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THERMAL PROPERTIES OF EXPANDED PERLITE FILLERS MODIFIED WITH ALUMINO-SILICATE GEL

Expanded perlite is commonly used in cryogenic and high temperature applications. This lightweight filler has excellent thermal conductivity but its use as the insulation in high temperature applications is limited to about 900°C. In this paper, the investigation's results of the thermal properties of expanded perlite modified by spraying with alumino-silicate gel are presented. The sol-gel method allows to prepare very homogenous and reactive gel that enables synthesizing mullite phase at relatively low temperatures. The gel is also easy to be sprayed or used as coating of different materials e.g. lightweight fillers like expanded perlite. Such fillers modified with alumino-silicate gel after firing above temperature of forming mullite have better high temperature stability and durability.

The DTA analysis shows that in case of alumino-silicate gel and gel modified perlite at 980°C the mullite phase is formed (Fig. 1). The powder X-ray patterns indicates that in case of gel and modified perlite the crystalline mullite phase is formed only above 1100°C (Figs 2 and 3). The physical thermal properties were also obtained. The thermal conductivity of samples were realized by steady-state method (20 and 50°C) and by hot wire method up to 1000°C. Obtained results show that modified perlite have still good thermal conductivity (Fig. 5). Figures 8 and 9 show saved porous structure of perlite grains reinforced with mullite crystals. Consequently, the thermal resistance and durability in high temperatures of such composites are significantly improved, up to 1300°C.

Key words: high-temperature insulation, perlite, mullite, sol-gel

WŁAŚCIWOŚCI CIEPLNE PERLITU EKSPANDOWANEGO MODYFIKOWANEGO ŻELEM GLINOKRZEMIANOWYM

Perlit ekspandowany jest popularnym materiałem używanym do termoizolacji w niskich i wysokich temperaturach. Charakteryzuje się bardzo niskim współczynnikiem przewodzenia ciepła, jednak jego wykorzystanie w aplikacjach wysokotemperaturowych jest ograniczone do około 900°C.

Opisano wyniki badań właściwości cieplnych perlitu ekspandowanego modyfikowanego żelem glinokrzemianowym. Zastosowanie metody zol-żel pozwala otrzymać jednorodny i wysoko reaktywny żel, z którego możliwe jest syntezowanie mulitu w stosunkowo niskiej temperaturze. Żel jest dodatkowo łatwy do natryskiwania lub powlekania nim innych materiałów, w tym lekkich wypełniaczy, jakim jest np. perlit ekspandowany. Perlit modyfikowany żelem glinokrzemianowym po wypale w temperaturze wystarczającej do powstania mulitu cechuje się znacznie podwyższoną odpornością i stabilnością termiczną w wysokich temperaturach.

Wyniki analizy DTA wskazują, że w temperaturze około 980°C z otrzymanego żelu glinokrzemianowego powstaje mulit (rys. 1). Analiza rentgenograficzna potwierdza występowanie fazy mullitowej, jednak duże ilości krystalicznego mulitu powstają dopiero w temperaturze przekraczającej 1100°C (rys. rys. 2 i 3). W pracy również określono cechy fizyczne modyfikowanego perlitu. Badanie współczynnika przewodzenia ciepła przeprowadzono metodą ustalonego strumienia ciepła (w temperaturach niskich) oraz metodą gorącego drutu w temperaturach wysokich, do 1100°C. Perlit wzmocniony fazą mulitową (po wypaleniu) posiada niewiele gorsze właściwości izolacyjne od perlitu niemodyfikowanego (rys. 5). Obserwacje mikroskopowe potwierdzają zachowanie porowatej struktury kompozytu, wzmacnianej przez kryształy mulitu (rys. rys. 8 i 9). W konsekwencji uzyskano kompozyt o dobrej odporności termicznej i o bardzo dobrych właściwościach izolacyjnych, który może pracować w znacznie wyższych temperaturach niż perlit niemodyfikowany.

