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Effects of in situ synthesized mullite whiskers on compressive strength of mullite fiber brick

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ABSTRACT

The method of in situ synthesis of mullite whiskers by gas-phase deposition and reaction was applied to improve the compressive strength of the mullite fiber brick. During the preparation process, silica sol, $Al(NO_3)_3$ solution and NH_4F solution were introduced into the fibrous brick in the form of ions or sol through vacuum impregnation and freeze drying, and the silica sol, $Al(NO_3)_3$ and NH_4F served as the silica sources, aluminum source and catalyst, respectively. Effects of process parameters (concentration of impregnation solutions, holding time, sintering temperature) on compressive strength and elastic modulus of the fibrous brick during the in situ toughening process were analyzed. SEM and XRD analysis results demonstrated that the mullite whiskers were synthesized on the surface of mullite fibers based on the reaction of AlOF and SiF_4. What is more, the whiskers on adjacent fibers intersected with each other and formed many unfixed lap-jointing points, resulting in the increase of compressive strength and elastic modulus. Although the density and thermal conductivity of the sample after the generation of mullite whiskers fabricated with the optimum process were 0.406 g/cm^3 and 0.1262 W/(m K), respectively, which were slightly higher than that of the raw fibrous brick (0.375 g/cm^3 density and 0.1069 W/(m K) thermal conductivity, respectively), the corresponding compressive strength and elastic modulus of the sample reinforced with the whiskers increased to 1.45 MPa and 42.03 MPa, respectively, which were much higher than that of the raw fibrous brick (0.39 MPa compressive strength and 6.5 MPa elastic modulus).

1. Introduction

Mullite has been widely employed as a high quality refractory material because of its good mechanical strength, excellent thermal shock, high creep resistance, low thermal conductivity, good chemical stability, and so on [1,2]. As a kind of high temperature structural materials, mullite fiber brick which was constructed by the mullite fibers has the advantages of low density, high porosity, low thermal conductivity, good resistance to thermal shock and has been widely used in aerospace and industrial fields [3,4]. However, the low mechanical property of the fibrous brick limited its further application. Therefore, it is significant to toughen mullite fiber brick and improve its compressive strength to meet a wider range of application requirements.

Many methods, including particle dispersion toughening [5,6], phase transformation toughening [7], and fiber toughening [8,9], have been introduced and applied to toughen ceramics in many researches, but these methods are not suitable for toughening the porous fibrous bricks. The compressive strength of the brick depends on the amount of binder in the lap-jointing points. Therefore, the compressive strength of the brick may be improved by adding more binder on the lap-jointing points; however, introducing too much binder would result in the decrease of the sample porosity and the deterioration of high temperature performance of the brick. The compressive strength of the brick can also be improved by increasing the number of lap-jointing points. In the snowstorm, pine trees can withstand the pressure of heavy snow and keep upright, which is attributed to the hierarchical structure of the pine tree. The pine tree consists of pine branches and pine needles, and the pine needles on adjacent pine branches intersect with each other and form many lap-jointing points, consequently enhancing the compressive resistance of the pine tree. Inspired by this interesting pine branches/pine needles hierarchical structure, we try to synthesize a similar hierarchical structure in the mullite fiber brick to improve the compressive strength of the fibrous brick. Compared to the pine tree, the mullite fibers in the brick have formed the skeleton structure

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similar to the pine tree branches. Therefore, we tried to in situ synthesize mullite whiskers on the surface of mullite fibers, and the whiskers on adjacent mullite fibers could intersect with each other just like the pine needles and form more lap-jointing points to improve the compressive strength of the mullite fiber brick.

A number of methods, such as molten salt assisted synthesis [10,11], mineral decomposition [12,13], and powder calcination [14], have been developed to produce mullite whiskers. However, the whiskers which are synthesized by molten salt assisted synthesis exhibit poor high temperature performance. Therefore, this kind of whiskers can't satisfy the fibrous brick's high temperature resistant requirements. During the process of mineral decomposition to synthesize mullite whiskers, a certain amount of sintering residue would be produced because of the impurities in the mineral raw materials. The sintering residue would block pores in the brick and lead to the decrease of the fibrous brick's porosity. For the method of powder calcination, it is difficult to introduce powders evenly into the fibrous brick. The uneven distribution of the powders will lead to the disorderly distribution of mullite whiskers. What is more, the disorderly distribution of mullite whiskers exhibits limited toughening effect to the brick. Therefore, these above methods are not suitable for in situ synthesized mullite whiskers in the fibrous brick.

In this research, we tried to introduce particles into the brick in the form of ions and sol in order to ensure the uniform distribution of the particles. Therefore, silica sol, $Al(NO_3)_3$ solution and NH_4F solution were introduced into the fibrous brick through vacuum impregnation and freeze drying. Among them, silica sol, $Al(NO_3)_3$ and NH_4F served as silica source, aluminum source, and catalyst, respectively. During the infiltration process, $Al(NO_3)_3$ and NH_4F would react into $(NH_4)_2AlF_5 \cdot H_2O$ and the formed $(NH_4)_2AlF_5 \cdot H_2O$ particles would evenly disperse in the brick. The microstructure and properties of the whiskers could be adjusted by tailoring the concentration of vacuum impregnation solutions, holding time and sintering temperature. The mullite whiskers' toughening effects on the compressive strength and elastic modulus of the mullite fiber brick were carefully analyzed and discussed in this paper.

