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Ceramics International 39 (2013) 4075–4079

CERAMICS INTERNATIONAL

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Preparation and microstructure of in-situ gel modified expanded vermiculite

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Received 26 October 2012; accepted 29 October 2012
Available online 5 November 2012

Abstract

Expanded vermiculite is an important thermal insulation material with a layered micro-porous structure. In this paper, modified expanded vermiculite was obtained using an in-situ gel method. Under experimental conditions of $n_{(\text{epoxy propane})}$:$n_{(\text{A1(NO3)3})}$:$n_{(\text{ethanol})}=5.5:1:30$, the alumina aerogel was distributed evenly in the structural gaps of the expanded vermiculite. The framework of the in-situ alumina aerogel is composed of sphere-like Al_2O_3 particles with a diameter of 40 nm and the pore size distribution is uniform with an average size of 45 nm. The modified vermiculite maintains a good multi-porous network structure, without any distinct signs of conglobation or collapse of the porous structure after being calcined at 900 °C and 1000 °C for 4 h. The modified expanded vermiculite show lower thermal conduction than the non-modified expanded vermiculites at all temperatures tested.

Keywords: Expanded vermiculite; Alumina aerogel; Insulation material

1. Introduction

Energy shortages are an important issue faced by countries all over the world, and the most effective way to solve the problem is to save energy. One of the main ways to do this is the development and application of insulation materials. Expanded vermiculite is an excellent insulation refractory material due to its low thermal conductivity and bulk density; moreover, the scale structure of its granule surface has the ability to reflect thermal radiation [1,2]. However, expanded vermiculite composite materials have relatively poor high-temperature insulation performance due to the spacing of the layers, which are relatively large at 10–20 μm. Since Kistler reported the properties of aerogels, many aerogels have been studied [3]. Aerogels have a high porosity (more than 90%), a high surface area and an extremely low density. In this paper, the in-situ gel method was adopted to modify the expanded vermiculite to improve its microstructure. As the pore sizes are from micro to nano, in the expanded vermiculite, its insulation performance is greatly enhanced.

2. Experimental procedures

Expanded vermiculite was bought from Weili Mining Co, Xinjiang, China, as a crude ‘superfine grade’. The particle size of the crude vermiculites was 0.05–1.0 mm.

$Al(NO_3)_3 \cdot 9H_2O$ was firstly dissolved in ethanol; while, the expanded vermiculite was soaked in ethanol for 2 h. Then, certain amounts of the expanded vermiculite that had been soaked in ethanol, propylene oxide (PO) and formamide were added to the clear $Al(NO_3)_3 \cdot 9H_2O$/ethanol solution. The reaction mixture solution was stirred for a certain period of time. The in-situ modified expanded vermiculite was obtained after the mixture solution stood at room temperature for a while.

A drying oven at 40 °C was used to age the in-situ modified expanded vermiculite for 24 h. Then the composite was soaked in a series of solutions of absolute ethanol at 60 °C for 48 h, with the ethanol being replaced every 24 h, and then a Teos ethanol solution (1:3 in volume) at 60 °C for 48 h, with the Teos ethanol being replaced every

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http://dx.doi.org/10.1016/j.ceramint.2012.10.261

24 h. Finally, the gel modified expanded vermiculite was washed with ethanol to get rid of the redundant Teos. Then after being dried in an oven for 48 h at 70 °C the treated expanded vermiculite was obtained.

The microstructures of the samples were observed by field emission scanning electron microcopy (FEI HK limited company Nova400 Nano SEM).

3. Results and discussion

3.1. Preparation process of alumina aerogel and influence of the structure

3.1.1. Effect of epoxypropane on the process and structure of alumina aerogel

The molar ratio of n(alcohol):n($Al(NO_3)_3$):n(formamide) in this reaction system was fixed at 30.0:1.0:0.8. Different PO/aluminum nitrate mole ratios (4.0, 4.5, 5.0, 5.5 and 6.0) were used to investigate the microscopic structure and gelation process of alumina aerogels. As can be seen from Table 1, gel formation time decreases when the mole ratio of n(PO):n(Al) increases. When the PO/aluminum nitrate mole ratio was 4.0, the gelation time was about 100 minutes. This significantly decreased to 5 minutes when the PO/aluminum nitrate ratio reached 6.0. This is attributed to the function of the PO in regulating the pH value of the reaction system; when a low concentration of PO is added, the pH value of the reaction system increases and the opening ring reaction of the PO captures protons. Subsequently, the rate of the $[Al(H_2O)_6]^{3+}$ hydrolysis and hydroxyl condensation reaction of the hydration aluminum ion decreases, so that the gelation time of the system is increased. On the other hand, when the concentration of PO reaches 6.0, the speed of the ring opening reaction is relatively high, so pH increases very quickly, and the rate of the $[Al(H_2O)_6]^{3+}$ ion hydrolysis and hydroxyl condensation reaction of the hydration aluminum ion increases sharply, so the gel forms very fast, which makes the structure and elasticity of hydroxyl alumina polymers generated by the hydration hydroxyl ion polycondensation loose and decreased [4].

