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MATERIALS
ENGINEERING

Thermal properties of calcium-aluminate based materials

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Abstract. Good cementing properties, fast setting and strong thermal performance make calcium aluminate a valuable raw material for use in the production of different types of new refractory materials, e.g., heat conductive/storage materials. The main aim of the study was to determine thermal properties of novel Nb-slag based materials with different fillers, and to clarify the optimal composition and technology. The preparation process of the studied materials was the following: mixing of components, casting into moulds and hardening of materials. To estimate potential application areas, the following thermal properties of CA-based materials were investigated: thermal behaviour, the coefficient of thermal expansion (CTE) and conductivity. For thermal analysis, small cylindrical specimens were cut out from produced materials, and plates sized 25 × 300 × 300 mm were used for conductivity studies. Different compositions of CA-based materials, the hardening process, and the influence of mechanical activation on the strength were analysed. The best thermal properties similar to the analogous reference materials were obtained by quartz sand and granite sand as filler materials. The thermal conductivity of the novel CA-based material is 1.5 times higher and the bending strength is about 3 times higher compared to commercial thermoplates.

Key words: materials science, calcium aluminate, refractories, thermal properties, disintegrator milling.

1. INTRODUCTION

Slags from metallurgy are primarily composed of silica with concentrations of constituents such as alumina, magnesia and other components which have the potential value for application. Moreover, technologies have emerged to recycle and reuse reprocessed slag in different building materials [1]. Niobium slag resulting from the aluminothermic process at Sillamäe metallurgical plant NPM Silmet AS, Estonia, contains mainly calcium-consisting aluminate (CA) and due to incomplete calcium-aluminothermic reduction some amount of the initial materials – mainly niobium oxide Nb_2O_5 (3–7%) and pure Nb up to 1% (depends on the batches) [2].

The technology of the separation of pure Nb, based on the disintegrator treatment of CA consists of the following steps: precrushing of big pieces, disintegrator milling and separation of the milled product to fine (<0.3 mm) and coarse fractions (>0.3 mm), followed by separative milling of the coarse fraction to separate pure Nb [2,3] (Fig.1).

Preliminary experiments were conducted to clarify the potential application area of ground CA as the main component of heat accumulation and heat-transfer materials. Similar alumina-silica based ceramic materials are used for accumulation (slow heat release) of heat in fireplace stoves and fireplaces [4]. Due to analogous compositions of niobium slag, it may be a potential material for refractory products.

It was demonstrated by our previous experiments [2,3] that CA-based materials have a high potential of application as the main component of refractory materials, especially in the form of heat transfer elements of stoves, fireplaces, etc. Our preliminary experiments showed that

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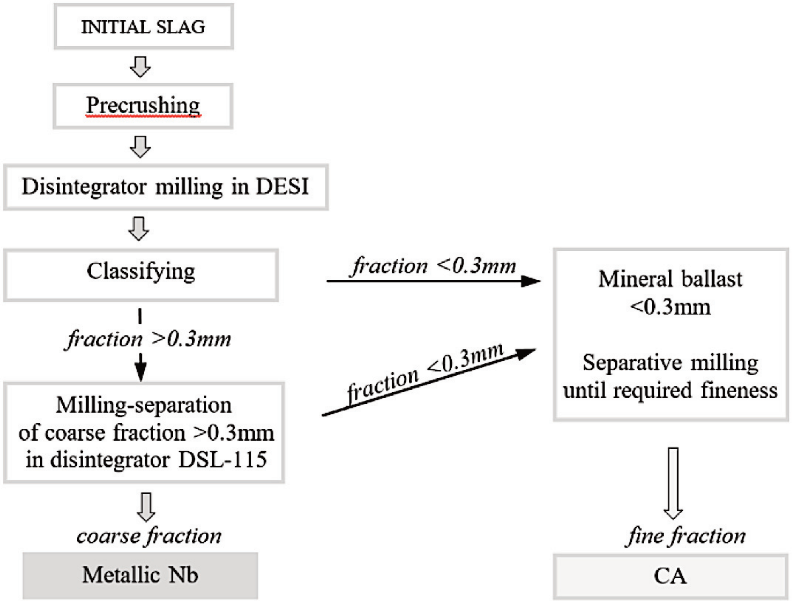

Fig. 1. Proposed scheme of milling of niobium slag and separation of metallic Nb.

