

Strength analysis of refractory concrete with SiO₂ microdust

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In the current paper, the investigation of the strength of refractory concrete with SiO₂ microdust is presented. The influence of the sintering temperature and the high temperature stream of combustion products is discussed. It is shown that the strength of the refractory concrete samples treated in the stream of combustion products depends on their preparation for working under such conditions. Due to a different degree of sintering the samples strength is not identical and decreases with the growth of sintering temperature.

Key words: Compressive strength, Microsilica, Refractory concrete, Sintering.

Introduction

In contemporary cement building materials various pozzolanic additives are used with cement: SiO₂ microdust, metakaolin, plasticizers, deflocculants and modifiers, due to which the nanostructures determining the material's properties are formed [1-3]. The phases of potassium hydroxide (CSH) formed in the cement materials during hardening are attributed to nanostructures. These structures have not been given a considerable scientific concern and today only a few descriptions are found in scientific literature. The formation of such phases has not been put under control yet. In this respect, it would be purposeful to control the properties of such materials on the microlevel and then proceed to the macrolevel of building materials.

SiO₂ microdust is a by-product formed during the production of silicon and ferrosilicon obtained by reducing quartz sand or quartzite with carbon at 2000 °C temperature. When cooled, SiO that is formed during the reaction gets condensed and oxidized into amorphous SiO₂ microdust. Such microdust is most often included into the composition of the building materials with its amount no smaller than 2% [4]. Microdust always contains admixtures, one type or another. Among them, carbon and its combinations-coke remains, silicon carbide and resin remains-make a considerable part. The major characteristic of SiO₂ microdust is the amount of SiO₂. It should be more than 85%. The particles of SiO₂ microdust are ultradispersive spheres ~0.15 μm in size, yet it also contains nanoparticles 5-30 nm in size. The specific surface of the microdust is close to 20 · 10³ m²/kg,

therefore it is hydroscopic. In the concrete mixture, the additive of SiO₂ microdust positively affects the rheological properties of the paste, the microdust fills in the gaps between the larger particles of cement and filling, which results in the decrease of water and cement demand for concrete paste and in the improvement of concrete's strength characteristics at high temperatures. At the temperature of 1000-1200 °C new compositions are formed under the impact of this additive and mutilisation takes place [5]. With the use of SiO₂ microdust additive (2-12%) in refractory concretes, the amount of cement in the mixture decreases 2-5 times and the material's strength characteristics at high temperatures get improved [6].

Concrete's thermal endurance is considerably increased when the additive of reactive aluminium oxide is used together with SiO₂ microdust [7]. The following three groups of aluminium oxide are most widely used [8]: calcinized aluminium oxide, calcinized low-alkaline aluminium oxide and reactive aluminium oxide. The size of the calcinized aluminium oxide crystals is 2-8 μm and they contain 0.1-0.5% Na₂O. The calcinized low-alkaline crystals have a smaller amount of Na₂O (no more than 0.1%). These materials may be either ground or non-ground. It should be maintained that reactive Al₂O₃ powder is marked by a smaller size of crystals-0.3-1.5 μm and an adequately larger relative surface (from 2000 m²/kg to 10000 m²/kg). They contain less than 0.1% Na₂O and only a few other admixtures. Some marks of reactive aluminium oxide show a monomodal or polymodal distribution of the particles [5]. For the regulation or improvement of the rheological characteristics of refractory concretes the plasticizers are used, which improve the mixture's diffusion, workability and have an effect on cement's hydration, concrete's density, its porosity and strength properties [8]. Their operation is

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determined by the fact that the forces of the system of water, cement and dispersive particles undergo alteration. It should be noted however that this mechanism has not been fully examined, yet the electrostatic, entropic and capillary effects or their combinations are mentioned [9, 10]. Actually, various plasticizers are used: proteins, sodium polyphosphates, polyacrylates, naphthalene sulphonates, melamine formaldehyde resin, lignosulphonates, etc. [7] Sodium polyphosphates and polyacrylates have a negative charge and therefore the principle of their operation is electrostatic dispersion, i.e., a strong push of the cement particles to a negative side. If the initial cement hydrates are composed in the concrete, then the plasticizing effects of this type of rheological modifiers disappear. The plasticizers that are most widely utilized today produce a double effect of dispersion in the system of cement and water-electrostatic and spatial. When they are used, the cement particles do not stick to each other even after the initial cement hydrates are composed. Polycarboxylate ethers belong to this group of rheological plasticizers, in which a polymer is composed of anionic and nonionic side chains. When absorbed by the cement particles, these chains foster their electrostatic repulsion and create an additional spatial repulsive effect [11, 12]. The modifying effect differs when an organic (polyacrylates, polycarboxylates) or inorganic (polyphosphates) modifiers are used. When polyphosphates are used, they stick to SiO₂ microdust and clean their surface from pollutants. When phosphates are used, the black films are formed on the surface of concrete during vibration, which are, in fact, organic plant waste separated from the surface of SiO₂ microdust. Such an effect has not been noticed with the use of organic deflocculants [13]. When aluminate cement is used in the heat-resistant mixture of concrete paste with a little amount of cement, the solution of sodium silicate may perform the role of a modifier, during the hydrolysis of which ions with a negative charge OH are formed. They get absorbed on the cement particles to produce a plasticizing effect. The analysis showed that [14], if compared with sodium tripolyphosphate, the solution of sodium silicate has its advantages: it is cheaper and more convenient to use. When plasticized with the solution of sodium silicate, the concrete with a small amount of cement demonstrates higher thermal endurance since with the help of this deflocculant the concrete's structure acquires a number of microdefects that compensate the stretches caused by the heating-cooling cycles.

