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Preparation and characterization of continuous alumina based fiber reinforced with orientated mullite whisker

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HIGHLIGHTS

- The orientated mullite whisker-reinforced alumina based fibers were prepared using spinnable sol.
- The axial direction of whiskers was consistent with the fibrous matrix.
- The addition of whisker enhanced the spinning viscosity while lowered the zeta potential of the sol.
- The addition of whisker reduced the spinning length but did not affect the compactness of the fiber.
- The tensile strength increased from 535.9 to 637.9 MPa at a whisker content of 1 wt.%.

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ABSTRACT

Single crystal mullite whiskers were directly added into the precursor sols to synthesis the orientated whisker-reinforced continuous alumina based fibrous matrix composite. The solid content and spinnable viscosity range were enhanced but the zeta potential was reduced by the addition of the mullite whiskers into the sol. The Al oligomers content increased while monomer and Al_{13} decreased with the increase of mullite whisker. After sintering at 1250 °C, the obtained compact nano grains fibers were reinforced with accordant axial direction whiskers which were orientated by the axial force derived from the spinning process. The phase composition and compact structure were not affected by the presence of the mullite whiskers, while the continuous spinning length became low. Although tensile strength of single composite fiber was decreased at a high mullite whisker content due to the low densification and cracks of composite fiber, whisker bridging and pullout during fiber fracture may have increased the strength at a mullite whisker content of 1 wt.% to 642.6 MPa.

1. Introduction

Compared to organic fibers and other inorganic fibers such as carbon fibers or carbide/nitride fibers, alumina based fibers are attractive because of their excellent properties at high temperature and oxidizing atmosphere environment. Mullite and corundum are the main phases of the alumina based fiber. Mullite ($3Al_2O_3{\cdot}2SiO_2$) is the only stable intermediate phase in the Al_2O_3–SiO_2 system at atmospheric pressure [1]. The creep resistance of mullite is much higher than alumina. So the existence of mullite phase improved the creep resistance of fiber significantly. The fiber is mainly used in two areas: as reinforcement of metals, ceramics or resins in the form of continuous fibers [2–4] and as high temperature insulating material in the form of mats, blankets, etc. [5]. Particularly it is irreplaceable as the reinforcement in high temperature ceramic matrix composites, which has been widely used as thermal insulation material of aerospace craft and as advanced engine components in the civil automotive industry. However, it is also facing challenges due to their low strength compared to carbon fibers or carbide/nitride fibers.

Ceramic whiskers have unique properties which result from their near-perfect structure. As the reinforcement of high temperature ceramic composites, it can enhance the mechanical and thermal properties. The major toughening mechanisms are crack deflection, whisker bridging and whisker pullout. The stable crystal structure of mullite is orthorhombic with edge-shared AlO_6 octahedral chains aligned in the *c*-direction and corner-shared crosslink (Si, Al)O_4 tetrahedrons [6]. Thus, the crystal grows faster along the crystallographic direction parallel to the *c*-axis, resulting in a high degree of orientation [7].

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Most studies of mullite-whisker-reinforced ceramics focus on the bulk composites. Li et al. [8] fabricated the self-reinforced porous mullite ceramics by a starch consolidation method with fly ash, $Al(OH)_3$ (or Al_2O_3) and the additive AlF_3. The in situ synthesized mullite whiskers formed an interlocking structure enhancing the mechanical strength of the porous mullite ceramics. According to Long [9], bar like mullite whiskers with width ranging from 0.05 to 3 μm were obtained by firing a mixture of kaolinite, aluminum fluorite and graphite. The reinforcement with the whiskers results in drastic improvement in wear resistance of aluminum alloy and less attack against the counter material in comparison with silicon carbide whiskers or alumina fibers. However, no reports have been found on the whisker-reinforced fibrous matrix composites. Fibers, the same as whiskers, have large aspect ratio, and were required to possess different characteristics in axial and radial directions for the application needs. Compared to the short lengths whiskers whose pullout in the reinforced ceramics is limited, continuous fibers arise much extensive fiber pullout in the matrix [10]. If the orientations of the whiskers and fibers could be met, the directional requirement of the mechanical properties between the reinforcement phase and the matrix should be combined excellently. Single crystal whiskers with small diameter are easy to be added into fibrous matrix in sol–gel processing. And the axial force derived from the spinning process coincidentally makes the orientations of the whiskers consist with the axial direction of the fibers.

In this work, orientated mullite whisker-reinforced continuous alumina based fibers were prepared by sol–gel method and subsequent heat treatment at 1250 °C. The mullite whiskers were synthesized from Al_2O_3, SiO_2 and AlF_3 powders. Its effect on the spinnable viscosity, solid content and molecular structure of the sol; and on the spinning length, composition, porosity and tensile strength of the fibers, as well as its orientation in the fiber were investigated.