CA-based materials have high mechanical properties and similar heat conductive properties (about 0.34 $W \cdot m^{-1}K^{-1}$ against 0.42 $W \cdot m^{-1}K^{-1}$ of commercial heat-transfer materials) [2].

2. EXPERIMENTAL

2.1. Initial materials

Niobium slag was subjected to impact milling in disintegrator DESI and a coarse ground product was subjected to separative milling in disintegrator DSL-115. The ground slag contained mainly calcium aluminates (CA) – fineness was <125 µm. Fresh and old CA (aged more than ten days) were used in our experiments. In order to have fresh mechanically activated CA, it was milled immediately before using (during the next 5 h).

The following CA-based mixtures were studied (Table 1):

– Pure CA (fresh and old);

– CA with additions of granite sand (GS), CEN Standard quartz sand (QS) and polarstone sand (PS). The fillers were obtained by disintegrator milling of granite gravel, standard QS and PS waste. The same chemical composition was shown after milling;

– CA with the addition of fly ash cenospheres of alumina silica (AC) (lightweight, inert, hollow sphere filled with inert air or gas – a typical byproduct of coal combustion at thermal power plants [Biotecha Latvia Ltd, Riga, Latvia], mainly consisting of SiO_2 and

Table 1. Composition of studied materials

Composition [wt%; conditions; fraction size]		Post-treatment
CA[a]	Filler	
[100; fresh and old]	–	Hardening at 20 °C / up to 54 days
[66, 50 and 34; fresh]	granite sand (GS) [34, 50 and 66; milled; <125 µm]	
[66, 50 and 34; fresh]	quartz sand (QS) [33, 50 and 66; milled; <125 µm]	
[66, 50 and 34; fresh]	polarstone (PS) [33, 50 and 66; milled; <125 µm]	
[75 (50 vol%); fresh]	ash cenospheres (AC) [25 (50 vol%); classified; <300 µm]	
–	portland cement [25] + standard sand [75; 2÷0 mm]	Hardening at 20 °C / 7 days

[a] fraction size <125 µm

Al_2O_3). The chemical composition of AC was studied previously in [5] and it has been approved as an efficient heat-resistant inert filler for ceramics [6] and lightweight concrete [7]. Figure 2 shows the SEM images of the filler materials used.

As a reference material, an analogous Cebud thermoplate CPA-K [8] and concrete (cement + standard sand) of hardened materials were prepared and tested for comparison.

For the study of mechanical properties, bending strength specimens sized 40 × 40 × 160 mm were prepared. For the thermal analysis, cylindrical specimens with ø7 mm were cut out from mechanical test pieces. For the study of thermal conductivity, the plates sized 300 × 300 × 25 mm were produced. The prepared mixtures of CA with fillers and addition of water (about 33%) were cast into moulds and densified by vibration. The procedure was as follows: preparation of components → mixing of mixtures → hardening at air 24 h → drying at 100 °C for 24 h. The density of CA-based materials with the fillers GS and QS was about 2.0 g/cm^3, with PS it was about 1.5 g/cm^3 and with AC about 1.3 g/cm^3.

2.2. Characterization of mechanical properties

Prismatic specimens were tested at three-point bending on a universal testing machine according to standard EVS-EN 196-1:2016 [9], determining the bend strength of the specimens. Then, the universal testing machine P-5 (50 kN) was employed, the distance between the points of support was 100 mm.