In this study, the strength of refractory concrete with SiO₂ microdust was investigated and was discussed the influence of the sintering temperature and the high temperature stream of combustion products on the compressive strength.

Experimental

The microstructure of the oxide materials is defined

by the size of powder grains and their composition, by modifying additives, the level of their distribution and sintering regime. Since ceramic materials have an imperfect structure they are always thermodynamically unstable. The produced sorts of SiO₂ microdust differ by their characteristics, the most significant of which are the amount of SiO₂ and the amounts of additives. Due to admixtures the quality of SiO₂ microdust varies. Although their amount in concrete makes only up to 0.5% of the total weight of the components, their effect on rheology and physical-mechanical properties of concrete mixture may be significant.

G-70 aluminium cement with the smallest amount of admixtures was chosen for the production of the samples, to which 5% of microsilica RW Fuller was added.

Table 1 shows the results of the analysis of SiO₂ microdust bulk density, moisture and mass losses at 1050 °C of temperature. X-ray analysis revealed that cristobalite starts crystallizing in the microdust at 1100 °C of temperature. According to the obtained data [15], the early formation of cristobalite is initiated by low valent cations of Na⁺ (rad. 0.98) and K⁺ (rad. 1.33)-the larger the amount of admixtures in SiO₂ microdust, the larger the amount of cations.

The composition of raw materials for the compressive strength experiments are shown in Table 2. After mixing the raw materials, specimens of 40 mm in width, 40 mm in height and 160 mm in length were formed and sintered at 800 °C, 1000 °C, 1300 °C. They were named as G800, G1000 and G1300, respectively.

Experimental studies of the influence of erosion and ageing processes on the compressive strength of the refractory specimens were carried in the special stand [16], in which the specimens were been under the sway of combustion product flow. The samples had been working in the eroding environment for 100 h, when the temperature of the working wall was 500 °C and

Table 1. Characteristics of SiO₂ microdust.

Bulk density / kg/m ³	Moisture / %	Mass losses at 1050 °C / %
254	0.88	2.6

Table 2. Batch composition of the specimens.

No.	Component parts	Percentage / Mass %
1	Aluminate cement Gorkal-70	8
2	Bauxite 0-1 mm	32
3	Bauxite 3-5 mm	32
4	Finely milled bauxite	18
5	Microsilica RW Fuller containing ~ 30 % nanoparticles	5
6	Ultradispersive alumina CTC-20	5
7	Water	6
8	Deflocculant FS-20	0.1

the speed of the stream of combustion products was 5 m/s.

The examined samples tested by compression with the use of Ton IPRAX (model 1543) Automatic Compression and Bend Test Plant type press with TONITRON (model 1510) automatic programmed control block allowing to determine, control and write down the compression parameters with the computer system of data processing control and visualization, and software TONISOFT 4 (model 0510.301). The ISO 6784 test standard was accepted.

Results and Discussion

The carried out compression revealed the relationships between the load power of the compressed samples (N/mm^2) and deformations (μm) that are presented in Fig. 1. These dependencies, both in the case of Sample 1 that was untreated in the stream of combustion products and in the case of Sample 2 that was tested in the stream of combustion products, were obtained by performing the tests under erosion conditions described in the section 2. The sample's material was sintered at $1300\text{ }^\circ\text{C}$.

The carried out compressive strength analysis demonstrated that the eroding surface of the material G1300 and the layer affected by erosion determined the alteration of the material's strength (Fig. 1). If the sample that did not work in an eroding environment got deteriorated at $172.22\text{ N}/\text{mm}^2$ (Fig. 1, Curve 1), the sample treated by the stream of combustion products, got deteriorated at $60.27\text{ N}/\text{mm}^2$ (Fig. 1, Curve 2). It is clearly seen that when the eroding material is in a fragile state, a number of processes that diminish the material's strength take place on its surface and in the neighbouring layers.