2. Experiments

2.1. Material preparation

Commercially available mullite fiber bricks (Hongda Crystal Fiber Co., Ltd, Zhejiang, China) were used as the starting materials. Alkaline silica sol, aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, analytically pure) and ammonium fluoride (NH_4F, analytically pure) were used to prepare vacuum impregnation solutions. Fig. 1 exhibited the process of in situ synthesis of mullite whiskers. Firstly, the fibrous brick was immerged into the silica sol (Fig. 1a) and impregnated in a vacuum environment for 15 min (Fig. 1b). Then, the fibrous brick was frozen for 30 min at −20 °C (Fig. 1c) and dried in the freeze-dryer (Fig. 1d). After the first impregnation, SiO_2 particles evenly dispersed around the lap-jointing points of the fibrous brick (Fig. 1d–i). Secondly, the fibrous brick was immerged into the $Al(NO_3)_3$ solution (Fig. 1a) and impregnated in a vacuum environment for 15 min (Fig. 1b). Then, the fibrous brick was frozen for 30 min at −20 °C (Fig. 1c) and dried in the freeze-dryer (Fig. 1d). After the second impregnation, Al^{3+} evenly dispersed around the lap-jointing points of the fibrous brick (Fig. 1d-ii). Thirdly, the fibrous brick was immerged into NH_4F solution (Fig. 1a) and after the vacuum impregnation and freeze drying, $(NH_4)_2AlF_5 \cdot H_2O$ particles was generated through the reaction of $Al(NO_3)_3$ and NH_4F and evenly dispersed around the lap-jointing points of the fibrous brick (Fig. 1d-iii). During the three times impregnation, the ratio of SiO_2, $Al(NO_3)_3$ and NH_4F was kept at 1:3:12 by mole. The amount of the impregnated particles in the brick was controlled by changing the concentration of these three impregnation solutions simultaneously. After the third freeze drying, the bricks were placed in a closed alumina crucible and sintered at different temperatures for different holding time. Therefore, the present paper was focusing on effects of the concentration of impregnation solutions, sintering temperature and holding time on the compressive strength and elastic modulus of the mullite fiber brick after in situ toughening.

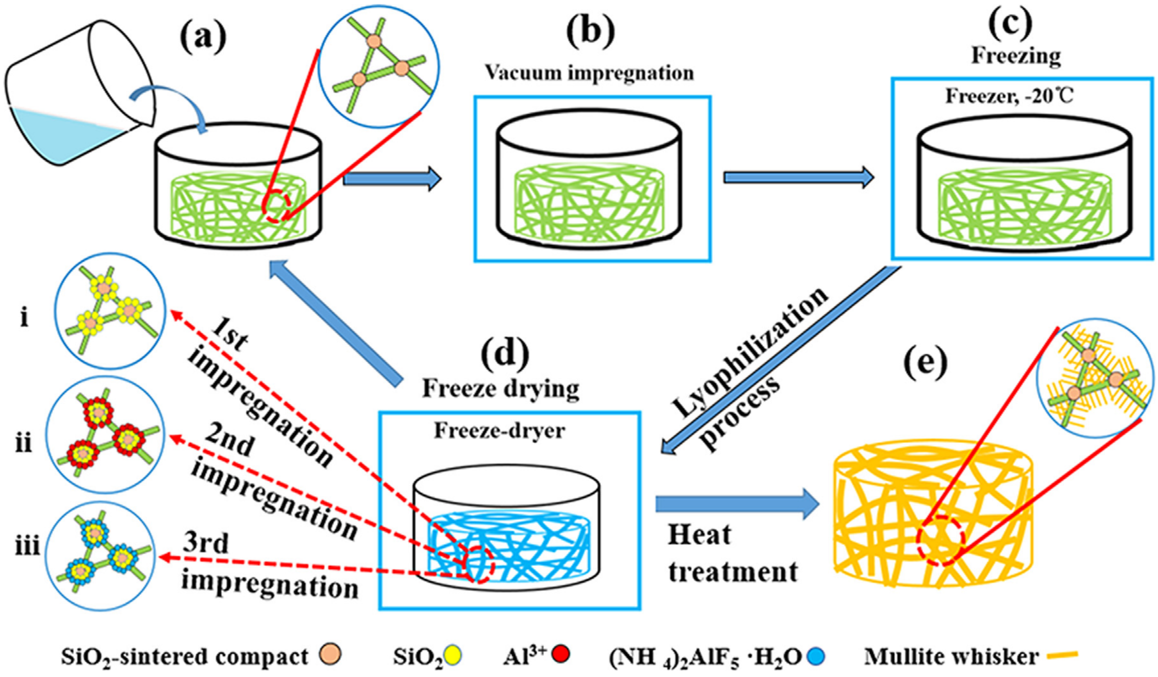

Fig. 1. Schematic diagram of the fabrication processes of mullite whiskers.