Słowa kluczowe: izolacja wysokotemperaturowa, perlit, mulit, metoda zol-żel

INTRODUCTION

Perlite is alumino-siliceous amorphous volcanic rock made of containing a small amount of combined water. When crude perlite ore particles are heated to plasticity (above 870°C), they expand to form large number of sealed glassy cells. The combined water vaporizes and the perlite expands four to twenty times its original volume. This expansion process creates the large number cells in the amorphous grains thus resulting in the excellent thermal conductivity of expanded perlite. Because of their unique multicellullar structure these lightweight perlite fillers can provide many advantages. Lightweight perlite fillers are effective bulk fillers, exhibit a uniform white color that has minimal effect on the color of the finished product. The particle shape promotes good bonding between the perlite and

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different matrixes e.g. cement paste, resins, etc. When used with other fire retardant materials, inert and inorganic perlite fillers can enhance fire resistance. Expanded perlite is also commonly used in cryogenic and high temperature applications, because of its very low thermal conductivity and relative durability and thermal stability, as well. 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. 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 and perlite grains melt fast.

One of the possibilities to improve the thermal stability of expanded perlite is chemical modification that leads to crystalline phases obtaining on the porous structures of perlite grains. The phase should be resistant to higher temperature, above 1000°C. The synthetic mullite is that material with such properties.

Mullite is one of the extensively studied crystalline alumino-silicate phase because of its excellent properties (high temperature durability and strength, low thermal expansion, creep resistance and good chemical stability). Usually, the 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 relative 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. Mullite can be obtained through the sol-gel method. The method allows to prepare very homogenous and reactive composition of reactants as gel which is possible to sinter at lower temperature as compared to the classical way. Second advantage is that by sol-gel method 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 gel obtained either by sol-gel or similar methods leading to the different precursor types [1-7]. The main difference between types of gel is their homogeneity: monophasic gels are homogenous at the atomic level and mullite formation occurs by exothermic reaction around 980°C [1, 2, 7]. In diphasic gels homogeneity is in the nanometer range but mullit formation occurs at higher temperatures because of diphasic gel consisting of discrete alumina and silica particles reacting independently above 1300°C for complete crystallization [1, 4, 5].

Hoffman et al. described several methods of making monophasic gels from tetraethyl silicate (TEOS) and aluminium nitrate solved in ethanol. The alumino-silicate gel obtained by polycondensation from nitrate and TEOS may be a suitable 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) [7].

The alumino-silicate sol may be excellent coating component, especially to obtain mullite on porous support e.g. expanded perlite. During heating, possible mullite formation from gel on grains allows improving the thermal stability and durability such fillers above the melting point of raw perlite. So, the significant increase in the range of expanded perlite working temperature above 1200°C is expected.

EXPERIMENTAL DETAILS AND TEST METHODS

In this study the expanded perlite class III from ZGM Zebiec S.A. (Poland) was used. Typical 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 1.

TABLE 1. **Physical properties of expanded perlite**
TABELA 1. **Właściwości fizyczne perlitu ekspandowanego**

class	III
bulk density, kg/m^3	125 ±15
density, g/cm^3	2.23÷2.40
melting point, °C	950÷1050
average particle size, mm	about 1.0
thermal conductivity*, W/mK	0.045÷0.059
water absorption, % V/V	30÷40
compression strength**, MPa	0.10÷0.40

* - in dry state at 20°C, ** - compacted condition

Composition and preparation of mullite gel is based on results presented in [7]. Alumino-silicate gel with stechiometric composition of the mullite was obtained by dissolving aluminium nitrate nanohydrate in absolute ethyl alcohol and by mixing it at room temperature with tetraethylsilicate (TEOS). Dilution mol ratio aluminium nitrate nanohydrate to alcohol was 0.05. The quantity of water used for hydrolysis of TEOS was from bonded water in aluminium nitrate nanohydrate. The bonded water was 27 mol of water per mol of TEOS. The gelling temperature was 60°C for 2 h. The solution for gelling was placed in a water bath. Obtained gel was dried for

48 h at 105°C under atmospheric pressure and then calcined at 600°C for 2 h. After calcinations samples of pure gel were heated up to 1300°C for 2 h.

Second series of samples were prepared by spraying alumino-silicate sol on the surface of expanded perlite grains by atomizer. Spraying process was led until the volume proportion of sol to perlite was 1:2 (that approximately means that the mullite phase to perlite ratio is about 1:4). Next treatments were similar to pure mullite gel, but the gelling process was realized in heating chamber because of large amount of prepared materials.

