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Short communication

Thermal stability of expanded perlite modified by mullite

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Abstract

Results of the thermal stability of expanded perlite modified by mullite are presented. Mullite was formed from alumino-silicate gel by sol–gel method. This method allowed us to obtain very homogenous and reactive gel and phase formation of mullite took place at relatively low temperatures. Expanded perlite modified with alumino-silicate gel after firing above the temperature of mullite formation had better thermal stability and durability during heating. The thermal stability of this material was examined up to 1400 °C.

Keywords: C. Thermal properties; D. Mulllite; Perlite

1. Introduction

In recent years, the tendency to obtain materials with better chemical and physical properties than traditional ones has been apparent. The growing requirements for such materials are indications because of technological progress. Their invention, improvement and application are also an important question due to economic factors. One of the possibilities to achieve new materials is chemical modification of traditional materials. Modification of expanded perlite is one of the ways to obtain materials of a new class with properties similar to, for example alumino-silicate fibers.

Perlite is a glassy volcanic rock of rhyolitic composition usually containing a small amount of combined water. Raw perlite when heated to an appropriate temperature (above 870 °C) expands and transforms into a cellular material of low bulk density. This expansion process occurs due to the presence of 2–6% of combined water in the crude perlite rock. Upon rapid heating, the chemical water held within the perlite vaporizes and creates bubbles in the heat softened rock. The formation of these bubbles allows perlite to expand even 15–20 times of its original volume and produces froth-like structure. This structure gives excellent insulation properties, low density and high porosity of materials. Moreover, perlite shows chemical inertness, fire resistance and high absorption of sound. All these properties make perlite an applicable material for many applications. The expanded perlite can be applied in the construction industry and horticulture market and as a filter aid and filler. This lightweight filler is used as insulating cover on the surface of the molten metal to prevent excessive heat loss during delays in pouring; to top of ingots, to reduce piping and decrease lamination; to produce refractory blocks and bricks or simply as fillers and in several important foundry applications. Miscellaneous applications of expanded perlite include fillers or extenders in paints, enamels, glazes, plastics, resins, and rubber; as well as a catalyst in chemical reactions and as an abrasive. Expanded perlite has excellent thermal insulation properties but its use as the insulation in high temperature applications is limited to about 900 °C. Above this temperature the insulation properties of perlite significantly decrease as perlite grains melt fast.

One of the possibilities to improve the thermal stability of expanded perlite is synthesis of mullite in-situ by sol–gel process on the porous structures of perlite grains. During heating, mullite formation from gel on perlite grains allows improving of the thermal stability and durability of such fillers above the melting point of raw perlite. The modified expanded perlite has much better properties than raw perlite.

Mullite is one of the extensively studied crystalline phase due to unique combination of features. It is the only stable phase in the SiO_2–Al_2O_3 system. Taking interest in mullite in traditional and advanced ceramics can be explained by its

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excellent properties: high thermal stability, chemical stability, low thermal expansion coefficiency, high temperature durability and strength and creep resistance.

Usually, mullite is formed during thermal decomposition of kaolinite and related materials to mixed oxides at high temperatures. The mechanism of mullite formation depends on the type of raw materials and their treatment methods. The reaction leading to mullite crystallization between bulk samples of alumina and silica occurs at relatively high temperatures, above 1500 °C. The process is determined by nucleation and growth at the interface between two phases. The main problem in classical method of mullite synthesis is poor homogenization of reactants and relatively high temperature of formation. Mullite can be obtained through the sol–gel method. The method allows to prepare very homogenous and reactive composition of reactants as gel that is possible to sinter at lower temperature than in the classical way. Second advantage is that by sol–gel method it is possible to obtain nanometric homogeneity and microstructure of products. Relatively high density of gel in green state may allow to sinter well densified mullite ceramics.

Mullite can be synthesized from monophasic and diphasic gels obtained either by sol–gel or similar methods leading to the different precursor types [1–10]. The main difference between the two types of gel is their homogeneity: monophasic gel is homogenous at the atomic level and mullite formation occurs by exothermic reaction around 980 °C [1,2,7]. In spite of homogeneity of diphasic gel that is in the nanometer range, the mullite formation occurs at higher temperatures because this gel consists of discrete alumina and silica particles reacting independently above 1300 °C for complete crystallization [1,4,5].

