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Influence of microsilica additive on thermal conductivity of refractory fireclay-based castable

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The effect of microsilica on the thermal conductivity of refractory fireclay-based castable was investigated. The experimental technique employed for thermal conductivity measurements was the hot-wire cross-array method. The temperature of measurements ranged from room temperature up to 1000 °C both for unfired and fired material. In unfired samples, thermal conductivity decreased to 600 °C due to hydration reactions. The thermal conductivity of fired samples increased with temperature and was higher by up to 8% for castable with microsilica. The results of ultrasonic wave velocity tests allow explaining the changes that occur in the structure of castable under heating.

Key words: refractory castable, fireclay, thermal conductivity, microsilica, ultrasonic wave velocity

1. INTRODUCTION

Refractory castable is widely used as refractory linings in many high-temperature industrial processes [1]. Recently, new materials with improved thermal properties have been employed in heating units. Special heating regimes are used for the first-time firing [2] of newly installed power plant refractory linings due to complex processes that occur in the raw castable, such as dehydration, carbonization, polymorphic changes of minerals, synthesis. The knowledge of the thermo-physical properties of newly developed materials is very important in engineering projects, since accurate heat transfer calculations must be taken into consideration.

Thermal conductivity of material is influenced by its own mineral characteristics, pore structure, chemical composition, moisture and temperature. Age, aggregate volume fraction, the amount of cement, types of admixtures, fine aggregate fraction, temperature, and the moisture status of specimen – the parameters that mostly affect the thermal conductivity of concrete – were considered [3]. Authors have concluded that aggregate volume fraction and the moisture condition of specimen are the factors mainly affecting the thermal conductivity of concrete. Water content has a drastic influence on the thermal conductivity of unfired concrete [4, 5] as well as on its physical properties. A denser material structure, better thermo-mechanical properties of new generation refractory castable can be obtained using microsilica additives which, together with a deflocullant, determine the lower water content in the castable [6]. The thermal conductivity of refractory concrete with such additives will certainly differ from the conductivity of conventional concrete. Therefore, it is important to ascertain the variation of thermal conductivity of castable with microsilica additive at the first heating-up schedule when essential changes in microstructure occur.

Conductivity is one of the physical characteristics whose measurement is very difficult. For refractory materials, the hot wire technique is considered to be an effective and accurate means of determining thermal conductivity [7]. Four variations of the hot wire method are known: the hot wire standard technique, hot wire resistance technique, two-thermocouple technique and the hot wire parallel technique [7]. The latter is most popular for investigating the thermal conductivity of refractory at high temperatures [8–10]. In this work, the effect of microsilica on the thermal conductivity of fireclay-based refractory castable was investigated.

2. METHODS

The experimental work was performed using Gorkal 40 alumina cement (AC) with Al_2O_3 content no less than 40%, manufactured by "Gorka" (Poland). Disperse chamotte and fireclay castable aggregates were obtained from fireclay scrap (Al_2O_3 ~30%).

Table 1. **Chemical composition and physical properties of RW-Fuller SiO_2 microsilica**

SiO_2	Al_2O_3	Fe_2O_3	C	CaO	MgO	K_2O	Na_2O	SO_3	pH	LOI,%	Bulk density, kg/m^3
96.06	0.20	0.05	0.6	0.25	0.4	1.2	0.1	0.35	7.5	0.44	200

Table 2. **Composition of refractory castable**

Castable components	Composition, %	
	B0	Bs-3
Fireclay aggregates	60	60
Alumina cement	25	25
Dispersed fireclay	15	12
Microsilica	0	3
Water	14.5	11
Deflocculant	0	0.05

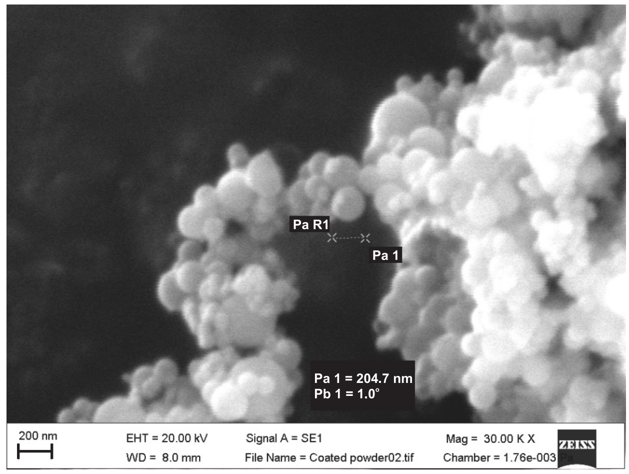

Fig. 1. SEM image of RW-Fuller microsilica

The chemical composition and physical properties of RW-Fuller brand SiO_2 microsilica (manufactured by RW Silicium GmbH, Germany) are summarized in Table 1. Microsilica is ultra-disperse spheres of the medium size ~150 nm. The size of part of spheres is less than 50 nm (Fig. 1). The deflocculant Castament FS 40 (a commercial product from BASF GmbH, Germany) was used to improve the placing properties of castable.

