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CATALITIC PROPERTIES OF PHYLLOSILICATES IN THE CONCENTRATED OXIDE SUSPENSION

FILOSILIKĀTU KATALĪTISKĀS ĪPAŠĪBAS KONCENTRĒTĀS OKSĪDU SISTĒMĀS

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Introduction

The investigated porous ceramic materials by direct foaming of ceramic concentrated suspensions are produced [1-3]. In concentrated suspensions pore formation depends on the rheological properties of the suspension such as viscosity, zeta potential and pH. Direct process of pore formation in ceramic suspension is concerned with a few problems. At first chemical process of gas elimination and conditions influences this process. The gas bubbles containing structure from the thermodynamic position is not stable and is exposed to change of structure, it means the gas bubbles have association tendency. At the same time the components of ceramic suspension flow out from the surface of gas bubbles. Both these kinetic processes: gas bubbles association tendency and suspensions flow are connected and can bring to decay of not solid pore structure [4]. The gas elimination reaction of metallic aluminium with water is the most important process by obtaining foamed ceramic materials by slip casting of suspensions. Besides, the viscosity of the suspension determines the possibility of forming spherical pores. A metastable pore structure within 1 hour during the pore formation and solidification process is developed. The chosen raw materials have defined zeta potentials and therefore they may influence the gas elimination rate. Aluminium reaction with water facilitates by catalytic minerals of the phyllosilicate class [5]. Kaolinite, illite and smectite containing clays in different relation with alumina are used. The influence of used clays on the pore formation process by reaction of aluminium with water is determined. Surface properties of clay minerals have influence on the rate of gas elimination reaction. At the same time pore formation and size depends on the viscosity of suspension and amount of aluminium powder.

Experimental

Zettlitz kaoline, Quaternary illitic clay of deposit Rauna and smectitic clay of deposit Saltiski for the preparation of water suspension together with alumina in ratio 1:1 for investigation of catalytic properties of phyllosilicates are used. Commercial alumina with plasma sprayed alumina is partially for the determination of grain size influence on the pore structure of sintered materials substitute. Amount of aluminium powder in these investigation is 0.4 wt. %. Devonian illitic clay of deposit Liepa, Quaternary clay of deposits Rauna and Livani by additive of 20 wt.% of alumina and amount of aluminium powder 0.1 wt.% are used for the investigation of possibility to obtain porous materials from Latvian clays.
Measure of zeta potential in very diluted suspensions – 0.1 wt.% (Zeta Potential Analyser, Brookhaven Instruments Corporation), pH of suspension, differential thermal analyses (company Paulik, Hungary), optical microscopy (Optical Stereomicroscope Leica 420), electron scanning microscopy (SEM FEI Quanta 200), X-ray difractometry (Ultima Plus, Japan), mercury porosimetry (Autopore IV), three point bending strength (Zwick: BDO-FB020TN) are applied.

Results and discussion

Determination of solid particle size and following zeta potential of investigated raw materials in much diluted suspension is given comparable properties. Stability of ceramic suspensions depends on particle size, shape and the surface properties of solid particles. Surface properties by the zeta potential induced between interacting particles can be characterised. The higher absolute zeta potential of raw materials is the term for the more stabile suspension. Kaolin in the composition takes effect not only on forming stable suspensions in association with alumina, but also catalyses the reaction of aluminium and water and stabilizes the pore structure after gas elimination. Kaoline provides bonding between alumina grains in the cast solidification process.

Table 1.

Grain size of solid particle, zeta potential and pH of diluted suspension

Component	Grain size, μ	Zeta potential, mV	pH
Kaoline	0.8	-25.4	10.8
Kaoline + alumina	1.22	-23.0	10.6
Smectite	0.34	-22.6	11.8
Smectite + alumina	0.66	-27.7	11.2
Smectitic clay	1.43	-9.72	11.6
Smectitic clay + alumina	1.35	-14.3	11.2
Illitic clay	1.5	-6.79	11.0
Illitic clay + alumina	1.2	-7.9	10.8
Alumina plasma sprayed	0.9	+48.4	10.8
Alumina, coarse grained	> 2	+14.7	11.9