Hoffman et al. [1] described several methods of making monophasic gels from tetraethyl orthosilicate (TEOS) and aluminum nitrate dissolved in ethanol. The alumino-silicate gel obtained by polycondensation from nitrate and TEOS may be an appropriate method for mullite processing. The microstructure of gel and consequently microstructure of mullite phase strictly depends on processing parameters (sol dilution, pH value, gelling temperature and water content).

Table 1
The notations of the starting sols

Sample notation	Al_2O_3:SiO_2 molar ratio	Aluminum nitrate nonahydrate to alcohol molar ratio
A1	1:1	0.05
A2	1:1	0.1
A3	1:1	0.15
B1	1.5:1	0.05
B2	1.5:1	0.1
B3	1.5:1	0.15
C1	2:1	0.05
C2	2:1	0.1
C3	2:1	0.15

Table 2
Physical properties of expanded perlite

Class	III
Bulk density (kg/m^3)	125 ± 15
Melting point (°C)	950–1050
Average particle size (mm)	About 1.0
Thermal conductivity[a] (W/mK)	0.045–0.059
Water absorption (%, V/V)	30–40
Compression strength[b] (MPa)	0.10–0.40

[a] In dry state at 20 °C.
[b] Compacted condition.

In the present study the thermal stability of modified expanded perlite by alumino-silicate gel with different Al_2O_3:SiO_2 molar ratio and different quantities of solvent was investigated. The thermal stability of the materials during the heating process up to 1400 °C was studied.

2. Experimental details and test methods

2.1. Preparation of samples

Samples were prepared by the following procedure. Alumino-silicate gels with different Al_2O_3:SiO_2 (1:1, 1.5:1, 2:1) molar ratios were obtained by dissolving aluminum nitrate

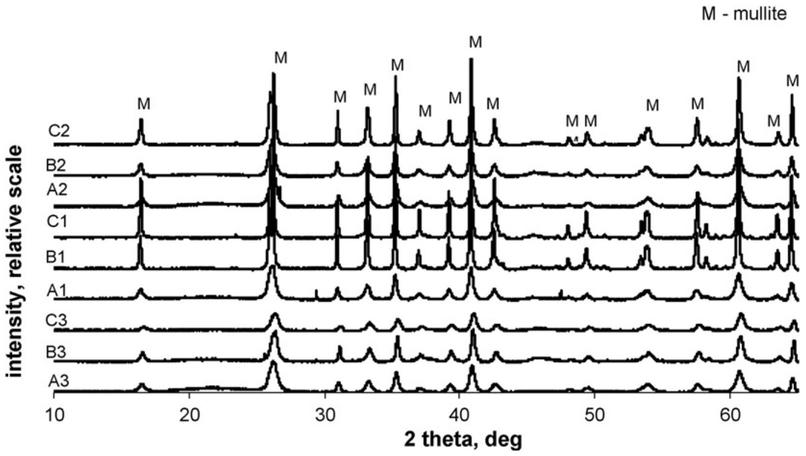

Fig. 1. XRD analysis of alumino-silicate gels fired at 1200 °C.

Table 3
Phases detected in alumino-silicate gels heated at 1200 °C

Sample notation	Phases detected	
	Main phase	In traces
A1	Mullite	Weak Al_2O_3
A2	Mullite	Weak SiO_2
A3	Mullite	Weak SiO_2
B1	Mullite	Weak SiO_2
B2	Mullite	Weak Al_2O_3
B3	Mullite	Weak Al_2O_3, SiO_2
C1	Mullite	Weak Al_2O_3
C2	Mullite	Weak Al_2O_3
C3	Mullite	Weak Al_2O_3, SiO_2