2. Experimental procedures

The mullite whiskers used as reinforcement phase in this study were obtained by heating the mixture of alumina nano-powders (α-Al_2O_3, 13 nm, Beijing Nachen, China), silica nano-powders (SiO_2, 30 nm, Merck KGaA, Germany) and aluminum fluoride ($AlF_3 \cdot 3H_2O$, chemical pure, Sinopharm chemical reagent, China, calcined at 280 °C to remove the crystal water) in an airtight alumina crucible at 1100 °C for 10 min with a fast heating rate. AlF_3 was used as the additive to promote the formation of mullite whiskers. The weight ratio of $[Al_2O_3]/[SiO_2]/[AlF_3]$ was 61.75:26.95:11.3 (as the stoichiometric composition of mullite). The sintered whiskers were grinded and dispersed, then used as one of the starting materials for the reinforced fibers. Acidic silica sol (SiO_2, 20 nm, pH value of 1.5, chemical pure, Zhejiang YUDA, China), aluminum chlorohydrate ($Al_2(OH)_5Cl \cdot 2H_2O$, average basicity of 1.92, daily chemical, YOTECH Chemical, China) and PVA ($[C_2H_4O]_n$, alcoholysis degree of 88%, polymerization degree of 2000, Shanxi Sanwei Chemical Industry Co., Ltd., China) were the rest of the starting materials for the fibrous composites and were used as Si source, Al source and spinning aids respectively.

Firstly, a transparent sol was obtained by mixing aluminum chlorohydrate and distilled water with vigorously stirring at room temperature. Then acidic silica sol and mullite whiskers were successively added with stirring for 3 h to obtain a mixture sol with the effective $[Al_2O_3]/[SiO_2]$ weight ratio of 85:15 (corresponding to 49% α-Al_2O_3 and 51% mullite after sintering) and different mullite whisker contents of 0, 1, 3 and 5 wt.%. Afterwards, 5 wt.% PVA solution was slowly added into the sol with magnetic stirring. The content of PVA was 7 wt.%. Finally, the sol was condensed at 60 °C using a water bath, and then kept at room temperature until an appropriate viscosity suitable for spinning was obtained. The spinnable sol was spun using a laboratory miniature dry-spinning apparatus (lab self-made) and collected by a bobbin winder to obtain the gel fiber. The gel fibers were dried at 40 °C for 2 h and then calcined in air at 1250 °C for 20 min. The samples were heated up to 800 °C with a very slow heating rate (less than 1 °C/min), and then to 1250 °C with a fast heating rate (more than 10 °C/min).

The synthesized whiskers and reinforced fibers were characterized by scanning electron microscopy (SEM, S-4800, HITACHI, Japan) and field emission transmission electron microscopy (FETEM, JEM-2100F, JEOL, Japan). The sintered fibers were ground into powders and tested by X-ray diffraction (XRD, Rigaku Co., Ltd., Japan) using D/max-3c diffractometer at 40 kV and 100 mA with Cu Kα radiation. The grain diameter and porosity of the fibers were obtained by the SEM photographs. Viscosity measurement of the spinning sols were carried out by using the HADV-2 viscometer (Shanghai Nirun Tech. Co., Ltd., Shanghai, China) at 25 °C. The solid content of the spinning sols were measured by thermo-gravimetric analysis/differential scanning calorimetry (TG/DSC, SDT Q600, TA, USA) with a heating rate 10 °C/min. The sample weight was 25 mg. The ^{27}Al nuclear magnetic resonance (NMR) spectra were obtained by using the AV 400M spectrometer (Bruker, Switzerland). The single fiber tensile strength of the fiber was tested by dynamic mechanical analysis (DMA Q800, TA, USA) at controlled force mode with force rate 0.002 N/min.

3. Results and discussion

3.1. Characterization of whiskers

Fig. 1 shows the microscopic appearance of whiskers synthesized from alumina and silica nano-powders with AlF_3 as the catalyst. A mass of well-developed prismatic crystals with an average diameter of 395 nm and aspect ratio of 24.45 was observed. The grinded whiskers practically added to the sol had a smaller aspect ratio of 10.12. Fig. 2 is the TEM micrographs of the whiskers, which demonstrates that the mullite whisker is single crystal. A lattice image with an average interval of 0.539 nm which corresponded to the (1 1 0) plane of mullite was clearly observed on the high-resolution electron microscopy (HREM) micrograph. The crystallographic orientation of the whiskers was examined by the selected-area electron diffraction (SAED) which confirmed that the elongated direction was the *c*-axis of the mullite, and the plane perpendicular to this photograph corresponded with the (1 1 0)

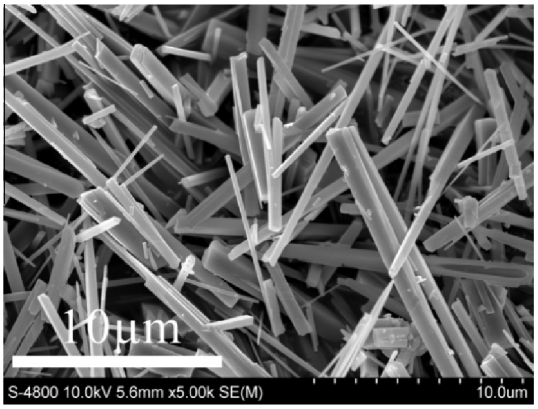

Fig. 1. SEM micrograph of whiskers obtained by firing the mixture powder at 1100 °C.