The rate of pore formation reactions and pore structure of obtained materials changes in cases of other clay minerals such as illite and smectite in corresponding clays. 0.1 % suspension of kaoline, illitic and smectitic clay has different zeta potential (Tabl.1). Kaoline has the highest absolute zeta potential – 25.4 mV, smectitic clay 22.6 mV and illitic clay 6.79 mV. Addition of alumina in its decreases the value of zeta potential in case of kaoline by relation 1:1 of alumina and kaoline. Zeta potential increases in two other systems with illitic and smectitic clay and alumina. At the same time alumina decreases the pH of suspension. Corresponding suspensions have equally different pH. The lowest pH shows suspension with kaoline, but the highest – with smectite and smectitic clay. Kaoline and alumina containing suspension has the fastest pore formation process, but suspension with smectitic clay – the slowest process. The differential thermal analyses of air-dry solid non-fired materials have different mass loss in temperature range until 110^0C. This effect is concerned with amount of aluminium hydroxide formed accordingly reaction of metallic aluminium with water and hydrogen gas elimination. In kaoline containing composition mass loss is higher and it is concerned with more active influence of kaolinite on reaction in comparison with other clay minerals. The shape of pores in kaoline is round and the layer of aluminium hydroxide around gas bubbles is thicker. Pore are prolonged in materials produced from illitic or smectitic clays and they are associated (Fig.1.)

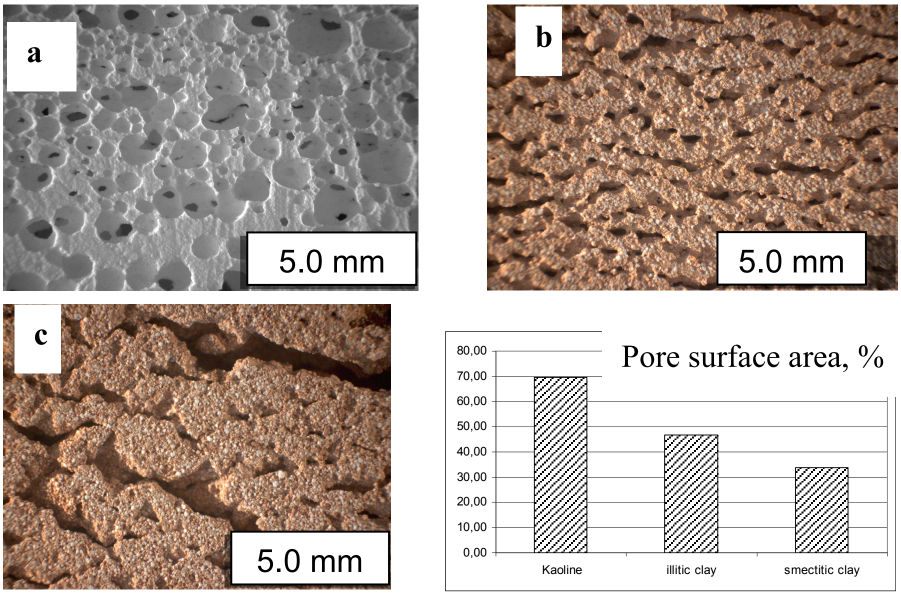

Fig.1. *Pore structure by optical microscopy of materials fired at temperature 950^{0}C: a- with kaoline; b – with illitic clay; c – with smectitic clay and pore surface area, %.*

The grain size of used raw materials is also significant. The part of alumina in composition with illitic clay is substitute with in plasma sprayed alumina. At first, the plasma sprayed alumina has highest absolute zeta potential 48.4 and by suspension preparing it is necessary to use more water because the viscosity of suspension is to high. By increasing of content of plasma sprayed alumina about 30%, the amount of necessary water by preparing of suspension increases two times in comparison with composition without plasma sprayed alumina. Pore size distribution in such materials is represented in Fig.2.