Fig. 1 shows the SEM micrographs of the in-situ alumina aerogel with different PO/aluminum nitrate mole ratios, which are 4.0 for Fig. 1(a), 5.5 for Fig. 1(b) and 6.0 for Fig. 1(c). In-situ alumina aerogel is a porous solid material with a loose continuous mesh structure, where the skeleton is formed from coalesced nanoscale alumina spherical particles. The amount of PO influences the structure and quality of the in-situ alumina aerogel; and, as can be seen from the framework structure plays an important role in the gel structure. When the PO/aluminum nitrate mole ratio is close to 4.0, the alumina gel framework structure is comparatively well formed, but a little fluffy. Yet when the ratio reaches 5.5, the alumina gel network structure is quite uniform; but, when the ratio exceeds 6.0, due to the rapid reaction of the gel system, the low polymer structure of the alumina aerogel formed by hydration hydroxyl aluminum ion polycondensation is loose, and the network is not so homogeneous. From the pore size distribution in the alumina aerogel it can be inferred that the amount of PO has a significant effect. When the PO/aluminum nitrate mole ratio is close to 4.0, pore size distribution is uneven, and the pore size is relatively large, as shown in Fig. 1(a). When the PO/aluminum nitrate mole ratio is 5.5, pore size distribution is even, as shown in Fig. 1(b). As the amount of PO increases the pore size distribution becomes more uneven and the pore size clearly decreases, as shown in Fig. 1(c).

The reason why in-situ alumina aerogels have distinct micro-structures under different mole ratios of PO and aluminum nitrate is due to the network structure of aluminum nitrate that differs greatly under different pH values. The alumina aerogel will possess a branched linear polymer structure when the solution pH is 4.5. However, when the solution pH value is higher than 6, the alumina aerogel has a body type polymer structure. When the amount of PO is relatively low (the mole ratio of PO/aluminum nitrate is less than 5.5), the solution pH value would be about 4.5, and it can be inferred that the alumina aerogel is mostly composed of polymerized alumina particles with branched linear structures. In the network structure of the alumina aerogel, the pore size of the body type structures is relatively small, showing microporous structure characteristics, while the pore size of the branched linear structures is larger. This results in alumina aerogels where the pore size distribution is uneven.

3.1.2. Effect of ethanol on the process and structure of alumina aerogel

In this reaction system, the molar ratio of PO, aluminum nitrate and formamide are fixed at 5.5:1:0.8, and the molar ratios of ethanol and aluminum nitrate were 22, 24, 27, 30 and 32. It can be seen from Table 2 that addition ethanol solvent influences the formation process of the alumina gel. The gelation time needed for the alumina gel was extended gradually as the molar ratio of the ethanol/aluminum nitrate in the system increased. This is because when the molar ratio of ethanol in the system increases, the concentration of the aluminum ions decreases, leading to a reduction in the rate of hydrolysis of the aluminum ions. The collision probability is smaller as the number of hydroxyl aluminum colloid ions per

Table 1
Gel formation time for different mole ratios of n(PO):n(Al).

Sample	1	2	3	4	5	6
nPO:n($Al(NO_3)_3$)	0	4.0	4.5	5.0	5.5	6.0
Time (min)	–	100	68	45	21	5