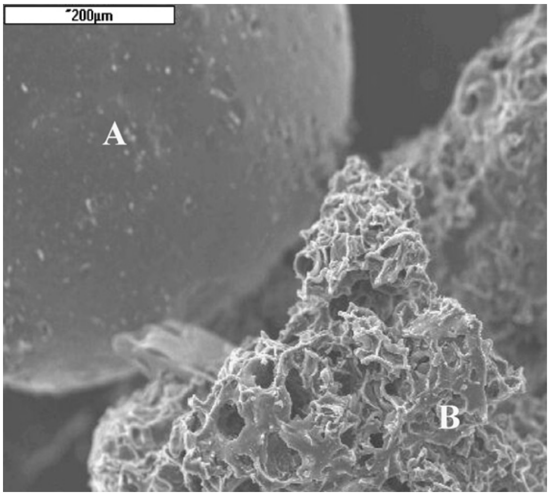

Fig. 2. Perlite grains heated at 1200 °C: A—without modification (molten) and B—modified by mullite gel (saved porous structure).

nonahydrate in absolute ethyl alcohol and by mixing it at room temperature with tetraethyl orthosilicate . Dilution mol ratio of aluminum nitrate nonahydrate to alcohol was 0.05, 0.1, and 0.15, respectively. The series of samples with different proportion of compounds are presented in Table 1. Water used for hydrolysis of TEOS was derived from bonded water in aluminum nitrate nonahydrate. The gelling temperature was 60 °C for 2 h. The solution for gelling was placed in a water bath. The obtained gels were dried for 48 h at 105 °C under atmospheric pressure and then calcined at 600 °C for 2 h. After calcination samples of pure gels were heated up to 1200 °C for 2 h.

Then, the expanded perlite was modified by sol. The mixtures with alumino-silicate sol were sprayed on the surface of expanded perlite grains by atomizer. Two gels which give the largest amount of mullite were chosen. Spraying process was continued until the volume proportion of green state of sol to perlite fillers was 1:2 which led to uniform coating of grains. Samples of modified perlite were treated similar to pure alumino-silicate gels up to 1200 °C. Next, samples were heated up to 1400 °C and their changes during heating were observed.

In this study the expanded perlite class III from ZGM Zebiec S.A. (Poland) was used. Mean chemical composition of perlite is SiO_2—65–75%, Al_2O_3—10–18, $K_2O + Na_2O$—6–9, $MgO + CaO$—2–6 and Fe_2O_3—1–5. The physical properties of perlite are presented in Table 2.

2.2. Characterization methods

Samples of products formed from gel and modified expanded perlite heated at different temperatures were investigated. Powder XRD patterns were carried out using a Philips X-ray diffractometer X'pert system with monochromatic CuK_α radiation. Microstructures of the modified perlite samples heated at different temperatures were investigated by the JEOL scanning electron microscope equipped with EDX LINK system. A maximum used magnification of 24,000× was used.

3. Results

The XRD patterns of alumino-silicate gels heated at 1200 °C are shown in Fig. 1. The results of the XRD analysis of the alumino-silicate gel samples have shown mullite phase. Small amounts of other phases were detected. All detected phases at 1200 °C are given in Table 3. In addition to mullite, a weak trace of Al_2O_3 was present in rich-alumina samples and SiO_2 in rich-silica samples were detected. The highest content of the