Two groups of samples were prepared. The first group contained samples of a conventional castable (B0) and the other of a castable containing microsilica and a deflocculant (Bs-3). The composition of the samples is shown in Table 2.

Cubes of both types of castable 70 × 70 × 70 mm, as well as samples with the dimensions 200 × 100 × 50 mm were formed. The thermal conductivity of both types of material (samples 200 × 100 × 50 mm) was determined experimentally using the standard hot-wire cross-array method [11]. First, thermal conductivity measurements of unfired samples (after 3 days of normal curing) were performed at 800 °C. After the first heating-up schedule, samples were fired for 4 hours at 1050 °C, and then measurements were carried out for the fired concrete at a temperature interval of 25 °C to 1000 °C. Later the samples were heat-treated for 4 hours at 1200 °C, and again thermal conductivity experiments were performed.

The cubes after 3 days of normal curing were dried at a temperature of 105 ± 5 °C for 48 hours and kept for three hours at the study temperatures (600 °C, 800 °C, 1000 °C and 1200 °C) in an electronic controller furnace and cooled. After that, the ultrasonic wave velocity in castable samples was investigated employing a Pundit 7 (the frequency of transducers 54 kHz).

3. RESULTS AND DISCUSSION

The thermo-mechanical and physical properties of refractory castable had been investigated and reported in detail elsewhere [12]. It can be briefly recapitulated that the density of hardened and fired castable with microsilica (Bs-3) was found to be ~9% higher, and its cold crushing strength was 2–3 times higher in the whole temperature range (20–1200 °C) than that of the microsilica-free castable.

Experimental results of thermal conductivity measurements of two types of unfired refractory castable are presented in Fig. 2 (dotted lines). The initial heating of high-temperature concrete causes physical and chemical changes induced by eliminating combined water. On the first heat-up, a drop in thermal conductivity occurs in the temperature range 25 °C to 500 °C. A decrease in thermal conductivity occurs as a result of binder dehydration or the loss of crystallization water [4, 12].

The thermal conductivity of the denser Bs-3 castable with microsilica was higher than that of B0 by up to 20% at room temperature and decreased to 5% at 400 °C. Densification of these materials and formation of a more continuous solid phase determined a slight increase in thermal conductivity at high temperatures (600–800 °C) (Fig. 2).

After the first heating-up schedule, the samples were fired at 1050 °C, and the thermal conductivity of the castable was measured again. Figure 2 (solid lines) shows that the thermal conductivity of fired samples was considerably lower than that of unfired ones in at a temperature up to 400 °C due to various microstructural changes that occurred as a function of temperature and time: water was driven off, and new phases and microcraks nucleated in the castable matrix.

The thermal conductivity of B0 castable samples fired at 1200 °C increased by 2% up to 8% at 20–200 °C (Fig. 3). A sharp increase in thermal conductivity was noted at 100 °C. It could be related to water adsorbtion observed also by others [4, 8]. In the temperature range 400 °C to 900 °C, the thermal conductivity of both castable samples fired at 1200 °C was slightly lower than after firing at 1050 °C. The possible reason may be additional cracks that appeared in the castable structure as the samples were heat-treated three times (up to 800 °C, 1050 °C, 1200 °C), i. e. they underwent stood three firing–cooling cycles. On the contrary, at lower temperatures, especially the conductivity of the conventional castable sample (B0) was up to 5% higher.