2.3. Characterization of thermal properties

The thermomechanical characteristics of the samples of heat-conductive materials were determined on Setaram Setsys 1750 CS Evolution dilatometer. Cylindrical specimens with a diameter of 7 mm and height of 15–16 mm

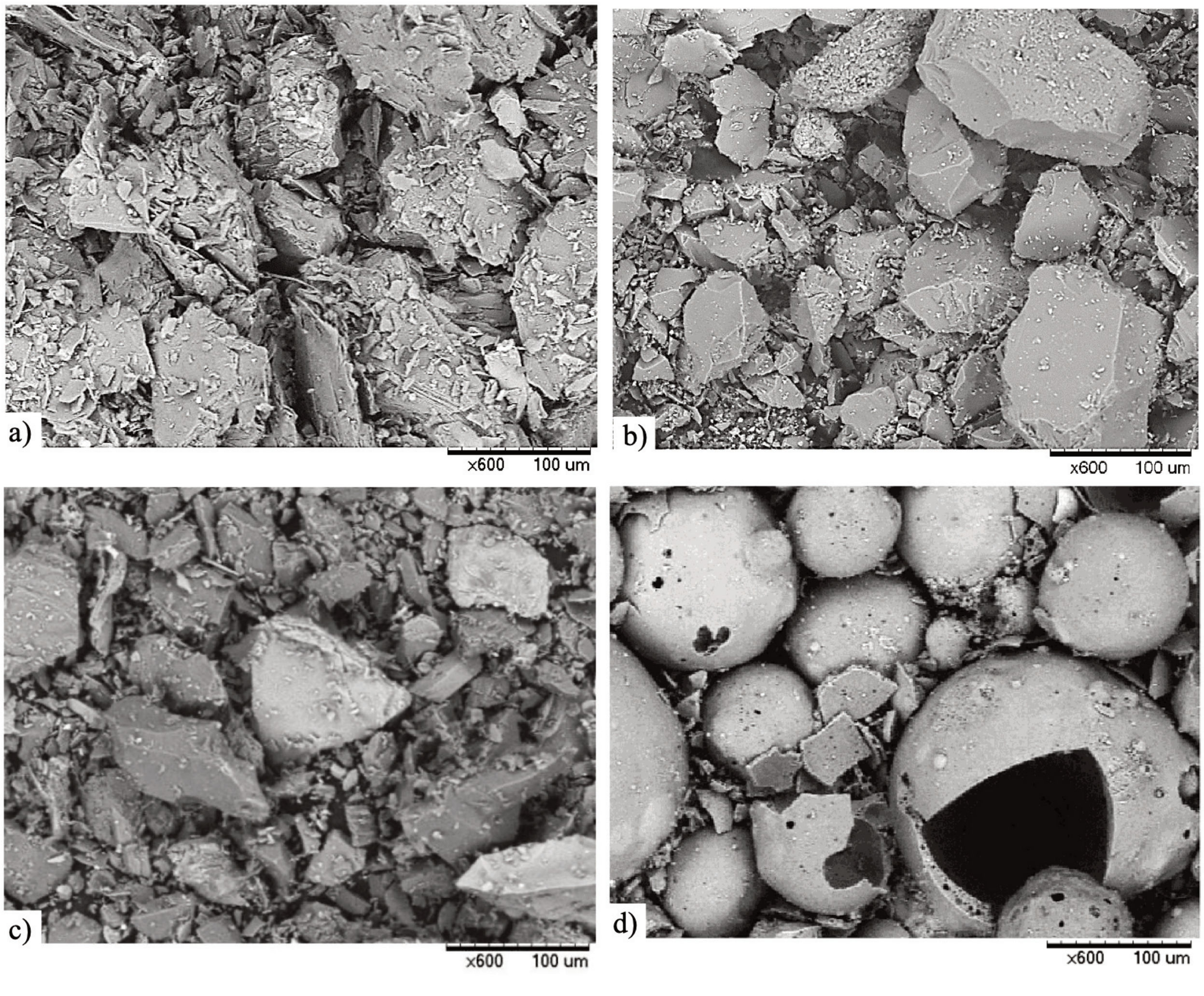

Fig. 2. Filler materials: a – granite sand, b – quartz sand, c – polarstone sand, d – fly ash cenospheres.

in a corundum sample holder were heated up to 1000 °C at a heating rate of 5 °C per minute and cooled down at the same rate in an Ar atmosphere. The diagrams DTDA–T and Δl%–T were plotted.