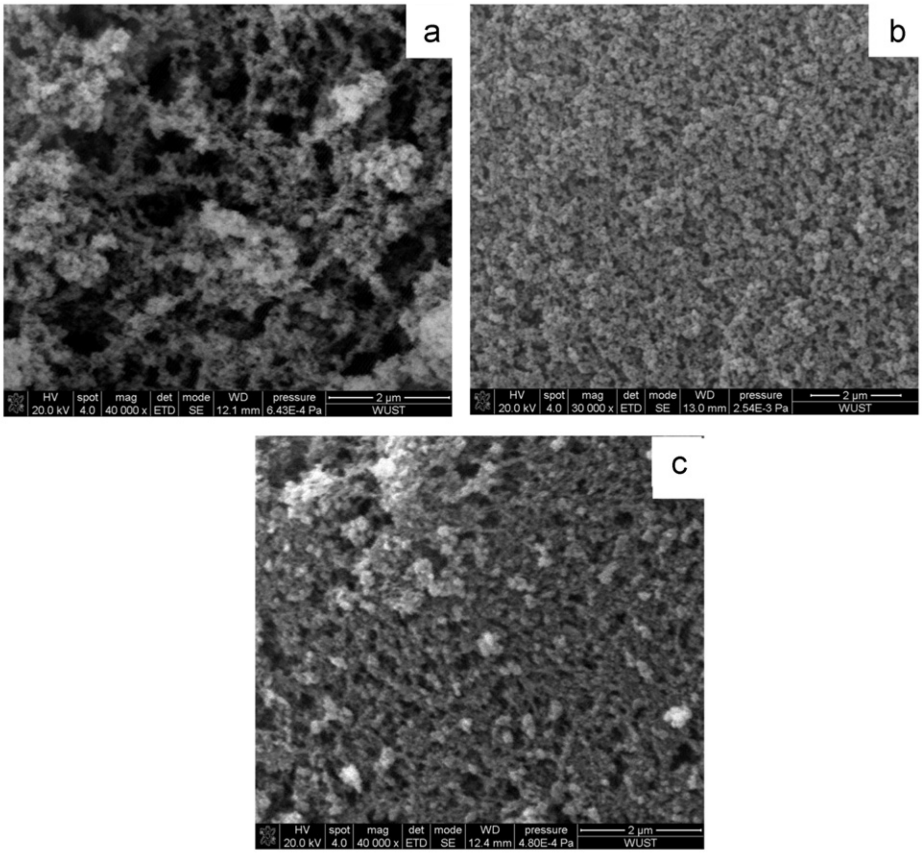

Fig. 1. SEM micrographs of alumina aerogel with different amounts of: (a) 4.0, (b) 5.5 and (c) 6.0.

Table 2
Gel formation time for different mole ratios of n(ethanol):n(Al).

Sample	1	2	3	4	5
n(ethanol):n(Al(NO$_3$)$_3$)	22	24	27	30	32
Time (min)	19	20	21	21	26

stere decreases, preventing the polymerization of the alumina gel, so the growth of the gel network slows down, leading to the extension of the gelation time [5].

From Table 2 it can be seen that the addition of ethanol had little effect on the gelation time. During the formation of the gel, both of the reaction rates of the aluminum ions hydrolysis and hydroxyl aluminum ions polymerization depended on the pH value of the system, which meant that pH was the key to the rate of gel time. In this system, the addition of ethanol has little effect on pH, so the gelation time changed little, remaining close to 21 min. However, the addition of ethanol has a great influence on formation of the gel network (Fig. 2). If the mole ratio of the ethanol/aluminum nitrate is too high or low it will be unfavorable for the formation of the gel network.

Fig. 2 shows the SEM micrographs of an in-situ alumina aerogel with different ethanol and aluminum nitrate mole ratios, which are 24 for Fig. 2(d) and 32 for Fig. 2(e). No matter whether the ethanol/aluminum nitrate mole ratio is 32 or 24, the network structure of the alumina aerogel is not perfect compared with the SEM micrograph of the alumina aerogel with a ratio of 30 (Fig. 1(b)). When the ethanol/aluminum nitrate mole ratio is 32 the alumina aerogel are fluffier than when the ratio us 24. The possible reason for this is that ethanol played the role of a solvent in this system, which dissolved the hydroxyl aluminum ions that were the products of the aluminum ions hydrolysis and polymerization processes. When the amount of ethanol is small (ethanol/aluminum nitrate mole ratio is 24), the hydroxyl aluminum ions could not be dissolved, so it began cooperating and forming hydroxide precipitation, leading to the imperfect network structure of the alumina aerogel and the compacting in some regions. When the ethanol/aluminum nitrate mole ratio increases to 32, the solvent could effectively prevent the hydroxyl aluminum ions from polymerizing, so the polymerization on the surface of the alumina aerogel is imperfect. The volatility of the ethanol in the drying process enhances the polymerization of the alumina aerogel, so the volume shrinkage of the alumina gel decreases to a degree, which causes the structure of the alumina aerogel to become fluffier, with more pores and larger pore sizes.

