Influence of the silicon carbide deposit on the thermal resistance of fire protection

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Abstract. The ceramics samples with structure of SiC-Al₂O₃-Fireclay having good thermal resistance were received. As materials were used: black α-SiC F-120, corundum α-Al₂O₃ F-1000 and Kudinovsky fire-clay. As a temporary technological bundle used polyvinyl alcohol (PVA). Thermal stability was determined by method of heat changes.

1. Introduction
Nowadays the main method of creating new unique in properties materials is combining of different materials – composites. Properties of materials in common with each other acquire properties of the new material and qualities of formed composites are unique.

Composites compete with common construction materials, for example aluminum, stainless steel, titanium. They are used in material producing relating to aviation, aerospace, chemical manufacture, automotive industry and medicine. Value of composites is high as known; this is due to the fact that complex producing, technologies and raw materials are really expansive. But in this case there is a saving resources in complex details producing due to reducing the number of components [1-2].

In recent decades the considerable attention was paid to the SiC-Al₂O₃ composite. The combination of silicon carbide and aluminum oxide will give us the certain ceramics composite materials with high durable and high chemical and temperature stability. This composite is characterized with multifunctional in usage, availability of raw materials, corrosion resistance and non-power-intensive production technology. Aluminum oxide and silicon carbide have unique complex of physic-mechanical properties such as high solidity, low coefficient of thermal expansion and also possibility of use in extreme conditions.

There are different types of composites: based on carbide-silicon (80-90 % SiC), carbide-silicone containing materials (10-30 % SiC), it depends on content quantity of SiC as matrix or reinforcing material.

It is not possible to obtain dense material from pure silicon carbide due to oxidation of SiC at high temperature up to 2000 °C in the air. For this reason the most used ceramics are contain different binders, as well as most carbide-silicon refractories are made with addition of α-Al₂O₃ and fire-clay because they do not oxidize in high temperature with air and they form the mechanism of liquid sintering. This way does not require high energy consumption.

Products with SiC-Al₂O₃-fireclay composition are characterized by high thermal conductivity, crack resistance, wear resistance and high temperature resistance. Ceramics of composition SiC-Al₂O₃ are widely used in ferrous and non-ferrous metallurgy due to high thermal properties [3].
Basic refractory materials in the metallurgical industry are dinas refractories, chamotte, periclase and also concrete materials. Dinas refractory contains more 93% of silicon carbide $\text{SiO}_2$. It has high durable and high operating temperature but heat resistance does not exceed on average $1–2$ water heat changes.

Chamotte refractories are one of the most used refractory materials and available. Chamotte contains $\text{SiO}_2$ and $\text{Al}_2\text{O}_3$ up to 45%. In one hand it has high heat resistance on average $10–20$ water heat changes but in other hand the strength is low, that is the main lack.

Periclase refractories are able to operate at high temperature about $1700\, ^\circ\text{C}$ and contain no less than $85\% \text{MgO}$. Heat resistance of periclase is low. It is on average $1–2$ water heat changes.

In the metallurgical industry, the main part of refractories are used in induction furnaces. Metal is actively mixed in these furnaces and it is possible to lead to destruction. Because the depth of the lining has to be about $10–15\, \text{cm}$, durable and chemical resistance ought to be high also.

2. Materials and Method
To obtaining refractory materials with high durable the mixture is added: SiC (F-120) with a content 20, 30, 35 mass %, $\text{Al}_2\text{O}_3$ (F-1000) in quantity of 55, 45,40 mass % and Kudinovsky field fire-clay content was the same in all of the mixtures 25 mass %. It is known that with increasing oxide phases initially, the porosity decreases and mechanical properties grow simultaneously.

Variation of the components content allowed us to study in detail the temperature resistance dependence of content SiC reinforcing component.

It is known that silicon carbide has high mechanical properties and high thermal conductivity. Because of this presence of coarse particles SiC allowed to obtain reinforced structure with high crack resistance. Using of fireclay with ceramic mixture allowed us to compensate low diffusion activity of SiC and $\text{Al}_2\text{O}_3$.

Use of the liquid-phase sintering principle allowed to achieve mutual dissolution of particles, which eventually led to activation of atoms diffusion process on the phase boundaries [4].

In this way the liquid-phase sintered material structure with particles of SiC, $\text{Al}_2\text{O}_3$ and silicate interfacial was formed.

Initial components were mixed in a roller mixer with addition of corundum balls with a diameter of 15 mm in proportion of 3:1 by weight during 2 hours. Using a greater number of grinding balls leads to fragmentation of particles.