Samples of gel and modified expanded perlite heated at different temperatures were investigated. The thermal analysis DTA were carried out on powder samples using a PERKIN ELMER Differential Thermal Analyzer DTA 7 in nitrogen atmosphere. Powder XRD patterns were recorded using a Philips X-ray diffractometer X'pert system with monochromatic CuK_α radiation. All samples were first heated up to 600°C for 2 h and then heated to the temperatures from 900 to 1300°C for 2 h. The heating rate was 5°C/min. Microstructures of the samples heated at different temperatures were investigated by the JEOL scanning electron microscope equipped with EDX LINK system. Maximal used magnification was 3500x. Physical properties of modified expanded perlite e.g. thermal conductivity were obtained after heating to 1200°C for 6 h. In this case the raw expanded perlite preheated up to 900°C was used as reference. The thermal conductivity of fillers at 20 and 50°C was measured by steady-state method using Fox 200 (LaserComp, Inc.). Samples were dried in 105°C to constant mass before these measurements. Thermal conductivity up to 1000°C were obtained by hot wire method. Before the measurement samples of fillers were put into frame and compacted by hand shaking.

RESULTS

Figure 1 shows the DTA traces of the pure alumino-silicate gel, expanded perlite samples and samples of modified one. For the pure gel (C curve at Fig. 1) near 200°C and about 450°C the endotermic peaks are visible. Those endothermic effects are responsible for drastically change of the gel weight. Those peaks are due to the dehydratation process of absorbed water and dehydroxylation of aluminium nitrate hydroxide. According to the results from [7] the changes are about 55%. Mullite formation from gel is obvious on 972°C from the small but rather sharp peak. For sample of modified expanded perlite by mullite gel the exothermic peak at 972°C is also visible but it is smaller because of the effect of „dilution" in perlite matrix. In case of raw perlite only the temperature of glass transformation (843°C) was recorded.

Results of X-ray analysis show that formation of crystalline mullite phase from the gel is reduced in temperature below 1100°C (Fig. 2). Only transient phase of alumina was observed. For samples fired at temperature equal 1100°C for 2 h small peaks of mullite are visible, but in this case the rate of crystalline mullite formation is still reduced. Above this temperature the crystallization and process of growth of mullite crystals is spontaneous and the large amount of mullite is formed. The elevated background X-ray pattern from amorphous phase decays according to growth of firing temperature that indicates the total amount of glass decrease.

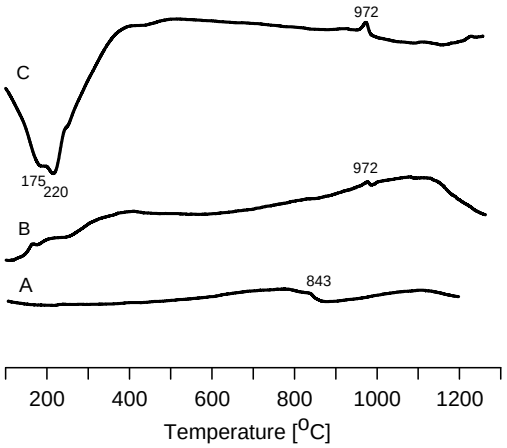


Fig. 1. DTA traces of samples: A - raw expanded perlite, B - perlite modified with mullite gel, C - mullite gel

Rys. 1. DTA próbek: A - perlitu, B - perlitu z dodatkiem żelu glinokrzemianowego, C - żelu glinokrzemianowego

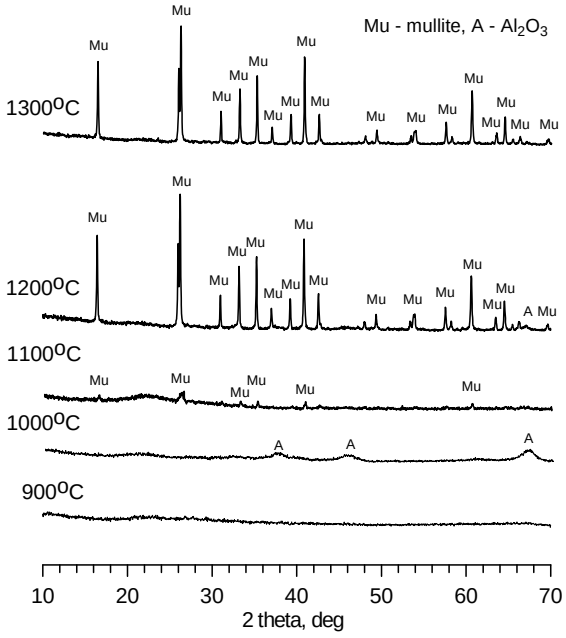


Fig. 2. XRD analysis of mullite gel heated at different temperatures

Rys. 2. Analiza rentgenograficzna żelu mullitowego ogrzewanego w różnych temperaturach

When modified perlite was heated up to temperature 1100°C the effect of crystalline mullite formation was

similar to raw perlite (also reduced) but in this case also disordered sodian anorthite forms. The crystallization of large amount of mullite is increased at temperature 1200°C and volume of glass phase is significantly reduced.