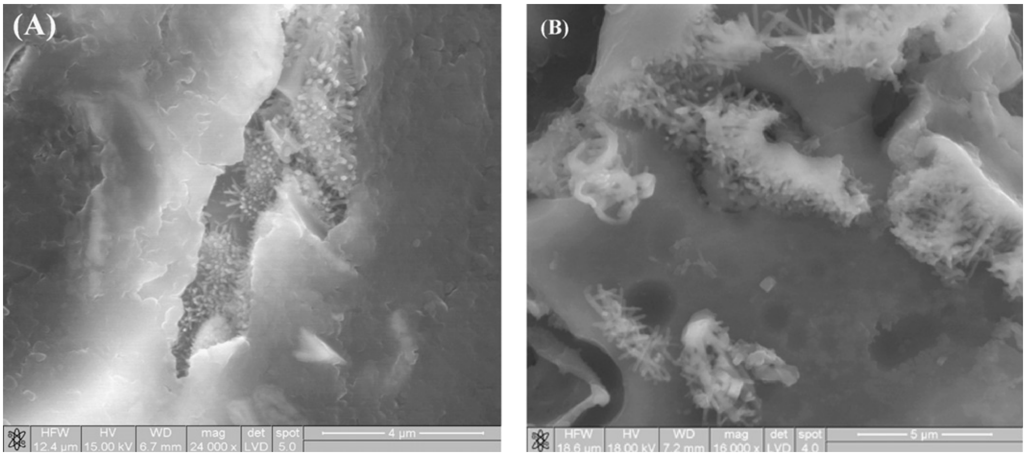

Fig. 3. Mullite crystals formed in perlite walls after firing at: (A) 1200 °C and (B) 1400 °C (composition B1).

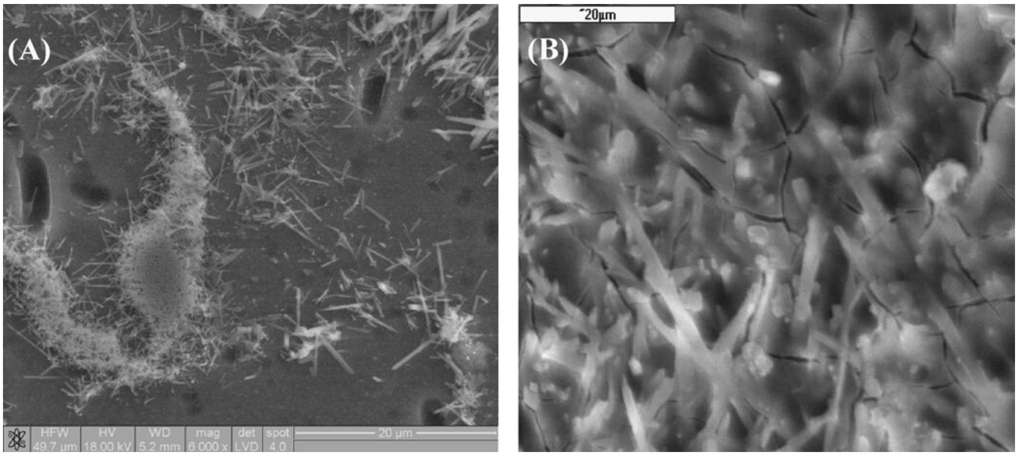

Fig. 4. Mullite crystals formed in perlite walls after firing at: (A) 1200 °C and (B) 1400 °C (composition C1).

formed mullite was found in samples from the gels with compositions B1 and C1. These two gels were chosen for further investigation.

Fig. 2 presents the SEM micrograph of the mullite phase synthesized on the expanded perlite at 1200 °C. The maximal application temperature of the raw expanded perlite is about 900–1000 °C. With softening, the process of the pores filling-up progresses. At the temperature of 1200 °C the completely melted grain (spherical shaped—A) of unmodified perlite is visible in contrast to the unmelted ones—B. Such modification allows to save the porous structure of grain and enables to use that as a filler at higher temperature than raw expanded perlite. Figs. 3 and 4 show the SEM micrographs of modified expanded perlite grains heated at 1200 and 1400 °C. The mullite forms needle-like crystals reinforcing walls of perlite grains (Fig. 4). After 4 h of heat treatment, the obtained mullite crystals from the amorphous gel had lengths above 5 μm (Fig. 4). It is noticed in Fig. 4(B) that the microcracking propagation is progressively impeded by the needle-like mullite crystals similar to the composites with brittle matrix reinforced by fibers. It can be seen from Figs. 3(B), 4(A) that mullite forms large agglomerates on the expanded perlite grains.

4. Conclusions

The thermal stability and durability of expanded perlite were improved by synthesis of mullite in-situ on the porous structures of perlite grains. Mullite has been obtained from alumino-silicate gel. Gel is sprayed on the surface of grains to improve the thermal stability and durability of raw expanded perlite above the melting point. The mullite forms needle-like crystals reinforcing walls of expanded perlite grains. The results show that chemical modification may lead to strengthening of expanded perlite microstructure by reinforcing with mullite crystals. This strengthening probably is one way to obtain the expanded perlite based materials that may be applied at higher temperature than raw expanded perlite.

Acknowledgement

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