Thermal conductivity was measured according to the standard EVS-EN 12667:2001 [10] using LaserComp FOX-304 Heat Flow Meter. In a heat flow metre, a specimen is positioned between two temperature-controlled plates. These plates establish a user-defined temperature difference (ΔT) across the sample. The resulting heat flux (Q/A) from steady-state heat transfer through the specimen is measured by two proprietary thin film heat flux transducers covering a large area of upper and lower sample surfaces.

The average heat flux was used to calculate the thermal conductivity (λ) and thermal resistance (R) according to Fourier's law. For thermal plates the optimal composition of CA:Filler (50:50) was selected considering technological as well as strength properties of the studied materials.

3. RESULTS AND DISCUSSION

3.1 Thermal Analysis

The DTDA-diagram shows old CA (Fig. 3), changes up to 100 °C are related to the emission of physically bound water. Changes in the range from 200 up to 400 °C are probably related to thermo-oxidation of the matter contained in Nb-slag as remains of the reduction process, and the change at 970 °C is probably caused by the formation of liquid phase.

The contraction-expansion behaviour of the samples of the studied materials by heating up to 1000 °C at the heating rate of 5 °C/min is presented in Fig. 4.

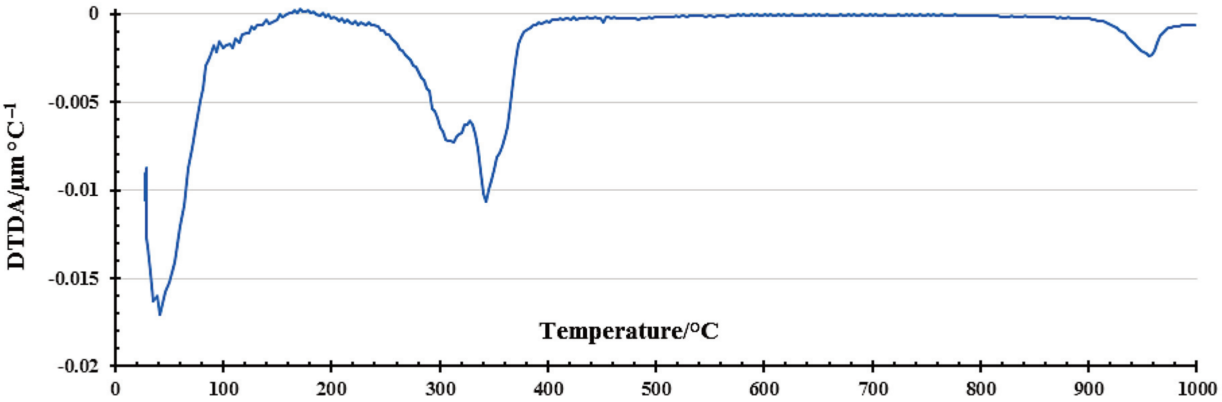

Fig. 3. Heating curve (DTDA-diagram) of CA.