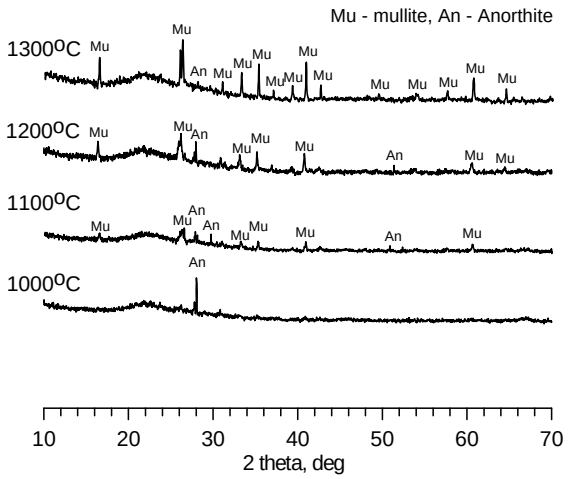


Fig. 3. XRD analysis of perlite modified with mullite gel fired at different temperatures

Rys. 3. Analiza rentgenograficzna perlitu modyfikowanego żelem mullitowym wypalanego w różnych temperaturach

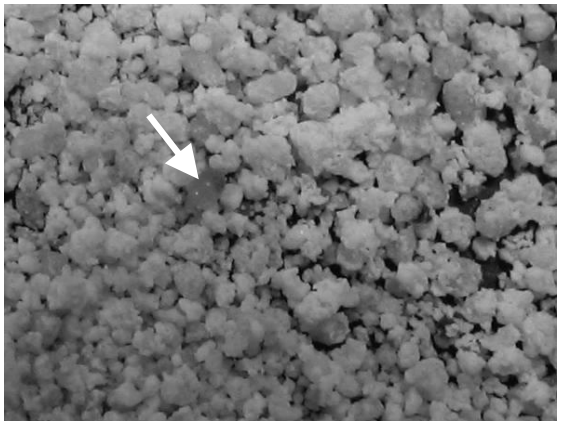


Fig. 4. General view of mullite modified perlite grains after heating at 1200°C for 6 h (arrow indicates molten grain of uncoated perlite)

Rys. 4. Ogólny widok perlitu modyfikowanego żelem mullitowym po wypaleniu w 1200°C przez 6 h (widoczne stopione ziarno perlitu bez modyfikacji)

According to results obtained from X-ray and DTA analysis the relatively large volume of sprayed perlite fillers (about 1÷2 dm^3) were prepared to physical tests. Preparation of such samples providing well homogeneity and uniform coating of each grain with alumino-silicate gel was another technological problem. One of the way of solving this problem was spraying gel on the very thin circulating perlite grains layer. Consequently, each particle of perlite was coated by spraying several times. Figure 4 shows the general view of the modified perlite samples after heating at 1200°C for 6 h. The arrow indicates that uncoated perlite grain has been melted in contrast to the coated grains preserved their original porous structure. The total number of them is small and their influence on the physical properties is rather insignificant.

Basic physical properties of perlite fillers are presented in Table 2. Bulk densities of raw expanded perlite fillers used in this work (class III) and perlite after firing at 900°C are similar, but in case of raw perlite is insignificant smaller (difference is about 20%). Likewise, the thermal conductivity of those samples obtained at 20°C in dry condition are quite similar, the differences are in error range of measurement method. Next heating of raw expanded perlite, above 1100°C, resulted in complete melting of grains. In case of modified perlite fired at 1200°C reinforced with mullite crystals the bulk density is about two times greater than unmodified one. The thermal conductivity of this sample obtained by steady-state method at 20°C in dry condition increases about 30% comparing to unmodified expanded perlite.