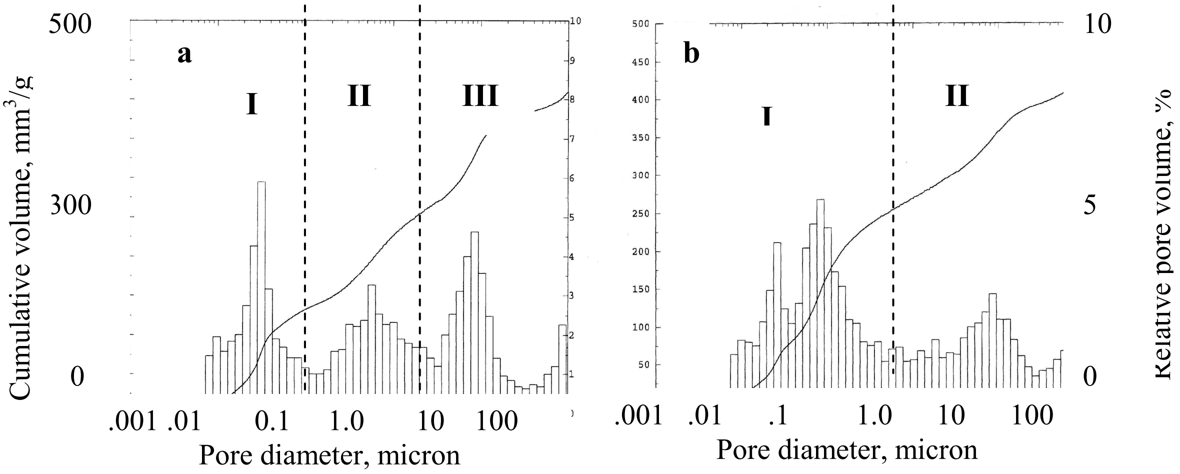

Fig.2. *Pore size distribution in fired samples: a – with commercial alumina powder; b –by partial substitution with plasma sprayed alumina.*

Pore size distribution in fired sample depends on the grain size of used alumina. Commercial alumina in system of illitic clay partially is substitute with plasma sprayed alumina. There are three pore size areas by use of commercial alumina (Fig.2a), but in sample with fine alumina two areas only (Fig.2b). In gas elimination process by solidification of suspension the greater pores are developed. By the sintering of green body the smaller pores are developed and pore size in this process depends on the grain size of raw materials and sintering conditions.

The pore formation process depends also on temperature. The rate of reaction by using of distilate water at temperature 40^0C is two times faster, but final volume of sample is similar (Fig.3).

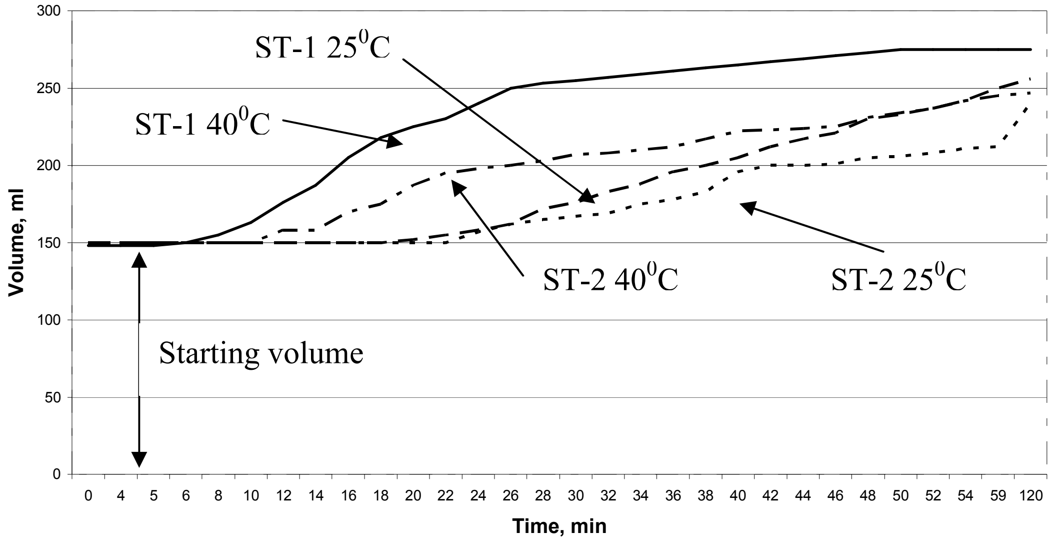

Fig.3. *Dependence of pore formation velocity on temperature*

Illite containing clays from deposits Liepa, Rauna and Livani for obtaining of porous thermal insulating ceramic materials are used. The ratio of clay and alumina is 4:1 and water content in suspension is in limits 28–35%. The pore structure of materials fired at temperature 1000^0C depends on used clays. Porous ceramic from lime less clay of deposit Liepa has small rounded pores (Fig.4a) with large surface 48%. Materials from other two lime rich clays have also different pore structure. There are small associate pores by use of clay deposit Rauna (Fig.4b) with pore surface 28% and max pore diameter 1.14 mm. Material contains large prolonged associate pores by use of clay deposit Livani (Fig.4c) with max pore diameter 2.89 mm and little pore surface – 27%. Thereby, the pore structure of materials obtained by chemical reaction of aluminium powder with water in alumina and clays systems depends also on admixture in natural clays. Carbonate content in clays and its grain size in pore formation process are significant. The carbonate grain size in clay deposit Livani is large – 0.8 mm and more.

Structure of acquired materials is determinate by SEM analyses (Fig. 5). Structure is composed of small grain matrix and stellar large crystals. Point analyses show different composition of these two structure parts. Large crystals comprise alumina, but matrix is composed of silicate and alumosilicate.

