Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Temperature-induced changes in morphology and microstructure of electrospun mullite nanofibers fabricated from a hybrid mullite sol

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ARTICLE INFO

Keywords:
Mullite
Electrospinning
Fibers
Crystallization
Microstructure

ABSTRACT

Mullite nanofibers with small diameter and high surface area are an ideal candidate as the reinforcements in composite materials, and have promising applications in the fields of catalysis, filtration, thermal storage and so forth. In this work, electrospun mullite nanofibers were successfully synthesized using a hybrid mullite sol. The morphology and microstructure of fibers calcined at different temperatures were investigated. The morphology of fibers synthesized at 900 °C is porous with coarse surface, and after crystallization it becomes compact with smooth surface. The densities of fibers increase with the increasing temperatures. At 1200 °C the surface of fibers becomes coarse again, as a result of the grain growth of mullite. The crystallization path of fibers was revealed that the Al-rich mullite ($4Al_2O_3{\cdot}SiO_2$) together with amorphous silica formed at 1000 °C, changed into mullite with higher silica contents as temperature further increased, and finally transformed into a stable $3Al_2O_3{\cdot}2SiO_2$ phase at 1200 °C. During this crystallization process, the flow of amorphous silica phase and the formation of mullite crystal structure benefit the densification of fibers, leading to the resultant fibers with fine and compact microstructure. The present findings can provide a guideline for the preparation of the promising high-mechanical mullite nanofibers and the synthesized nanofibers display great potential as reinforcements in structural ceramic composites.

1. Introduction

Mullite ceramics have a wide range of applications such as electronic devises, optically translucent ceramics and high-temperature structural materials due to its low thermal expansion coefficient and conductivity, high creep resistance and corrosion stability together with suitable strength and fracture toughness [1–3]. Ceramic nanofibers and nanotubes which are produced by electrospinning have potential applications in the areas of mesoscopic physics, fabrication of nanoscale devices and more [4–9]. Mullite nanofibers with small diameter produced by electrospinning are an ideal candidate as reinforcements in composite materials, leading to an improvement in the mechanical properties [10–13]. Owing to their high surface area, the nanofibers also have potential applications in the fields of catalysis, filtration, thermal storage and so forth [4,6,14,15]. Recently, many researchers [10,11,16–21] successfully fabricated mullite nanofibers using electrospinning method combined with conventional sol-gel process. The sol or solution they adopted for electrospinning contains polymeric template as well as an aluminosilicate precursor sol. As a result, the matrix polymer and aluminosilicate precursor in the as-spun fibers have to be calcined into mullite at an elevated temperature, in order to remove all organic components. The removal of all organic components introduces defects like voids or cracks. These defects can affect mechanical properties and limit the application of the fibers as reinforcements for structural ceramics composites. Therefore, the densification during the calcination process is of critical importance to improve the quality of nanofibers.

In the past decades, there are extensive researches [22,23] on the densification of mullite, which indicate the densification of mullite is strongly related to the crystallization path. Based on the homogeneity level of precursor sols, there are three types of crystallization path. When using monophonic sol, a precursor sol with molecular homogeneity, the crystallization path is named Type I that fibers crystallize directly into single mullite phase at a low temperature (~980 °C). The crystallization path of nanofibers synthesized by Chen et.al [17] and Mohammad Ali Zadeh et al. [19,20] were corresponding to this type. Even though this type of crystallization path displays good uniformity of nanofibers, the densification of these fibers is difficult due to the very slow mullite diffusion rate. On the other hand, there is another type of crystallization path, Type II, based on the diphase sol which is a precursor sol with nanometer-level homogeneity. Type II is a two-step crystallization. An alumina phase is first crystallized at around 1000 °C

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https://doi.org/10.1016/j.ceramint.2017.11.200
Received 30 August 2017; Received in revised form 8 November 2017; Accepted 27 November 2017
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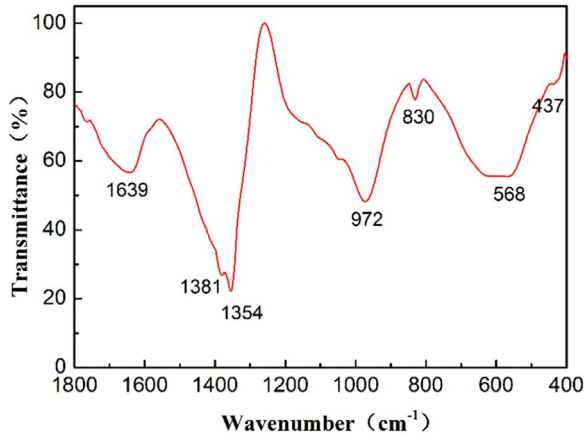

Fig. 1. FT-IR spectra in the range from 400 to 1800 cm^{-1} of the dried precursor gel.

with the silica phase still exists in an amorphous state, and then mullite crystallization in the nanofibers starts at approximately 1200 °C. Using polymethylsiloxane and aluminum tri-sec-butoxide as the silicon and aluminum source Dong et.al [11] obtained a diphase sol for electrospinning. They found the flow of the vicious silica-rich phase helped the densification process. But this silica phase usually remains in the final product, which deteriorates the optical and mechanical properties of the material.

