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Mullite-zirconia fibres produced by internal crystallization method: Microstructure and strength properties

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ABSTRACT

Mullite-zirconia ceramics produced by powder metallurgy methods or directional solidification are well-known materials that combine the high creep resistance of mullite and the enhanced fracture toughness of a composite microstructure. These features provide a potential for the use of the material as a fibrous reinforcement for metal and ceramic matrices to obtain high-temperature fibrous composites. In this study, the microstructure and room- and high-temperature strength of mullite-ZrO_2 fibres produced by the internal crystallisation method (ICM) were evaluated. The ICM provides a high productivity rate of fabrication technologies and, therefore, a potential to produce fibres suitable for structural applications. The room- and high-temperature strengths of the ICM fibres were comparable to those of the corresponding ceramics obtained by melt crystallization.

1. Introduction

Oxide fibres have attracted the attention of the composite community since the beginning of the modern composite era in the 1960s, because the first composites of that time were considered the future high-temperature materials [1–3], and oxides were potential reinforcements.

Sapphire whiskers seemed to have the potential to reinforce a nickel matrix. However, the first experiments with sapphire-whisker/nickel-matrix composites showed their inefficiency owing to numerous reasons [4]. The experiments revealed that the composites obtained at a low fabrication temperature had an interface strength that was too low to provide the composites with a sufficiently high strength. In addition, enhancing the fabrication temperature created a change in the whisker geometry owing to a partial dissolution of alumina in the nickel matrix.

This created an interest in single crystalline oxide fibres obtained by edge feeding growth (EFG) [5], laser heated pedestal growth (LEFG) [6], and micro-pulling-down (MPD) [7]. These methods of making single crystalline and eutectic oxide fibres from the melts produced fibres of perfect microstructures and excellent mechanical properties. However, the low productivity rates of the fabrication technologies based on these methods made the fibres too expensive to be used in structural materials.

Therefore, polycrystalline oxide fibres became an alternative to fibres crystallised from the melts. A review of the development of this fibre was presented by Bunsell [8]. The high strength of the polycrystalline fibres at low temperatures was determined by their nanostructures. However, these microstructures were unstable at a high temperature; therefore, the fibres only retained their high strength at temperatures up to approximately 1000 °C. Moreover, the grain boundary creep lowered the creep resistance of the fibres at temperatures higher than approximately 1200 °C.

Therefore, the author (STM) searched for an oxide fibre crystallization method that could fabricate a single crystal and eutectic fibres at a high productivity rate. The internal crystallisation method (ICM) that he and Kazmin developed [9,10] could be used to produce model metal matrix composites. Then, it was determined that the ICM could be used to produce a family of oxide fibres [11–15]. A review of the microstructures and mechanical properties of the fibres is given in Refs. [16,17]. The fibres produced by the ICM have a special shape: it is formed by two nearly plane surfaces and two concave ones. The fibre microstructures presented in Section 2 below show clearly this peculiarity.

Various oxide fibres obtained by the ICM have been used in a number of the composite systems, including a nickel-based matrix [18–22], a TiAl matrix [23], an oxide-fibre/high-entropy-alloy-matrix composite [24], and oxide-fibre/oxide-matrix composites [25].

In this study, the fabrication, microstructure, and strength of new fibres composed of mullite and zirconia were evaluated. Mullite-ZrO_2 ceramics produced by powder metallurgy methods [26,27] or directional solidification of eutectic and off-eutectic compositions [28,29] are known materials that combine the high creep resistance of mullite and the enhanced fracture toughness of a composite microstructure. Mullite/ZrO_2 directionally crystallised ceramics have a high strength at

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Table 1
Compositions of the raw mixtures of oxides used to crystallize fibres, wt%.

	ZrO_2	SiO_2	Al_2O_3
E-1 (C_1)	30	20	50
E-2 (C_2)	67	10	23
E-4	68	8	24
E-6 (C_3)	16	24	60

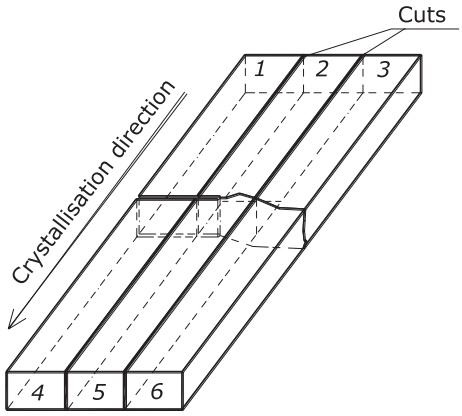

Fig. 1. Schematic of the composite sub-specimens MXYZW1 through MXYZW6, where M = V or C, and X, Y, Z, and W were digits. Hence, MXYZW is the serial number of an original specimen (i.e., V1221) and the fifth digit determines the location of a sub-specimen (sub-specimens 1–3 are located at the top of the original specimen, in a zone where fibre crystallisation starts, those numbered 4–6 are at the bottom).

temperatures up to 1400 °C [29]. These features provide a potential for the use of the material as a new fibrous reinforcement for metal and ceramic matrices to obtain high temperature composites. It is important to point out that the development of high temperature MMCs and ceramic matrix composites is possible only if we have a variety of the fibres characterised by various mechanical, physical and chemical properties.

