In-situ Synthesized Mullite Whiskers on the Surface of Aluminum Silicate Fibrous Felts with Low Thermal Conductivity and High Compression Rebound Performance

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Abstract. In this study, in situ synthesized mullite whiskers on the surface of aluminum silicate fibrous felts was prepared by gas-phase deposition and reaction. Effects of the concentration of impregnation solutions on the density, thermal conductivity, microstructure and the compression rebound performance of the fibrous felts during the in situ synthesized mullite whiskers process were analyzed. The mullite whiskers were generated on the surface of aluminum silicate fibrous felts through gas-phase deposition and reaction of AlOF and SiF₄, which proved that the mullite whiskers could form on the aluminum silicate fibers in this process. The results showed that the materials fabricated at the optimum process showed a high compression resilience ratio (94.6%) after compression to a compressive strain of 10%, meanwhile the density and the thermal conductivity of the sample fabricated at the optimum process were 0.1536 g/cm³ and 0.04102 W/(m*K), respectively.

1. Introduction

Heat-sealing/insulation materials have been widely used in various engineering applications. Fibers with excellent high-temperature properties are always used to prepare the heat-sealing/insulation materials. For example, as a promising heat-sealing/insulation materials [1], aluminum silicate fibrous porous ceramics exhibit excellent properties, such as low density, low thermal conductivity, high heat-resistance, high thermal shock resistance and high temperature creep-resistant properties [2,3]. It is reported that aluminum silicate fibers are mainly used as high temperature insulating material in the form of mats, blankets, boards [4], which could be used at 1500°C [5]. Therefore, aluminum silicate fibers are suitable for making fibrous porous ceramics that requires high level of heat resistance. Compression rebound performance of aluminum silicate fibrous felts can’t meet the demands in practical devices. One alternative strategy to solve this problem is by introducing some rigid materials into the aluminum silicate fibrous felts [6]. It is known that mullite whiskers, a kind of rigid materials, possess many attractive properties like high melting temperature, low thermal conductivity, low thermal expansion, low dielectric constant, good thermal shock resistance, excellent chemical inertness and high mechanical strength at high temperatures. The mullite whiskers are usually used as toughening phase in high temperature structure materials, and a number of methods have been developed to produce mullite whiskers into the mullite framework [7-9]. However, the formation of mullite whiskers on the soft substrates are seldom studied. Liu prepared mullite whiskers on the surface of the soft silica-fiber-woven material [10]. The raw material she used to fabricate mullite...
whiskers was AlF_3 powder and SiO_2 powder, however for the method of powder calcination, it is difficult to introduce powders evenly into the fibers. The uneven distribution of the powder will lead the disorderly distribution of mullite whiskers. Therefore, this method is not suitable for synthesized mullite whiskers.

In this study, in situ synthesized mullite whiskers on the surface of aluminum silicate fibrous felts was prepared by gas-phase deposition and reaction. Among them, silica sol and Al(NO_3)_3 served as the silica sources and aluminum source of the mullite whiskers' growth. NH_4F was used as the catalyst to promote the formation of mullite whiskers. After being heat treated at 1200°C for 2 h, the hierarchical structural mullite fibrous felts/mullite whisker material was formed. The microstructure and properties of the whiskers could be adjusted by tailoring the concentration of vacuum impregnation solutions and sintering temperature. The effects of formation of mullite whiskers on the density, thermal conductivity, microstructure, and the compression rebound performance of the aluminum silicate fibrous felts were carefully analyzed and discussed in this paper.

2. Experiments

2.1. Material preparation

In this work, commercially available aluminum silicate fibrous felts used as the substrate were purchased from Hongda Crystal Fiber Co., Ltd., Zhejiang, China. The raw aluminum silicate fibers possess a diameter in the range of 5-10 μm. Alkaline silica sol, aluminum nitrate (Al(NO_3)_3·9H_2O, analytically pure) and ammonium fluoride (NH_4F, analytically pure) were used to prepare vacuum impregnation solutions. The alkaline silica sol was purchased from Jiangtian Chemical Co., Tianjin, China. Aluminum nitrate nonahydrate (Al(NO_3)_3·9H_2O, analytically pure) and ammonium fluoride (NH_4F, analytically pure) were purchased from Guangfu Chemical Co., Tianjin, China.

Firstly, the fibrous felt was added into the silica sol and put into a vacuum circumstance for 20 min to make the fibers uniformly dipped by the silica sol. Then the fibrous felt was frozen for 30 min at -20°C and removed to the freeze-dryer at -50°C until the ice in the felt sublimated completely. After the first impregnation, SiO_2 particles evenly dispersed around the surface and the lap-jointing points of the fibrous felt. Secondly, the fibrous felt was put into the Al(NO_3)_3 solution, and then the felt was put into a vacuum circumstance to make the fiber uniformly dipped by the Al(NO_3)_3. After that, the felts were frozen and put into the freeze dryer as the steps mentioned before. Thirdly, the fibrous felt immersed into NH_4F solution and after the vacuum impregnation and freeze drying, (NH_4)_3AlF_6 particles was generated through the reaction of Al(NO_3)_3 and NH_4F and evenly dispersed around the surface and the lap-jointing points of the fibrous felts. During the three times impregnation, the mole ratio of silica sol, Al(NO_3)_3 and NH_4F was kept at 1:3:12. The contents of silica sol in this experiment were 0 wt%, 0.03 wt%, 0.1 wt%, 0.16 wt% and 0.33 wt%. At last, the felts dipped by silica, Al(NO_3)_3 and NH_4F were placed in a closed aluminum crucible and sintered at different temperatures for 2 h.