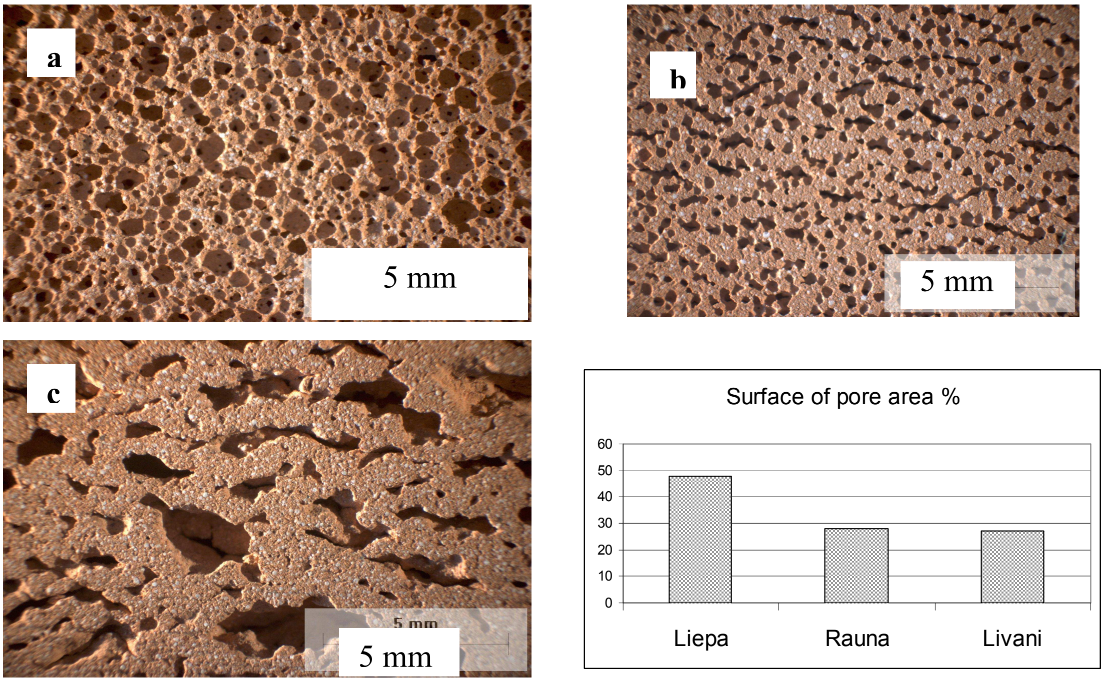

Fig.4. *Pore structure by optical microscopy of materials from different Latvian clays fired at temperature 1000^{0}C by additive of commercial alumina and aluminium powder: a – clay of deposit Liepa; b – clay of deposit Rauna; c- clay of deposit Livani.*

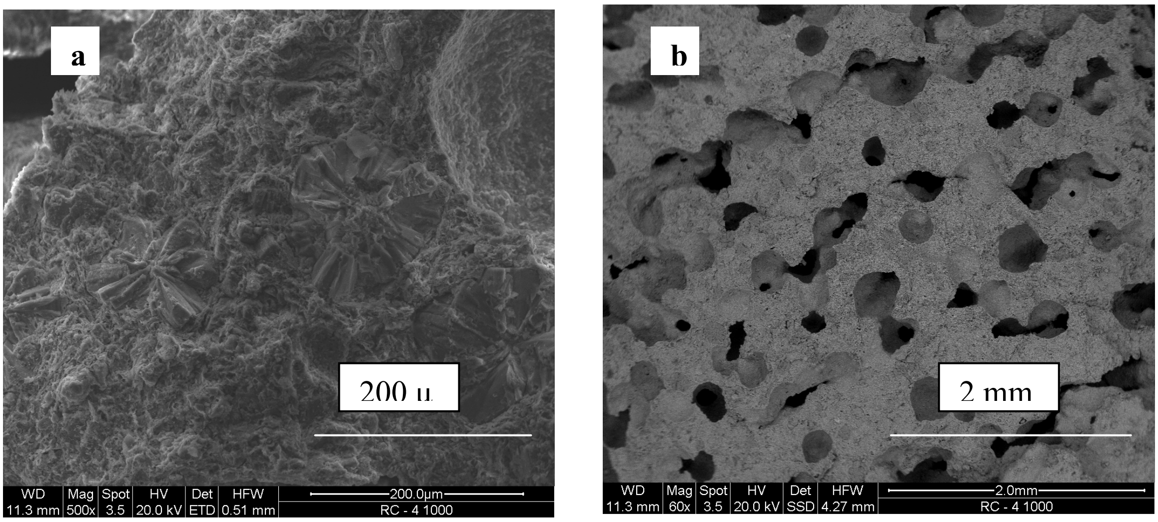

Fig.5. *SEM analyses of material from Quaternary clay deposit Rauna by additive of 20% commercial alumina sintered at temperature 1000^{0}C.*

SEM micrograph (Fig.5b) shows two different pore size areas: large pore are developed by gas elimination, but small pore are formed by sintering in result of decomposition of carbonates, which contain clay.