Changes in the thermal conductivity of castables correlate with the results of ultrasonic wave (UW) velocity in samples, measured after firing them at different temperatures. Castables subjected to dehydration are known to develop microcracks which result in a softening of the material (a process readily monitored by measuring the UW velocity in specimens). As we

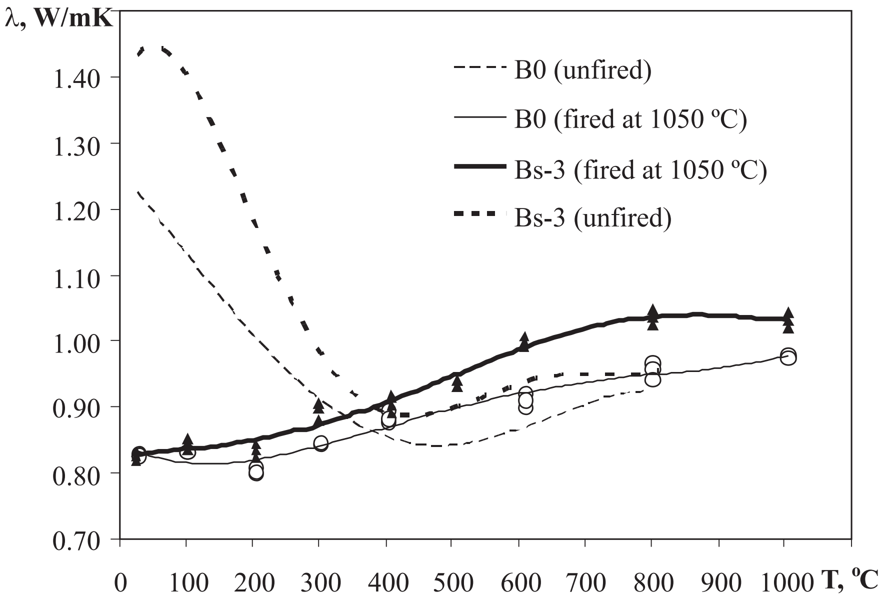

Fig. 2. Comparison of thermal conductivity of unfired and sintered refractory castable

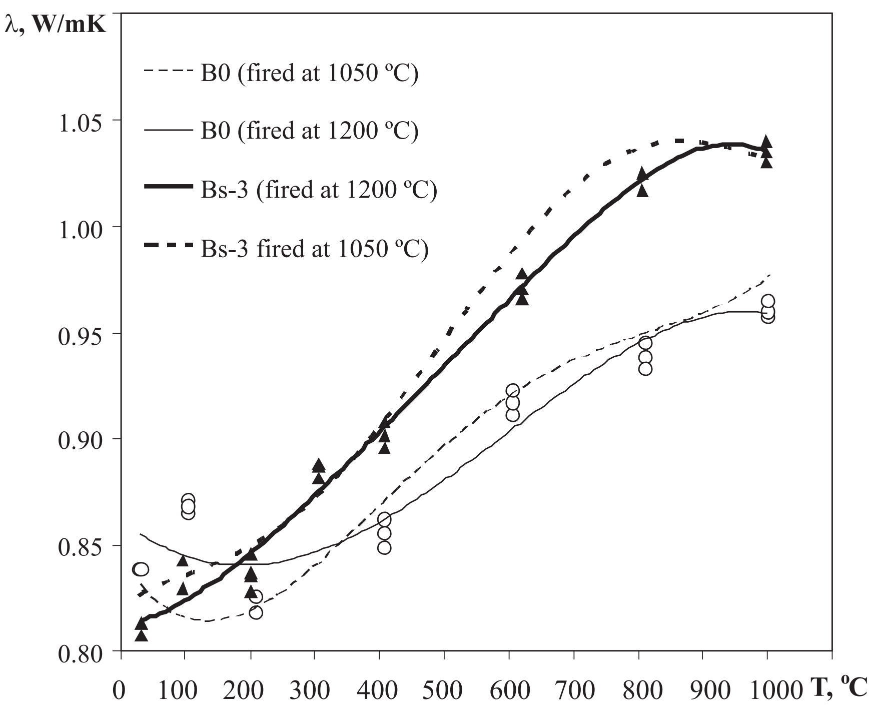

Fig. 3. Thermal conductivity of sintered at different temperatures refractory castable as a function of temperature.