3.2. Microstructure of in-situ aluminum gel modified vermiculite

Fig. 3 gives the SEM micrographs of the in-situ alumina gel modified vermiculite prepared by the above optimal processes. As seen in Fig. 3(f), the alumina aerogel is distribute evenly in the structural gaps of the expanded

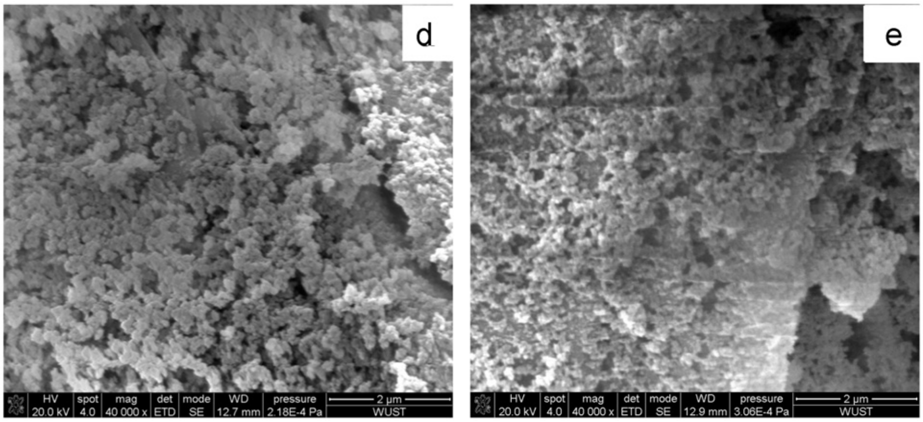

Fig. 2. SEM micrographs of alumina aerogel with different amounts of ethanol: (d) 24 and (e) 32.

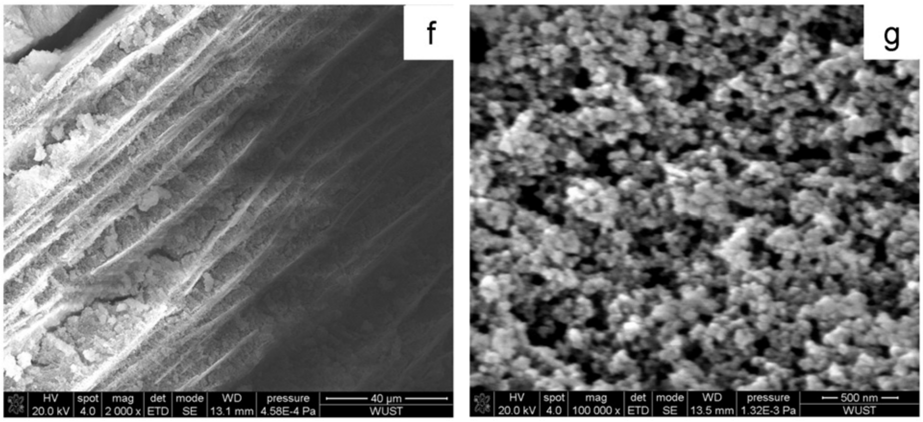

Fig. 3. SEM micrographs of in-situ alumina gel modified expanded vermiculite.

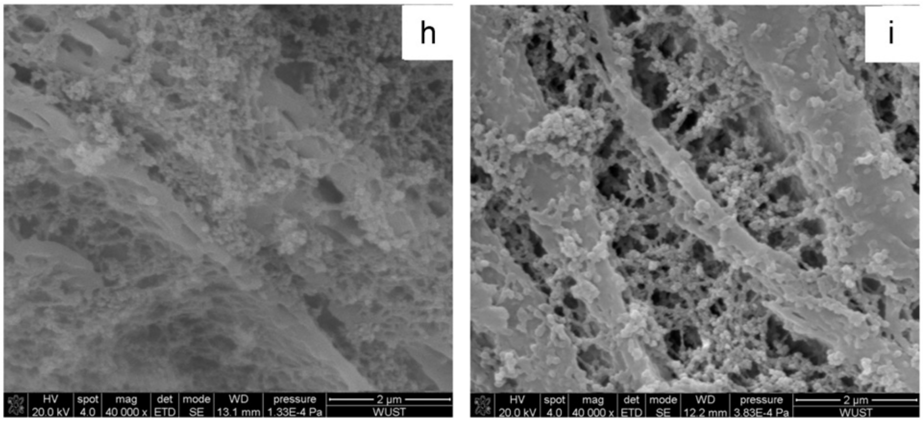

Fig. 4. SEM micrographs of in-situ alumina gel modified vermiculite: (h) calcinated at 900 °C for 4 h and (i) calcinated at 1000 °C for 4 h.

vermiculite by the in-situ gel method, and the framework of the alumina aerogel is make up of sphere-like alumina particles. The particle diameters were uniform with the mean being 40 nm (Fig. 3(g)); while the pore size was 45 nm, which is typical of mesoporous materials. The insulation performance of the material at high temperatures is enhanced by this special microstructure.