TABLE 2. **Bulk densities and thermal conductivities of perlite samples**

TABELA 2. **Gęstość pozorna i współczynnik przewodzenia ciepła perlitu**

Samples	Bulk density, kg/m^3	Thermal conductivity at 20°C, W/mK
Raw expanded perlite	118 ±20	0.051 ±0.003
Perlite fired at 900°C	150 ±21	0.053 ±0.002
Perlite fired at 1200°C	completely molten	
Modified perlite fired at 1200°C	311 ±17	0.070 ±0.002

The most important property of fillers assigned to the high temperature applications is their thermal conductivity. Mullite reinforced expanded perlite has low thermal conductivity, changes typically for insulation materials working at high temperatures. In comparison to the unmodified fillers thermal conductivity is greater about 20% but the exponential plot of this property is similar. The thermal conductivity of modified perlite obtained at 1000°C is about 0.23 W/mK. Dependence of thermal conductivity on temperature is shown at Figure 5.

Figure 6 shows the micrograph of modified expanded perlite after spraying the sol, gelling at 60°C and drying at 105°C for 48 h. In spite of significant loss water during drying the gel has rather good bond to grains. Arrows indicates the places covered with gel.

The maximal temperature of use the raw expanded perlite is about 900÷1000°C. With the softening, the process of the pores collapsed progress. At temperature equal 1200°C the completely melted grain (spherical shaped) of unmodified perlite is visible in contrary to the modified ones. Such modification allows to save the porous structure of grain and enables to use that fillers at higher temperature than raw expanded perlite (Fig. 8).

Mullite forms bead or needle-like crystals reinforcing walls of perlite grains. Bead-shape mullite crystals occasionally may be found in clusters with dimensions of single forms limited to 1 μm (Fig. 9).

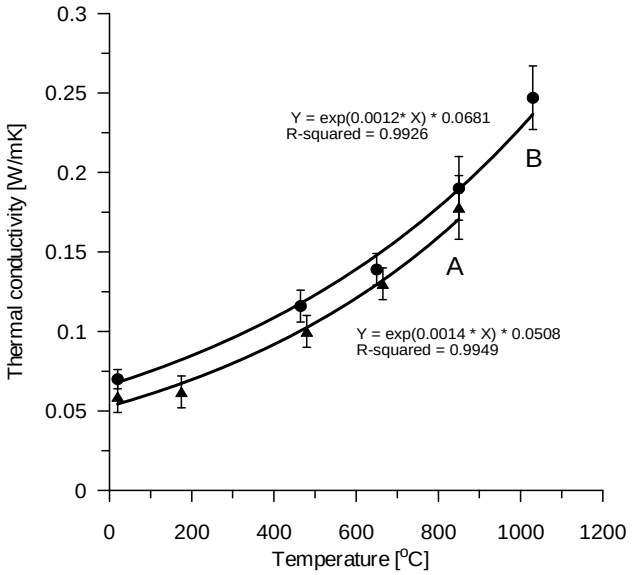


Fig. 5. Thermal conductivity of perlite at different temperatures: A - raw expanded perlite, B - mullite modified perlite

Rys. 5. Współczynnik przewodzenia ciepła perlitu w funkcji temperatury: A - perlit ekspandowany niemodyfikowany, B - perlit modyfikowany mullitem

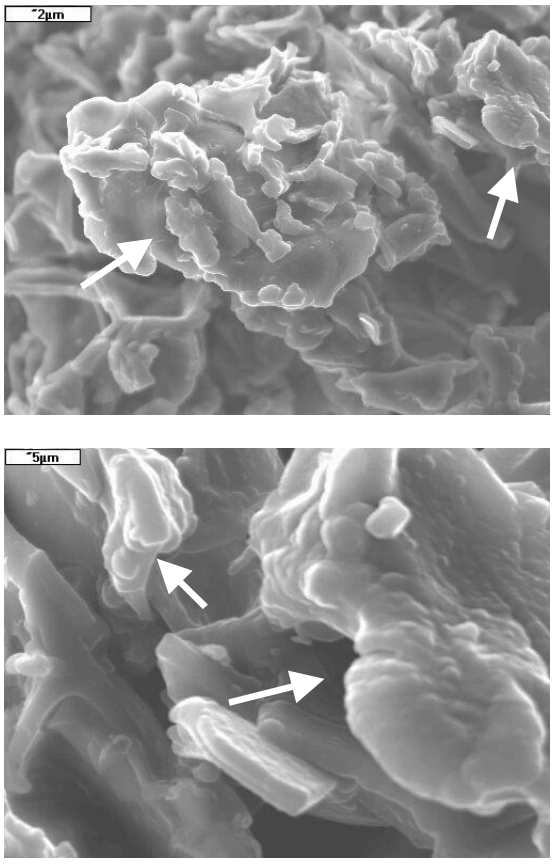


Fig. 6. SEM observations of perlite grains coated with alumino-silicate gel, dried at 105°C (A - 1000x, B - 3500x)