Type III adopts the hybrid sol [24–26], a monophasic sol as classified in Refs. [23,27]. The phase transformation sequence of Type III involves a metastable phase Al-rich mullite which is first crystallized at temperature close to 1000 °C and a stable mullite ($3Al_2O_3{\cdot}2SiO_2$) formed at final stage around 1200 °C. The typical feature of type III is the relatively low mullitization temperature and the exist of vicious silica-rich phase which benefits the fiber fabrication. However, the influence of this crystallization path on the densification process has not yet been understood.

In this study, a hybrid sol which consists of the Aluminum isopropoxide (AIP), aluminum nitrate (AN) and tetraethyl orthosilicate (TEOS) system together with polyvinyl butyral (PVB) polymer was prepared as starting materials for electrospinning. The morphological and microstructural features of the nanofibers calcined at different temperatures were investigated. The mullite crystallization path of fibers was revealed and corresponding to Type III. Furthermore, the crystallization and densification behavior during calcination process were discussed in details, as well as their influences on the properties and applications of the mullite nanofibers.

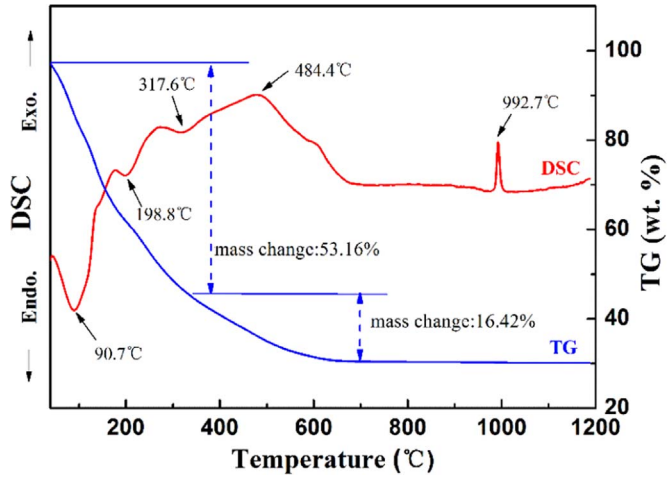

Fig. 3. TG-DSC curves of the as-spun fibers.

2. Experimental procedure

2.1. Materials

AIP ($C_9H_{21}O_3Al$), AN ($Al(NO_3)_3{\cdot}9H_2O$) and TEOS ($SiC_8H_{20}O_4$) were used as alumina and silica sources. PVB ($(C_8H_{14}O_2)_n$) with aldehyde acetal groups between 45% and 49% was used as polymeric template in the electrospinning solution.

2.2. Preparation of the electrospinning solution

The molar ratio of AIP/AN/TEOS/deionized water/ethanol was set to be 2:1:1:25:25 [18–20], so as the mole ratio of Al_2O_3/SiO_2 in the calcined fibers would close to be 3:2. The precursor sol was prepared by adding AIP and TEOS to AN solution and the mixture was stirred vigorously at room temperature for 20 h to obtain a clear sol. Then the sol was heated at 80 °C, using a water bath under reflux condition to complete the hydrolysis process. The electrospinning solution was fabricated by mixing the precursor sol and polymeric solution (PVB content of 5 wt%) with mass ratio of 1:2, and stirring at 40 °C for 1 h.

2.3. Preparation of the mullite nanofibers

The solution was contained in a capillary with an iron pin connecting to a high-voltage generator. A voltage of 9.5 kV was applied to

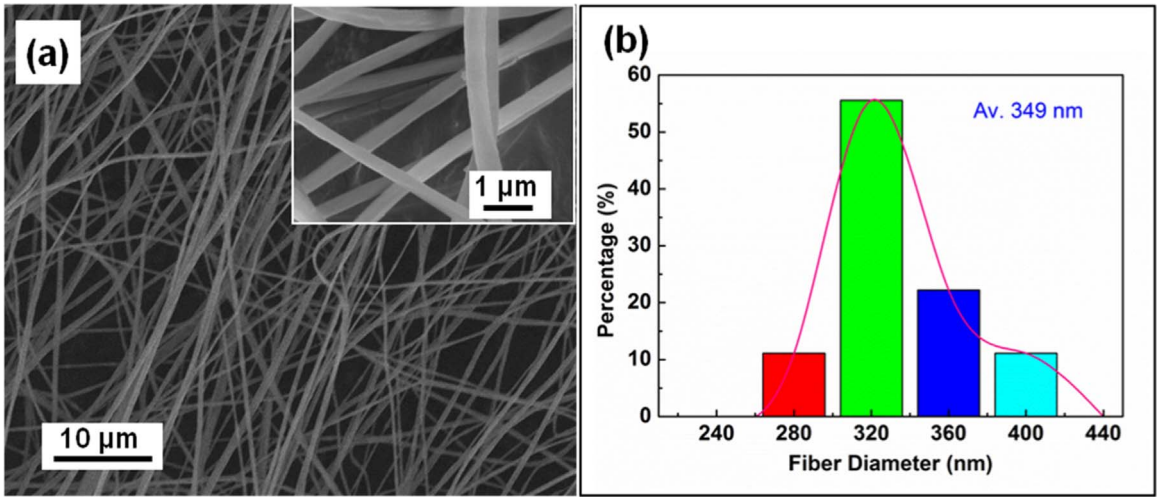

Fig. 2. (a) SEM images of the as-spun fibers and (b) the corresponding diameter distribution of the fibers.

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