As a temporary technological bundle was used the 8% aqueous solution of polyvinyl alcohol in quantity of 7 mass %. For uniform distribution of particles and bundle the mixture was sowed. With addition of the temporary technological bundle it occurs wetting and lubrication of particles surfaces. It allows to reduce friction between particles and improves their movement at high pressure. Due to this it was possible to achieve the closest packing at pressure. Also an important factor was using fireclay powder and aluminum oxide with the particular size smaller than particles of silicon carbide. It allowed us to obtain high density of samples.

The samples were formed by semi-dry pressing from the obtained mass. Pressing pressure was 100 MPa and cylindrical samples sizes were $d=\text{h}=35\, \text{mm}$. The samples were dried at a temperature of $23-25\, ^\circ\text{C}$ during 24 hours and burned in air at a temperature of $1400\, ^\circ\text{C}$ with 4 hours of isothermal aging. With this temperature it occurs formation of liquid phase with more fusible phase of fireclay.

It begins the process of liquid sintering at which a liquid phase spreads along grains boundaries of aluminum oxide and silicon carbide and pulls them together with filling the pores. Simultaneously the grains and structure become larger.

The main advantage of liquid sintering mechanism is impossibility of pores formation but it is possible the formation of large grains in the structure influencing on the physic-mechanical properties.
3. Results and discussion
The obtained testing results of average density, open porosity and water absorption are shown in the table 1. The results of density and porosity were determined by the hydrostatic weighing.

| Content Al₂O₃:SiC:fire-clay, mass. % | ρ, g/cm³ | P, % | W, % |
|---------------------------------|---------|-----|-----|
| 50;25;25                        | 2.72    | 12  | 5   |
| 45;30;25                        | 2.55    | 13  | 6   |
| 40;35;25                        | 2.53    | 15  | 6   |

The content of pores and defects in the volume of the material affects the material strength and heat-resistance. There is an increase in the stress gradient at thermal shock, eventually there are breaking cracks. Cracks propagation occurs if the energy of crack spread is more than the restraining energy [5].

Obtained material’s heat resistance was measured by heat-changes method. The samples were heated to 1000 °C in the silicate furnace with carbide-silicon heaters then cooled instantly in water at a temperature of 22-25 °C. This method allows to obtain results about thermal resistance on a par with actual operating conditions of refractories use. With instant cooling there is a stress gradient on the surface and inside of structures. By the number of heat-changes it is possible to judge the cycles of use in production. Results of the experiments are shown in table 2. The samples with the greatest content of SiC (35 mass %) were destroyed firstly.

| Material | Quantity of heat changes before crack appearance | Quantity of heat changes before destruction |
|----------|-----------------------------------------------|-------------------------------------------|
| 25 mass % SiC | 4                                           | 47                                        |
| 30 mass % SiC | 5                                           | 28                                        |
| 35 mass % SiC | 5                                           | 24                                        |

This is due to the fact that the presence of an oxide phase and reinforcing components allows to reduce the spread of main cracks in the ceramic structure. Coefficient of thermal expansion difference is weakens the adhesion between particles of SiC and oxide phase. This mechanism allows to restrain the cracks spread along the SiC boundaries, increasing the spread way. Eventually it requires more energy consumptions. Cracks in this material spread and pass around the grains of silicon carbide with intergranular mechanism at high temperature and thermal stresses [3-5].

An important factor is equal distribution of SiC particles in the Al₂O₃ matrix, it was a dominating role. With the increase SiC concentration there is a local congestion and agglomeration particles that leads to formation of unreinforced areas. These areas contribute to passing of break cracks through the material structure.

On the pages 1, 2 and 3 showed polished surfaces and character of SiC particles distribution. It is obviously that with increasing of SiC content occurs a local congestion as indicated earlier. Type cracks spreading (in the images below) characteristic for thermal shock and contracting-compressing thermal stresses.
4. Conclusions
A study was conducted to determine ceramics SiC-Al₂O₃-fire-clay properties of heat resistance and results allow us to make conclusions:

- Ceramic properties are investigated: density, porosity and water absorption. Porous samples with high density were obtained.
- By the method of heat changes the values of heat resistance with different SiC content were determined. As a result of experiments it was found that the samples with the content of 25 % have the best thermo mechanical properties due to SiC particles spread in the ceramic structure. This affected the increase in crack resistance.
- Developed material containing 25 mass % of SiC has high thermo mechanical properties, about 47 heat changes. This exceeds the standard chamotte and high-alumina refractories which are used nowadays in metallurgy.

References
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Figure 1. SiC particles spread (a - 25 mass %, b – 30 mass %, c – 35 mass %)