Rys. 6. Mikrografia SEM ziaren perlitu z naniesionym żelem glinokrzemianowym, suszonych w 105°C

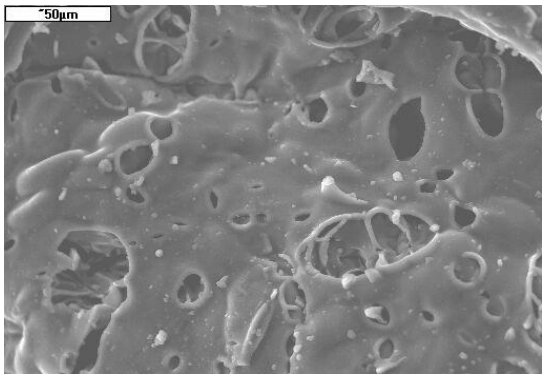


Fig. 7. SEM observations of raw perlite grain heated at 1000°C

Rys. 7. Mikrografia SEM ziarna perlitu wypalanego w temperaturze 1000°C

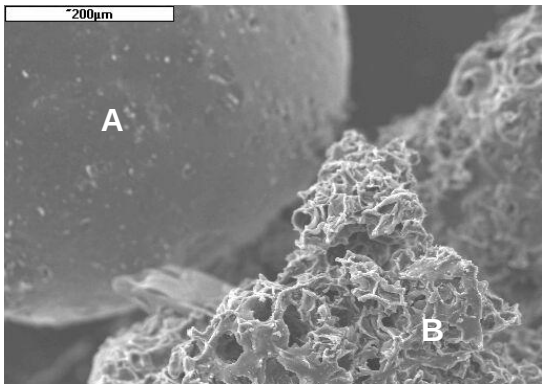
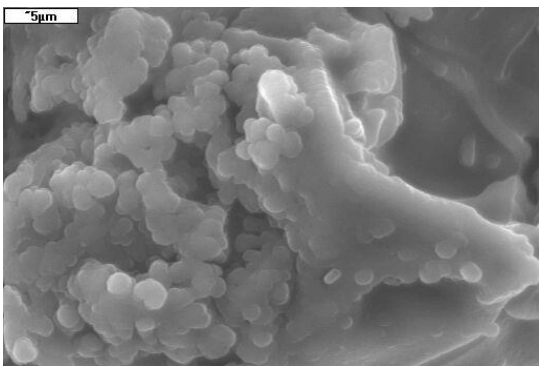


Fig. 8. Perlite grains heated at 1200°C: A - without modification (molten), B - modified by mullite gel (saved porous structure)

Rys. 8. Ziarna perlitu wypalane w temperaturze 1200°C: A - bez modyfikacji (stopione), B - modyfikowane żelem glinokrzemianowym (zachowana struktura porowata)



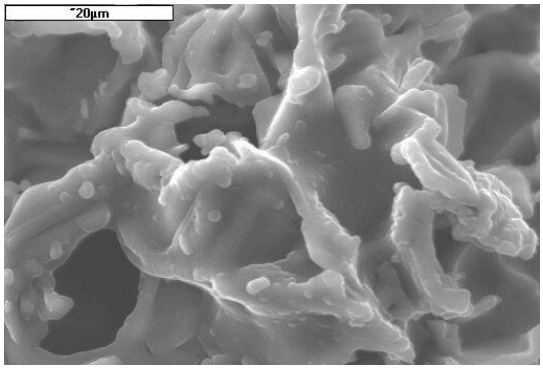


Fig. 9. Mullite crystals formed in perlite walls after firing at 1200°C

Rys. 9. Mullit przerastający ścianki ziarna perlitu wypalanego w temperaturze 1200°C

CONCLUSIONS

The alumino-silicate gel is an excellent coating component to obtain mullite phase, especially on porous support e.g. expanded perlite. Mullite forms from gel during heating already near 1000°C but only above 1100°C the large amount of mullite phase is formed. When the gel is sprayed on fillers or covers their surfaces grains the modification allows improving the thermal stability and durability of raw expanded perlite above the melting point. Consequently, obtained material may work at higher temperature up to 1300°C saving the porous structure and its insulation properties. Thus, the expanded perlite strengthened with mullite obtained through sol-gel method using spraying technique allows to obtain new insulations material. It may be potentially used in wide range of high temperature applications simply as fillers or as composite components.

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