2.2. Characterization

Raw materials and sintered samples were identified by X-ray diffraction (XRD, Rigaku D/max 2500 v/pc). Microstructure of the raw and sintered samples was observed by scanning electron microscope (SEM, TDCLS-4800). The compression-resilience performance was tested by an electronic universal testing machine(CSS-44001) with the speed of 0.2 mm/min. The thermal conductivity of fibrous felts was measured by a hot disk thermal analyzer (XIATECH, TC3000, China).

3. Results and discussion

3.1. The formation mechanism of the mullite whisker

Figure 1a-c show the SEM images of the fibrous felt after first, second and third impregnations and freeze drying, respectively. Figure 1d shows the SEM image of fibrous felt after heat treatment. The surface of the aluminum silicate fibrous felts was smooth before impregnation. It could be seen in
Figure 3a–c, many micron particles evenly dispersed on the surface and the lap-jointing points of the fibers. As we can see from Figure 1d, dense mullite whiskers uniformly formed on the aluminum silicate fibers after heat treatment.

As shown in Figure 2, when the fibrous felts were dipped three times, the peak of the \((\text{NH}_3)_3\text{AlF}_6\), aluminum silicate and \(\text{NH}_3\text{NO}_3\) could be seen. We suggested that \((\text{NH}_3)_3\text{AlF}_6\) was produced by the reaction of \(\text{Al(NO}_3)_3\) and \(\text{NH}_3\text{F}\). After sintered at 700°C, it could be seen that only the peak of mullite and aluminum silicate exited, and it means that \((\text{NH}_3)_3\text{AlF}_6\) and \(\text{NH}_3\text{NO}_3\) decomposed completely at this temperature. In the heat-treating stage, the \((\text{NH}_3)_3\text{AlF}_6\) firstly decomposed into \(\text{AlF}_3\), gaseous \(\text{NH}_3\) and HF. With the increase of heating temperature, the \(\text{AlF}_3\) reacted with \(\text{O}_2\) to produce gaseous AlOF. Then the \(\text{SiO}_2\) powders transformed into gaseous \(\text{SiF}_4\) under the catalysis of gaseous AlOF. As the sintering temperature increased to 800°C, topaz began to generate (Figure 2), the gaseous AlOF and \(\text{SiF}_4\) reacted with each other and formed transient phase topaz. The X-ray diffraction pattern kept the same from 800°C to 1100°C. When the temperature reached 1200°C, topaz disappeared and transformed into mullite. As the sintering temperature increased to 1300°C, only mullite was observed in the sample.

3.2. Effects of the concentration of impregnation solutions on compression-resilience performance

Fig. 3 illustrates the SEM microstructure of in situ synthesized mullite whiskers on the surface of aluminum silicate fibrous felts with different impregnation concentration. If the felt was dipped with 0.1 mol/L \(\text{Al(NO}_3)_3\), it could be observed that only some short nanorods formed on the surface of the fibers (Fig.3a). With the increase of the concentration of impregnation solutions, the aspect ratio of the mullite whiskers increased (Fig.3b). When the impregnation concentration of \(\text{Al(NO}_3)_3\) was 0.5 mol/L, the whiskers on the surface of fibers became more flourish, but the length of the whiskers decreased (Fig.3c). It could be seen from Fig.3d that if the concentration of \(\text{Al(NO}_3)_3\) solutions was 1.0 mol/L, the length and the width of the whiskers rose sharply, meanwhile the interspace among the fibers was filled by mullite whiskers.
Figure 2. XRD patterns of the samples after sintered at different temperatures.

![XRD patterns](image1)

**Figure 3.** SEM morphologies of the fibrous felts after dipped with different solutions: (a) 0.03 mol/L silica sol, 0.1 mol/L Al(NO₃)₃ solution and 0.4 mol/L NH₄F solution, (b) 0.1 mol/L silica sol, 0.3 mol/L Al(NO₃)₃ solution, and 1.2 mol/L NH₄F solution, (c) 0.16 mol/L silica sol, 0.5 mol/L Al(NO₃)₃ solution, 2.0 mol/L NH₄F solution, (d) 0.33 mol/L silica sol, 1.0 mol/L Al(NO₃)₃ solution, 4.0 mol/L NH₄F solution. Other process parameters: the holding time was 2 h, the sintering temperature was 1200 °C.