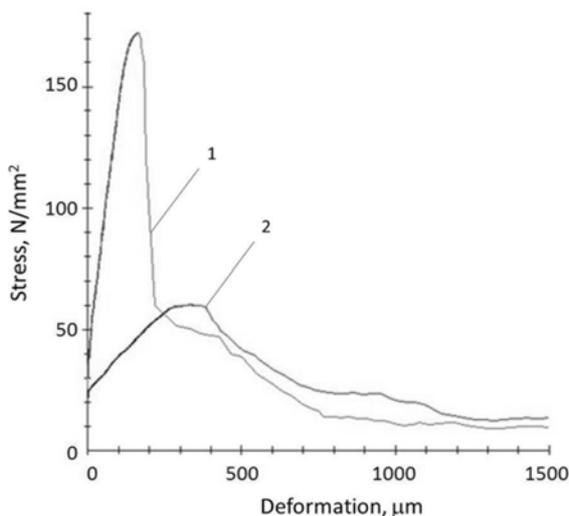


Fig. 1. Compressive strength of sample G1300 of refractory concrete: 1-the sample untreated by the gas stream, 2-the sample treated by the stream of combustion products.

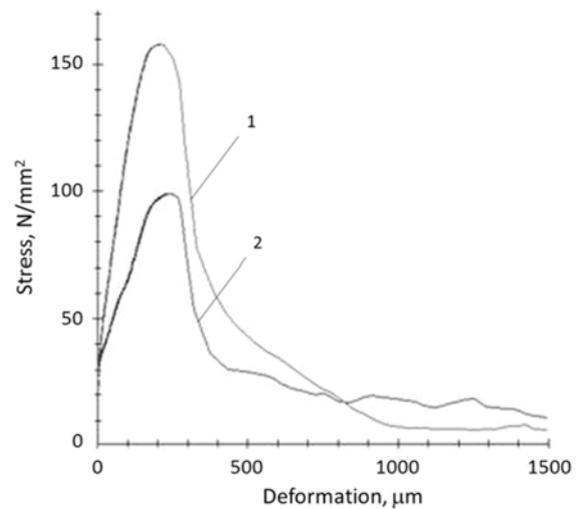


Fig. 2. Compressive strength of the samples G1000: 1-the sample untreated by the gas stream, 2-the sample treated by the stream of combustion products.

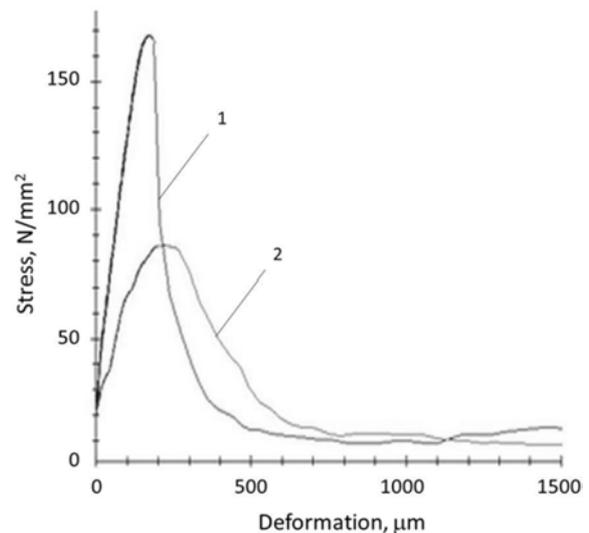


Fig. 3. Compressive strength of the samples G800: 1-the sample untreated by the gas stream, 2-the sample treated by the stream of combustion products.

Two types of the samples G1000 were used in another experiment-the samples untreated by the gas stream and the samples that had been working in the eroding environment. The compression test results are presented in Fig. 2.

In the case of the untreated sample, its compressive strength was $\sigma_c = 157.91\text{ N}/\text{mm}^2$ (Fig. 2, Curve 1). Meanwhile, in the case of the sample treated by the stream of combustion products, its compressive strength reached only $98.95\text{ N}/\text{mm}^2$ (Fig. 2, Curve 2), i.e., it was 1.6 times lower than that of the untreated sample.

The tests of the compressive strength of refractory concrete sintered at $800\text{ }^\circ\text{C}$ were carried out with the untreated samples and the samples treated under the conditions of erosion. The results are shown in Fig. 3.

Table 3. Stretch quantities of the untreated samples and the samples treated by the stream of combustion products.

No	Sintering temperature / °C	Untreated sample σ_{c1} , N/mm ²	Treated sample σ_{c2} , N/mm ²	σ_{c1}/σ_{c2}
1	1300	172.22	60.27	2.86
2	1000	157.91	98.95	1.60
3	800	168.15	85.97	1.96

The compressive strength of the untreated sample in the group of the samples produced by sintering at 800 °C was $\sigma_c = 168.15$ N/mm² (Fig. 3, Curve 1). The compressive strength of the sample treated in the stream of combustion products was $\sigma_c = 85.97$ N/mm² (Fig. 3, Curve 2).