2. Methods

2.1. Crystallisation of fibres

The ICM described in details in the publications cited in the Introduction was used to crystallize the fibres in the Al_2O_3-SiO_2-ZrO_2 system.

The four compositions of the fibres obtained and studied are listed in Table 1. The compositions E-1, E-2, and E-6 corresponded to ceramics C_1, C_2, and C_3, respectively, studied in reference [28]. The composition E-1 corresponded to the mullite/ZrO_2 eutectic, and E-2 was a zirconia rich off-eutectic composition. The composition E-6 was a mullite rich off-eutectic composition. The composition E-4 shifted from E-2 to zirconia.

The specimen shape, shown in Fig. 1, is explained as follows. First, the fibre crystallisation began from the top of the original composite specimen. After production, the composite specimens with a size of approximately 5 X 15 X 65 mm^3 were used to measure the critical stress intensity factor of the oxide-fibre/molybdenum-matrix composites (the notch of a length of about ½ of the specimen height is shown in Fig. 1). Then, it was cut into six sub-specimens for testing in 3-point bending at room and high temperatures. Sub-specimens MXYZW1 through MXYZW3 are located in the upper part of the original specimen where fibre crystallisation starts; three other sub-specimen are within a steady state fibre growth. The data obtained in these tests and together with the strength of the molybdenum matrix given in reference [30] were used to calculate the fibre strength. The fibre microstructure and their properties are expected to change along the original specimen length, hence the cross-sections to study the microstructure were chosen at about 5 mm from the top and bottom of the original specimen, respectively.

For pure mullite fibre crystallised under the ICM conditions, there was an unsteady portion when the fibre microstructure changed and a stable portion of the microstructure [14,31]. Hence, the crystallisation of mullite-zirconia fibres could have similar features.

2.2. Observation of fibre microstructures

Typical SEM-micrographs of the fibres of various compositions obtained at various crystallisation rates are shown in Figs. 2–5. The X-ray spectra of the fibres of the E-1, E-2 and E-4 compositions obtained at a crystallization rate 50 mm/min are shown in Fig. 6. The fibres were milled to prepare objects for the X-ray experiments. The powder was placed in a ditch of a diameter of 5 mm and a depth of 1 mm. The ditch was made of amorphous quartz and the quantity of the powder was small. This influenced spectra at low angles but did not affect the conclusions about the fibre phase composition.

2.3. Measuring fibre strength

The fibre volume fraction V_f of the specimens were between 0.35 and 0.40. The strength values of the fibre were evaluated from the strength data of the composites. The molybdenum matrix was recrystallized when heated to approximately 1800 °C in the composite fabrication process. Therefore, the bending strength values of the matrix were 450, 100, 80, and 70 MPa for temperatures of 20, 1000, 1200, 1300, and 1400 °C, respectively. The average value of the fibre volume fraction in the composite specimens was 0.37. The effective fibre strength, which is the strength of a fibre in a matrix, was a more important fibre characteristic than the strength measured by testing the separate fibres. In an appropriately designed composite, the matrix repairs the surface defects in the fibre and improves the strength [32]. However, tests on separate fibres at room temperatures were performed by measuring the strain when the fibre was bent over a sequence of rigid cylinders and observing the fibre breaks [33].

3. Results and discussion

3.1. Fibre microstructure

The micrographs (Figs. 2–5) and X-ray spectra (Fig. 6) of the fibres showed the following characteristic features of the fibre microstructures.

(1) The microstructure of the fibres in the one composite specimen contained different sizes of the zirconia inclusions (“white” phase) and configurations of the inclusion systems. This could be the result of the complicated temperature field in the oxide/molybdenum block during the crystallisation process. Nevertheless, typical microstructures were found. They were shown in the larger magnifications in the SEM-micrographs.
(2) The microstructures changed along the fibre length.
   a. The characteristic size of the microstructure of the fibres of the eutectic composition (Fig. 2) decreased as the cross-section moved away from the region where crystallisation began (Specimens C0288 and C0289). In addition, the mullite phase contained large straight formations (Specimen V1009). In both cases, the fibre strength increased along the specimen length from the top to bottom.