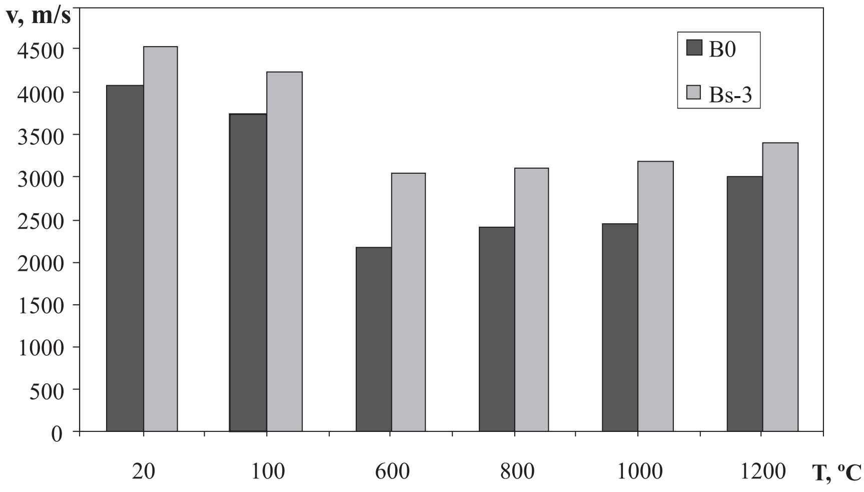

Fig. 4. Ultrasonic wave (UW) velocity in samples of castable

can see (Fig. 4), the UW velocity of B0 and Bs-3 castable specimens fired at 600 °C decreased by 46% and 33%, respectively, in comparison with the UW velocity in the hardened specimens. The decrease in UW velocity in microsilica-free specimens was higher than in Bs-3 specimens. This distinction should be explained by the specific hydration of additional phases CSH and CASH (nanostructures [13]) formed by the interaction between cement and microsilica.

The highest increase in USP velocity for the firing range 600–1200 °C was found in B0 (36%) (in Bs-3 about 15%), which may be explained by a specific sintering in castables free of microsilica. A comparison of binders prepared from Gorkal-40 alumina cement without microsilica and with microsilica added [13] has shown that in the specimens containing microsilica the percentage of aluminosilicate was reduced, whereas the percentage of gehlenite and ferrite phases increased, and anorthite and cristobalite were observed to form. In the binder without microsilica, the latter two species did not form. In the microsilica-free binder sintered at 1000–1200 °C, the percentage of ferrite phases increased significantly: these phases promoted the structural sintering.

4. CONCLUSIONS

Thermal conductivity of a conventional refractory fireclay castable and of castable with microsilica additive was measured experimentally by the standard hot-wire cross-array method. A drop in thermal conductivity with increasing the temperature to 600 °C for unfired samples was a result of dehydration reactions. The thermal conductivity of fired samples increased with the temperature. The thermal conductivity of samples with microsilica additive was by 5% to 8% higher than that of conventional castable in the whole temperature range. Changes in the thermal conductivity of unfired and fired samples of castables can be explained by their structural changes indicated by ultrasonic wave velocity.

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SiO_2 MIKRODULKIŲ PRIEDO ĮTAKA UGNIAI ATSPARAUS BETONO ŠILUMOS LAIDŽIUI

Santrauka

Standartiniu karštos vielelės (kryžiaus) metodu buvo išmatuotas tradicinio ir su ultradispersinių SiO_2 mikrodulkių priedais ugniai atsparaus betono šilumos laidis. Neišdegto betono šilumos laidis kylant temperatūrai iki 600 °C ženkliai mažėja dėl betone vykstančių dehidratacijos procesų. Aukštoje temperatūroje išdegtų bandinių šilumos laidis kylant temperatūrai palaipsniui didėja. Ugniai atsparaus betono ir su SiO_2 mikrodulkėmis šilumos laidis didesnis už tradicinio betono vos 5–8 % visame temperatūrų intervale. Ultragarso impulso greičio tyrimo rezultatai leidžia paaiškinti pokyčius betono struktūroje jį kaitinant.

Raktažodžiai: ugniai atsparus betonas, šamotas, SiO_2 mikrodulkės, šilumos laidis, ultragarso impulso greitis

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ВЛИЯНИЕ МИКРОКРЕМНЕЗЕМА НА ТЕПЛОПРОВОДНОСТЬ ЖАРОСТОЙКОГО БЕТОНА

Резюме

Влияние дефлокулианта и микрокремнезема на теплопроводность жаростойкого бетона исследовано экспериментально – стандартным методом горячей проволоки. С повышением температуры до 600 °C теплопроводность необожженного бетона понижалась в результате дегидратации бетона. После обжига теплопровод-ность обоих бетонов с увеличением температуры повышалась. Результаты измерений скорости ультразвука в образцах бетона позволили объяснить изменения в структуре бетона при его нагревании.

Ключевые слова: жаростойкий бетон, шамот, микрокремнезем, теплопроводность, скорость ультразвука