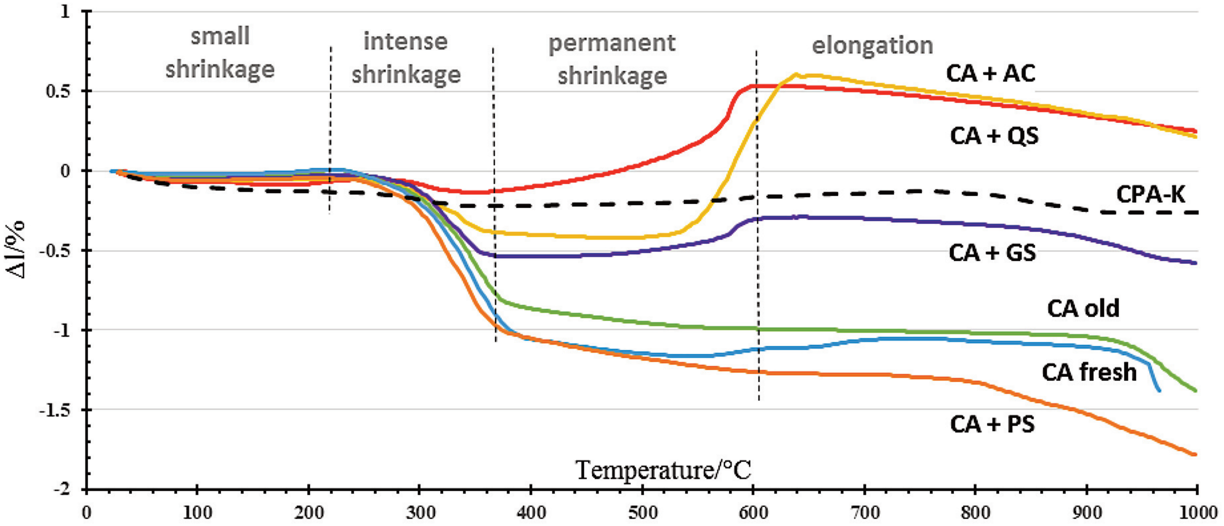

Fig. 4. Shrinkage-expansion curves of CA-based materials.

As the graph shows, up to 180–200 °C low shrinkage (up to –0.1%) can occur. Then, starting from 260 °C, deep shrinkage of bodies up to 340–380 °C follows, which is the most significant for pure CA (fresh –1.03%, old –0.85%). Starting from 400 °C, stabilization takes place.

The behaviour of composites (except CA+QS) notably differs from the behaviour of pure CA. Shrinkage is less dependent on the temperature; shrinkage of CA+GS occurs up to 360 °C (up to –0.5%) and then it stabilizes.

The composition containing quartz sand (CA+QS) behaves in a slightly different way: shrinkage is low (–0.2%) up to temperature 480 °C and then an expansion follows up to 580 °C (up to +0.5%), after which it is stabilized. The thermal behaviour of CA+AC body is characterized in an analogous way: starting from 550 °C notable elongation occurs (+0.6%) and then stabilization from 600 °C up to 1000 °C.

3.2. Behaviour of CA in the hardening process

Our preliminary experiments demonstrated that in the hardening process a notable increase occurs in the temperature of hardenable specimens, first, with CA that was just milled.

For this propose, a special study with pure CA with the particle size <125 µm was carried out – old (milled earlier and aged) and fresh (just milled) CA were used. Hardening time was 16 h.

Figure 5a illustrates that the temperature at the hardening of specimens made from fresh materials increases up to 100 °C whereas with specimens of old CA, the temperature is not significantly increased. It reveals mechanical activation in the high velocity impact milling process. The mechanical activation of materials due to the disintegrator milling was demonstrated in our earlier work [11,12]. It causes a notable increase in the mechanical properties as well as in the bending strength; materials made from fresh milled CA demonstrate up to 2 times higher strength (Fig. 5b). It takes about two days to achieve the necessary minimal strength level, e.g., 4 MPa with old CA, while with fresh CA only 10 h are required. One of the ways to suppress this phenomenon is to use ballast materials, i.e., inert fillers. With fillers, noticeable heating of cast mixture was not observed and was similar to old CA.

3.3. Optimization of composition

To suppress the high activity of fresh CA, inert filler materials such as granite sand, polarstone sand and CEN Standard sand – quartz sand were used. The studied mixtures consisted of filler materials from 33% to 66%. The materials were made by the same technology: mechanical mixing of components, casting of mixtures into moulds, densification by vibration and hardening at room temperature for 24 h, followed by drying at 100 °C for 24 h. Three prismatic specimens were subjected to the bend load at the three-point test. The results of the bending test are given in Fig. 6.

At all studied compositions, increase in the filler content causes a decrease in the bending strength. In the case of fillers GS and QS with the content over 50%, a deep decrease in the strength can be seen (Fig. 6a and 6b). Up to that point, with the increase of the filler content, flexural strength decreases proportionally. At the same time, the strength of materials increases with the use of fresh filler materials that were immediately disintegrator milled, being 30% higher (GS and QS) except for PS (Fig. 5b).