Conclusion

Structure of porous ceramic materials produced by direct pore formation in result of chemical reaction of aluminium with water in suspension depends on the kind of clay minerals. Structure is achievable more homogeneous with round pores by kaolinite. Different clay minerals by additive of alumina obtain different yield stress, which establish gas durability. Smectite minerals have the best yield stress [6] and therefore porous structure of materials from smectitic clay contain large prolonged pore parallel to clay mineral plates.

Anyone producing of porous ceramic by pore formation during solidification of suspension from different raw materials demand to establish the ratio of components, amount of aluminium powder and limit of sintering temperature. Porous building ceramic from clay of deposit Liepa with additive of alumina fired at temperature 1000^0C has the bulk density 0.95 g/cm^3, compressive strength 10.2 N/mm^2.

This method is preferable by environmental protection because restrict emission of carbon oxide, which eliminate by using of combustible additive for pore formation.

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V.Švinka, R.Švinka, A.Actiņš, A.Butlers, I.Zaķe, I.Sidraba. Filosilikātu katalītiskās īpašības koncentrētās oksīdu suspensijās. *Iegūta poraina keramika no mālu un alumīnija oksīda koncentrētas suspensijas (mitruma saturs 28-35%) tiešā poru veidošanas ceļā metāliskam alumīnija pulverim reaģējot ar ūdeni. Mālu minerāli, pateicoties daļiņu virsmas lādiņam, ko raksturo zeta potenciāls, veido stabilas suspensijas. Izdaloties ūdeņradim ķīmiskās reakcijas rezultātā, mālu minerāli saista izveidojušos poru struktūru, kura saglabājas pēc izžāvēšanas un apdedzināšanas. Kaolinīta, illīta un smektīta gadījumā iegūta atšķirīga šo materiālu struktūra, jo šiem minerāliem ir atšķirīgi virsmas lādiņi. Iegūto materiālu poru struktūra ir atkarīga arī no dabīgo mālu mineraloģiskā sastāva. Dažādi piemaisījumi mālos (karbonāti, smiltis) ietekmē ūdeņraža izdalīšanās procesu un suspensijas viskozitāti. Vislabākās katalītiskās īpašības ir kaolinītam, kuram ir arī vislielākais absolūtais zeta potenciāls.*

V.Svinka, R.Svinka, A.Actins, A.Butlers, I.Zake, I.Sidraba. Catalitic properties of phyllosilicate in the concentrated oxide suspension. *Porous ceramic from clay and alumina concentrated suspensions (water content 28-35%) in the direct process of pore formation by reaction of metallic aluminium powder with water are obtained. Clay minerals form stable suspension thanks surface charge of particle surface, which is characterize by zeta potential. Clay minerals associate the developed pore structure after hydrogen elimination. After drying and sintering structure remains. Different materials structure is obtain by use kaolinite, illite or smectite because particles of these minerals have different zeta potential. Pore structure of obtained materials*

depends on the mineralogical composition of clay. Various admixtures (carbonate, sand) influences hydrogen elimination process and viscosity of suspension. The best catalytic properties characterises kaolinite with the highest zeta potential.

В.Швинка, Р.Швинка, А.Ацтиньш, А.Бутлерс, И.Заке, И.Сидраба. Каталитические свойства филосиликатов в концентрированных суспенсиях оксидов. *Получена пористая керамика из концентрированных суспенсий глины и оксида алюминия (содержание воды 28-35%) в прямом процессе порообразования при взаимодействии порошка металлического алюминия с водой. Глинистые минералы образуют стабильные суспенсии благодаря поверхностному заряду глинистых частиц, который характеризуется зета потенциалом. При выделении водорода в результате химической реакции глинистые минералы связывают образовавшуюся пористую структуру, которая сохраняется после сушки и обжига. В случае каолинита, иллита и смектита получены материалы с различной пористой структурой. Пористая структура полученных материалов зависит также от примесей (карбонаты, песок) в глинею Наилучшие каталитические свойства имеет каолинитю*