Fig. 4 shows the density and thermal conductivity of the fibrous felts dipped with different solutions. The density and thermal conductivity of the raw fibrous felt were 0.1445 g/cm³ and 0.0309 W/(m*K), respectively. With the rising of the concentration of solution, the density and thermal conductivity increased.
conductivity of the samples increased. The volume density and thermal conductivity of the frameworks were 0.1473–0.1554 g/cm³ and 0.0316–0.04451W/(m*K), respectively. Heat transfer in a fibrous insulation material occurs through conduction, convection, and radiation. In our work, the thermal conductivity of the fibrous felts was measured at room temperature, the influence of heat radiation could be ignored, so the process of transferring heat was mainly effected by heat convection and heat conduction. Meanwhile, the fibrous felts/mullite whisker materials have low heat convection velocity because they have large specific surface area and great friction on the surface of fibers. Meanwhile, the hierarchical fibers/whiskers structure had long heat transfer path which was benefit for lowering the velocity of heat conduction and preventing the thermal conduction and thermal convection. These reasons lead to high heat insulating performance and low thermal conductivity.

Figure 4. Density and thermal conductivity of the fibrous felts after dipped with different solutions: (a) 0.03 mol/L silica sol, 0.1 mol/L Al(NO₃)₃ solution and 0.4 mol/L NH₄F solution, (b) 0.1 mol/L silica sol, 0.3 mol/L Al(NO₃)₃ solution, and 1.2 mol/L NH₄F solution, (c) 0.16 mol/L silica sol, 0.5 mol/L Al(NO₃)₃ solution, 2.0 mol/L NH₄F solution, (d) 0.33 mol/L silica sol, 1.0 mol/L Al(NO₃)₃ solution, 4.0 mol/L NH₄F solution. Other process parameters: the holding time was 2 h, the sintering temperature was 1200 °C.

The compression-rebound tests were expected to be carried out below the elastic limit. Therefore, all of the compression-rebound data were tested by setting the compressive strain as 10%. Fig. 5 shows the compression rebound curves of fibrous felts dipped with different solutions. It should be noted that the compression resilience ratios of samples dipped with 0.1 mol/L Al(NO₃)₃, 0.3 mol/L Al(NO₃)₃ and 0.5 mol/L Al(NO₃)₃ showed good compression rebound performance, and the compression resilience ratios were 91.5%, 92.8% and 94.6%, nearly 100% (Fig. 5a-c). Meanwhile, with the increase of the impregnation concentration, compression rebound performance improved remarkably (Fig. 5a-c), and the fibrous felts after dipped with 0.5 mol/L Al(NO₃)₃ showed the best compression rebound performance (Fig. 5c). The mullite whiskers on adjacent fibers intersected with each other and formed many lap-jointing points, consequently enhancing the compression rebound performance of the fibrous felts. However, the compression resilience ratio of the fibrous felts dipped with 1.0 mol/L Al(NO₃)₃ was only about 18.2%. It could be seen that the length and the diameter of the mullite whiskers improved sharply, so that the fibrous felts could not provide enough space to move under the pressure.
Figure 5. Compression rebound curves of the fibrous felts after dipped with different solutions: (a) 0.03 mol/L silica sol, 0.1 mol/L Al(NO₃)₃ solution and 0.4mol/L NH₄F solution, (b)0.1mol/L silica sol, 0.3mol/L Al(NO₃)₃ solution, and 1.2mol/L NH₄F solution, (c) 0.16mol/L silica sol, 0.5 mol/L Al(NO₃)₃ solution, 2.0 mol/L NH₄F solution, (d) 0.33 mol/L silica sol, 1.0 mol/L Al(NO₃)₃ solution, 4.0mol/L NH₄F solution. Other process parameters: the holding time was 2 h, the sintering temperature was 1200 °C.

4. Conclusions
The following conclusions can be drawn through investigations of the effects of in situ synthesized mullite whiskers on the on the density, thermal conductivity, microstructure, and the compression rebound performance of aluminum silicate fibrous felts:

(i). Silica sol, Al(NO₃)₃ solution and NH₄F solution could be introduced into the fibrous felt in the form of ions or sol through vacuum impregnation and freeze drying. The mullite whiskers were generated on the surface of aluminum silicate fibrous felts through gas-phase deposition and reaction, and the mullite whiskers formed on the surface of fibrous felts.

(ii). Impregnation concentrations and sintering temperature played an important role in improving the compression rebound performance. The optimum impregnation parameters to in situ synthesize mullite whiskers were 0.16 mol/L silica sol, 0.5 mol/L Al(NO₃)₃ solution, 2.0 mol/L NH₄F solution, the sintering temperature of 1200 °C and the holding time of 2 h. The results showed that the materials fabricated at the optimum process exhibited low density, low thermal conductivity and good compression rebound performance. The samples showed a high compression resilience ratio of 94.6% after compression to a compressive set of 10%. Meanwhile the density and the thermal conductivity of the sample fabricated at the optimum process were 0.1536 g/ cm³ and 0.04102 W/(m*K), respectively.
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