Notable influence of hardening time on the strength was observed. The samples gained half of their strength in the first 14 days of hardening. Over time (42 and 56 days), the rate of increase in the flexural strength slowed down.

Adding polarstone as a filler has a strong effect on the strength. The dependence of the decrease in strength on the amount of filler has a pronounced linear character (Fig. 7).

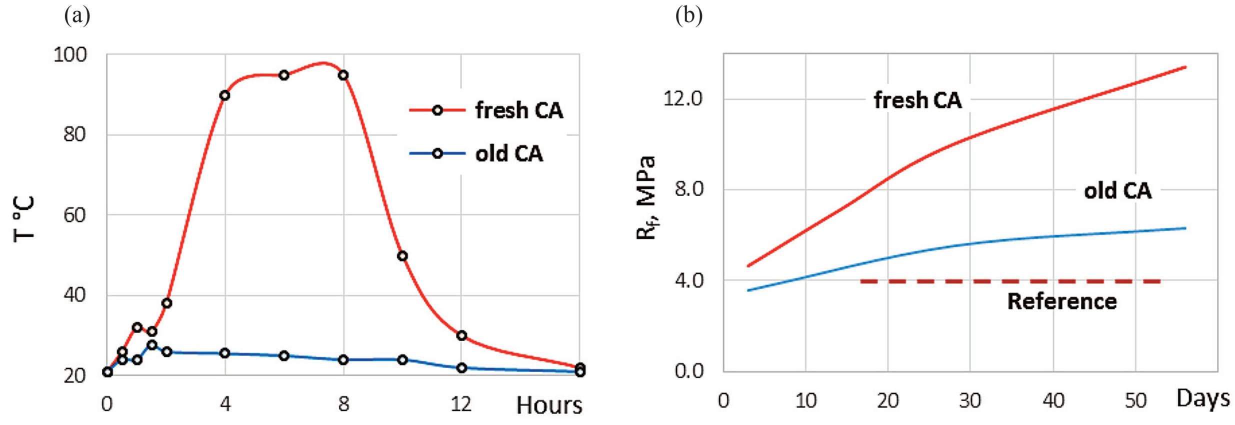

Fig. 5. Influence of mechanical activation on the behaviour and properties of CA: (a) self-heating at the hardening process; (b) increase in flexural strength Rf during hardening.

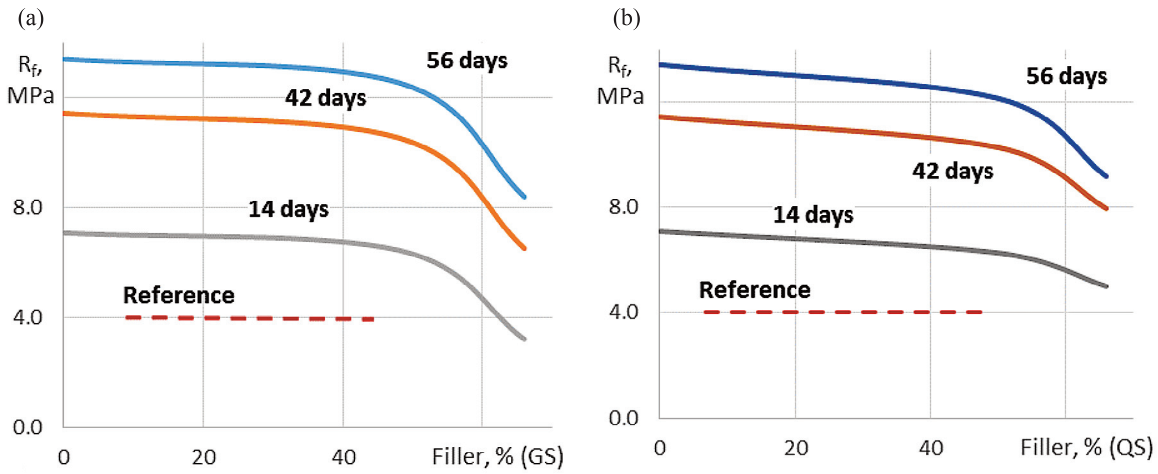

Fig. 6. Dependence of flexural strength on the amount of filler in the mixture: a – granite sand, b – quartz sand.