As seen from Fig. 4(h) and (i), after being calcined at temperatures of 900 °C and 1000 °C for 4 h, the in-situ alumina gel modified expanded vermiculite maintained a good multi-porous network structure, without any distinct signs of conglobation or collapse of the porous structure. The pore size of the calcined samples increased when compared to non-calcined samples (Fig. 3) due to volume

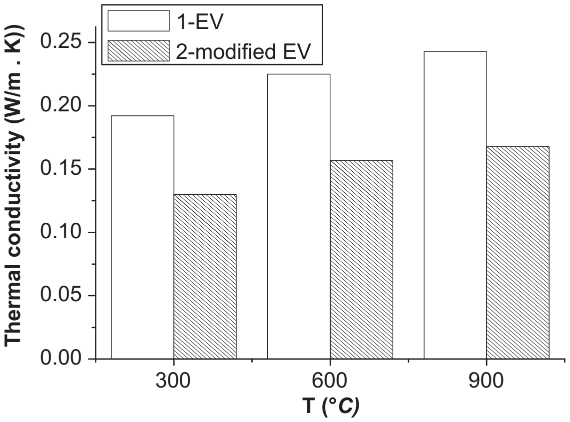

Fig. 5. Thermal conductivity of composites of modified expanded vermiculite.

shrinkage. The pore size distribution remained uniform, indicating an improvement in the microporous structure obtained from the in-situ modification of expanded vermiculite by alumina gel that is permanent. After being calcimined at 900 °C, the skeleton of the alumina aerogel, which existed in the layer gap, is still composed of nanometer-sized particles, but the structure tends to transform from a three-dimensional structure to a linear structure. Likewise, the alumina aerogel is also composed of linear structure alumina particles after being calcimined at 1000 °C. A result of the pore sizes being bigger due to the linear structure is that they become uneven. The special microstructure is of benefit as it reduces the contact area of alumina particles and the surface or volume diffusion of the alumina aerogel, thereby preventing high temperature calcinations effectively, and enhancing the high-temperature thermal stability of the aluminum aerogel.

3.3. *Properties of in-situ alumina gel modified vermiculite*

As seen from Fig. 5, the thermal conductivity of the modified expanded vermiculite was lower than that of expanded vermiculite, and had better insulation properties. The thermal conductivity of the modified sample increased slightly in the temperature range 600 °C–900 °C. Nano level pours in the modified samples played a very important role in obstructing heat transfer, especially at high temperatures.

4. Conclusions

1) The modified expanded vermiculite has been developed by as an in-situ gel under experimental conditions of $n_{(\text{epoxy propane})}$:$\text{n}_{(\text{Al (NO3)3})}$:$n_{(\text{ethanol})}=5.5:1:30$.
2) The microstructure of the modified expanded vermiculite has been determined: the alumina aerogel is distributed evenly in the structural gaps of the expanded vermiculite, the framework of the in-situ aluminum aerogel is made up of sphere-like Al_2O_3 particles, the particle size is fairly uniform with the mean particle diameter being 40 nm and the pore size being 45 nm.
3) The modified expanded vermiculite maintained a good multi-porous network structure, without any distinct signs of conglobation or collapse of the porous structure after being calcined at the temperatures of 900 °C and 1000 °C for 4 h.
4) The modified expanded vermiculite show lower thermal conduction than the non-modified expanded vermiculites at all temperatures tested.

Acknowledgments

The authors are grateful to the process No. 2012CB722702 of 973 plans to pre-research subprojects, and the Science and Technology Department of Hubei Province and Ministry of Science and Technology for financial support under the process Nos. 2011CDZ053 and 2010CDA028 of the Hubei Province Natural Science Foundation Project.

References

[1] G.S. Hu, Z.Y. Li, Y.P. Zhu, W.G. Zhang, Preparation of vermiculite powder with high expansion and high quality—II. Thermal expansion of vermiculite, The Chinese Journal of Process Engineering 6 (2006) 763–767 in Chinese.
[2] J. Matins, R. Fernandes, Hydrophobic expanded vermiculite as a cleaning agent for contaminated waters, Water Science and Technology 26 (1992) 2297–2299.
[3] S.S. Kistler, Coherent expanded-aerogels, Journal of Physical Chemistry 36 (1932) 52–64.
[4] L.B. Mao, R.Y. Zhang, Study on preparation of alumina aerogel, Materials Review 20 (2006) 16–20 in Chinese.
[5] Theodore F. Baumann, Alexander E. Gash, Sarah C. Chinn, Synthesis of high-surface-area alumina aerogels without the use of alkoxide precursors, Chemistry of Materials 17 (2005) 395–401.