (AM) fibre showed cavity and surface porosity possibly due to shrinkage and gas

evolution during solidification. XRD patterns of the as-spun IMS AM fibre showed the formation of α -Al₂O₃ and δ -Al₂O₃ phases. DTA results of the as-spun AM fibre showed a phase transformation ranging from 1185 to 1297 °C. This was identified as a phase transformation of δ -Al₂O₃ to α -Al₂O₃ by analysing XRD results from the AM fibres which were heated up to 1297 °C and then quenched.

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