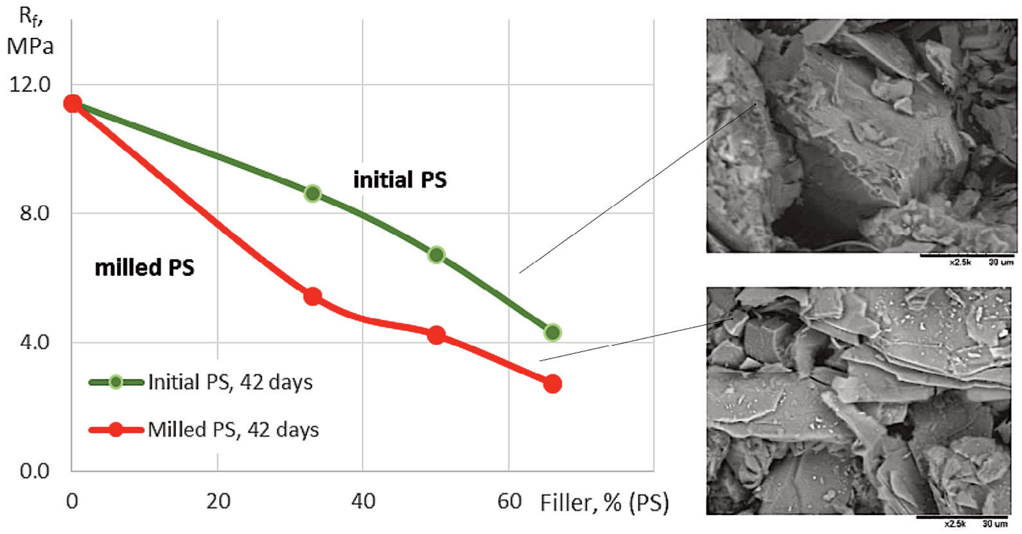

Fig. 7. Dependence of flexural strength on the amount of polarstone in the mixture.

Better strength was observed when using a non-milled PS filler, which can be explained by a change in the morphology of PS particles as a result of milling. Due to the lamellar structure of PS particles, we obtained flake powder (Fig. 7).

3.4. Thermal conductivity of CA-based materials

The results of the thermal conductivity study are provided in Fig. 8 and Table 2. The figure indicates that the CA+QS material has better conductivity, being about 55% higher than the reference material CPA-K, followed by the CA+GS material (about 29% higher) and CA+PS (10% higher).

Taking into account the mechanical and thermal properties as well as the economic aspect, CA-based materials with a quartz sand filler are more prospective.

4. CONCLUSIONS

1. Novel calcium-aluminate (CA) – Nb-slag based materials were obtained and prospects for application as heat conductive materials have been demonstrated.
2. Based on the study of mechanical and thermal properties of CA-based materials of different compositions and conditions, we can draw the following conclusions:

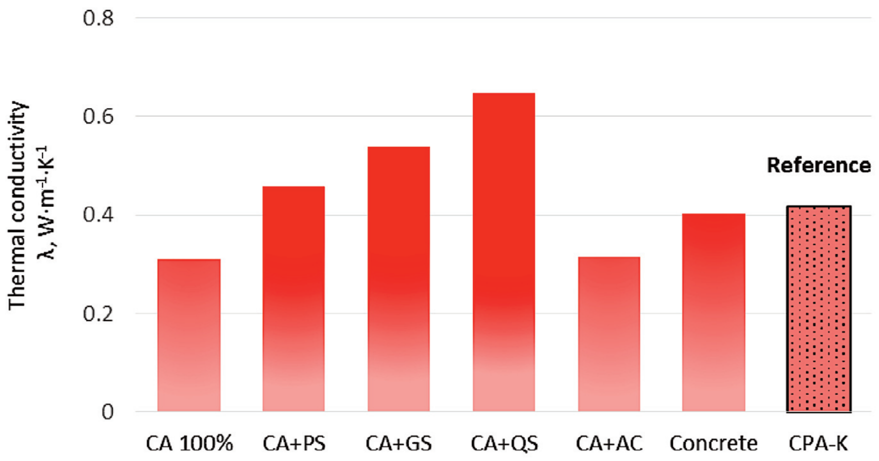

Fig. 8. Thermal conductivity of CA-based materials.