When analysing the given data (Table 3) it is worth remembering that during the sintering of the samples at 800 °C, a number of processes take place in the concrete with SiO₂ microdust, such as: partial hydration of the newly formed calcium silicates, hydration of unhydrated cement particles; CaO hydration; pucolanic reaction between SiO₂ microdust and the newly formed calcium hydroxide, and CaO carbonization [17]. It should be noted here that due to the mentioned processes the microfractures are filled with the newly formed products and the material gets partially strengthened. The same has been observed during the given analysis.

When determining the porosity of the concrete without silica fume and of the concrete with silica fume, as it has been observed in the paper [18], the dependence of the specific surface of the pores on temperature is parabolic and the maximum is reached at 500 °C of temperature. It claims that during the first period of incandescence the temperature gradient causes thermal pressures, due to which the microfractures are formed and grow in number, and the volume of the pores and their surface increases. At the temperatures higher than 500 °C Ca(OH)₂ is divided and CaO is formed, whose surface is very large and easily reacts with silicates and SiO₂ microdust. Now the crystals are formed that fill in the pores and thus diminish porosity.

Since the tested material was produced with a smaller amount of cement (G-70), therefore the used high quality thick fillings, i.e., boxites TMD (Al₂O₃ + H₂O) are amorphous structures, whose density is 2.4-2.5 g/cm³ and amount is 1-3. The new properties of concretes (mechanical, thermal, technological, etc.) obtained in such a way are obviously more favourable than the properties of ordinary concretes [19]. It should be noted here that under the treatment by the stream of

combustion products the erosive properties of these materials have not been analysed and therefore the carried out research is unique and offers useful information about the material's behaviour in the stream.

Conclusions

This investigation demonstrated that the strength of refractory concrete depends on the erosion processes and its products preparation for working under such conditions. Due to a different degree of sintering the strength is not identical and decreases with the growth of sintering temperature.

References

1. M. R. Rezaie, H. R. Rezaie and R. Naghizadeh, *Ceram. Int.* 35 (2009) 2235-2240.
2. Yu. E. Pivinskii, *Refract. Ind. Ceram.* 48 [6] (2007) 28-38.
3. H. Fan, Y. Li, Y. Huang, S. Sang, Y. Li and L. Zhao, *Mat. Sci. Eng. A-Struct.* 545 (2012) 148-154.
4. B. Myhre, in *Proceedings of the Unified International Technical Conference on Refractories*, Orlando, Florida (2005) p. 191.
5. H. Hommer and K. Wutz, in *Proceedings of the Unified International Technical Conference on Refractories*, Orlando, Florida (2005) p. 186.
6. S. Goberis, I. Pundiene, R. Stonys and V. Antonovic, in *Proceedings of XI Conference on Refractory Castables*, Prague (2005) p. 86.
7. S. Berrin Gürel and Akýn Altun, *Powder Technol.* 196 [2] (2009) 115-121.
8. P. Kokechejj-Lorenc, *Refract. Ind. Ceram.* 7 (2004) 82-84.
9. R.G. Horn, *J. Am. Ceram. Soc.* 73 (1990) 1117-1135.
10. E. Sakai and M. Daimon, in "Materials Science on Concrete IV" (The American Ceramic Society, 1995) p. 91.
11. K. Wutz, in *Proceedings of the 7th United International Technical Conference on Refractories*, Cancun, Mexico (2001) p. 892.
12. H. Hommer, in *Proceedings of 10th Biennial Worldwide Congress on Refractories*, aDresden, Germany (2007) p. 401.
13. A. R. Studart, V. C. Pandolfelli, E. Tervoort and L. J. Gauckler, *J. Eur. Ceram. Soc.* 23 [7] (2003) 997-1004.
14. S. A. Goberis, V. Antonovic, I. Pundiene and R. Stonys, *Refract. Ind. Cer.* 48 [2] (2007) 123-127.
15. Ch. Wohrmeyer, F. Simonin, Ch. Parr and Ch. Alt, in *Proceedings of the Unified International Technical Conference on Refractories*, Orlando, Florida (2005) p. 408.
16. R. Abraitis, E. Blazevicius, D. Abraitis, S. Bockus and A. Ciuplys, *Mechanika* 17 [6] (2011) 687-691.
17. G. Villain, M. Thiery and G. Platret, *Cement Concrete Res.* 37 (2007) 1182-1192.
18. C. Parr, F. Simon, W. Mucha and C. Wohrmeyer, *Pol. Ceram. Bull.* 88 (2005) 123-137.
19. V. Vydra, F. Vodak, O. Kapickova and S. Hoskova, *Cement Concrete Res.* 31 (2001) 1023-1026.