Table 2. Thermal conductivity and density of different compositions compared to the reference material

CA <125µm	Density g/cm^3	Thermal conductivity λ W/(m·K)	λ compared to CPA-K
CA $_{\text{old}}$	1.9	0.34	25% lower
CA $_{\text{fresh milled}}$	2.0	0.31	25% lower
CA+PS*	1.4÷1.6	0.46	10% higher
CA+GS*	1.6÷1.7	0.54	29% higher
CA+AC*	1.2÷1.3	0.31	25% lower
CA+QS*	1.8÷2.0	0.65	55% higher
Concrete	2.0	0.40	about the same
CPA-K	2.0÷2.1	0.42	Reference

* Filler content 50%

– Mechanical milling of CA is accompanied by activation of the ground material due to the fresh surfaces formed. As a result, this hardening process is more intensive, producing higher strength (up to 2 times). At the same time, an increase in the temperature in the hardening process results in the decrease in density and distortion of the material. It can be suppressed by optimizing the composition by the use of fillers.

– Optimal CA : filler proportion in fresh CA-based materials is 40–50% : 60–50% . Increase in strength by using a filler is about 10–15% (for GS) and 25–30% for QS and PS.

– With regard to thermal properties, the composition of CA with granite and quartz sand fillers is favourable. The thermal conductivity properties are 30–50% higher and strength properties about 3 times higher than these of the reference thermoplates.

ACKNOWLEDGEMENTS

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Kaltsiumaluminaadi baasil materjalide soojusomadused

Priit Kulu, Dmitri Goljandin, Rainer Traksmaa, Tiit Kaljuvee ja Andre Gregor

Kaltsiumaluminaadi (CA) teeb väärtuslikuks toormeks mitmesuguse kuumuskindla ehituskeraamika valmistamisel selle head tsementeerivad omadused, kiire kivistumine ja hea termopüsivus.

Käesoleva töö eesmärgiks on olnud uurida põhikomponendina kaltsiumaluminaati sisaldava nioobiumräbu (Nb-räbu) baasil mitmesuguse täiteainega materjalide soojusomadusi, määratlemaks nende optimaalset koostist ja tehnoloogiat.

Nb-räbu ümbertöötlus sisaldas järgmisi etappe: peenendamine, eeljahvatus, separatsioonjahvatus nioobiumi eraldamiseks ja CA peenfraktsiooni saamiseks. Materjalide valmistustehnoloogia oli järgmine: komponentide segamine, valamine vormidesse koos vibrotihendamisega ja kuivatamine koos kivistumisega. Hindamaks uudse materjali potentsiaalseid kasutusvõimalusi, uuriti järgmisi soojusomadusi: termopüsivus, soojuspaisumine ja soojusjuhtivus. Selleks valmistati termoanalüüsi tarvis silindrilised proovikehad läbimõõduga 7 mm ja soojusjuhtivuse määramiseks plaadid mõõtmetega 25 × 300 × 300 mm. Uuriti CA-baasil materjalide erinevaid koostisi, täiteaineid, mehaanilise aktivatsiooni ja kivistumisprotsessi mõju materjalide tugevusele ja soojusjuhtivusele. Parimate mehaaniliste ja soojusomadustega materjal, lähedane kaubanduslikele plaatidele, saadi peene CA ja täiteainena kvarts- ja graniitliiva kasutamisel. Uudsete soojusplaatide mehaaniline tugevus oli umbes kolm korda kõrgem ja soojusjuhtivus umbes 1,5 korda parem, võrreldes kaubandusliku CPK termoplaadiga.