FORMATION OF KAOLIN REFRACTORIES HEATED IN DIFFERENT GASEOUS ATMOSPHERES

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Refractories made from raw materials that contain 41-42% Al₂O₃ are used in linings of blast-furnace shafts and the critical parts of other furnaces. They provide highly resistant linings in heating units compared with firebrick [1-3]. The heating and cooling cycles and the body and gaseous-media compositions are important in the formation of the structure and phase composition of the refractories.

The raw material for our investigation consisted of Polozhe and Novoselits kaolins (see Table 1). Analysis of the grain-size composition shows that with a rise in the amount of coarse fractions from 0.02 to 0.06 mm, the SiO₂ content increases sharply, while the proportion of Al₂O₃ diminishes (Fig. 1). In the Novoselits kaolin, besides the main material — kaolinite and quartz — there is some hydargillite, marcasite, pyrites, rutile, epidote, leucocryst, biotite, muscovite, microcline, and iron hydrated micas. The total refractive index of the kaolinite is 1.562 ± 0.003. The marcasite and pyrite bond the main mass of iron impurities. The iron in both kaolins is distributed as oxides, hydroxides, low-solubility silicates, and hydrated micas; and it is bonded with the kaolinite in the form of isomorphous impurities.

Thermal analysis of the Novoselits kaolin shows that at 310-315°C there is an endothermic effect, indicating the decomposition of the hydargillite, at 410°C an exothermic effect for the oxidation of pyrite (FeS₂) and pyrrhotite (FeS₁₋ₓ). Oxidation of the sulfides commences at 380°C with heat evolution according to the reaction FeS₂ + 1.5O₂ = FeO + SO₂, 2SO₂ + O₂ ⇌ 2SO₃.

The oxidation process occurs in two stages: adsorption of molecular oxygen and dissociation into atomic oxygen; then diffusion of the oxygen atoms deep into the lattice of the sulfide, and reverse diffusion of SO₃. With enlargement of the grains of FeS₂ we note an extension of the exothermic effects towards the higher temperatures. The magnitude of the exothermic effect for the decomposition of hydargillite at 430°C is affected by the exothermic effect for the oxidation of FeO, which is noted at 250-375°C; its rate also depends on the particle sizes. The thermogram for pyrite shows an endothermic effect at 700-715°C with a high peak in reducing conditions, which is due to the polymorphic inversion of the pyrrhotine from the monoclinic to hexagonal modification. This indicates the preservation of sulfur compounds of iron at temperatures above 700°C.

The two kaolins were used to press specimens, and these were then fired at 1600°C in oxidizing (air) and reducing (coke filling) conditions. The fired specimens were treated with a water solution of HF, and we then measured the amount of HF-insoluble residues (IR). It is shown that in reducing conditions the mullite-forming reaction in the kaolin begins earlier than in the specimens fired in oxidizing media, and the reaction shifts toward the lower temperatures by 100-200°C. This is connected with the earlier formation of the liquid phase in reducing conditions (Fig. 2). A more marked influence is exerted by the reducing atmosphere on the refractory made of Polozhe kaolin, which contains more of the low-fusible oxides (3.23%) than Novoselits (2.47%). The iron in the Novoselits kaolin is present as pyrite, which helps sintering and mullite-formation in oxidizing conditions to a greater extent than Fe₂O₃ in the Polozhe specimens. In the Polozhe kaolin the iron takes the form of Fe₃O₄.

TABLE 1. Chemical Composition of Kaolin and Chamotte,* %

<table>
<thead>
<tr>
<th>Material</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>TiO₂</th>
<th>Fe₂O₃</th>
<th>FeO</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>Δm_calc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polozhe kaolin PLK-V</td>
<td>46.59</td>
<td>36.92</td>
<td>0.78</td>
<td>1.08</td>
<td>Tr.</td>
<td>0.77</td>
<td>0.20</td>
<td>0.02</td>
<td>0.08</td>
<td>13.26</td>
</tr>
<tr>
<td>Novoselits kaolin KN-0</td>
<td>44.10</td>
<td>38.40</td>
<td>1.13</td>
<td>0.60</td>
<td>0.50</td>
<td>0.03</td>
<td>0.11</td>
<td>0.13</td>
<td>14.82</td>
<td></td>
</tr>
<tr>
<td>Chamotte from PLK-V</td>
<td>54.94</td>
<td>41.70</td>
<td>1.01</td>
<td>1.23</td>
<td>Tr.</td>
<td>0.41</td>
<td>0.05</td>
<td>0.35</td>
<td>0.10</td>
<td>-</td>
</tr>
<tr>
<td>Chamotte from KN-0</td>
<td>52.24</td>
<td>44.53</td>
<td>1.63</td>
<td>0.83</td>
<td>&quot;</td>
<td>0.47</td>
<td>0.05</td>
<td>0.19</td>
<td>0.20</td>
<td>-</td>
</tr>
</tbody>
</table>

*Calculated content of mullite in chamotte from PLK-V 58.0%; in chamotte from KN-0 61.7%.
Fig. 1. Change in SiO\textsubscript{2} content (1) and Al\textsubscript{2}O\textsubscript{3} content (2) in Novoselits kaolin in relation to the grain-size composition.

Fig. 2. Relationship between the amount of insoluble residues $c_{IR}$ during firing of pressings made from Novoselits kaolin (1, 3) and Polozhe kaolin (2, 4) in oxidizing (1, 2) and reducing (3, 4) conditions and the firing temperature $t$.

of Fe\textsubscript{2}O\textsubscript{3}, which in reducing conditions changes into the active FeO form, reacting with SiO\textsubscript{2} and other oxides to form a readily fusible melt that helps mullite crystallization.

After firing at 1000°C in reducing conditions the amount of insoluble residue was 5.6% for Polozhe and 3.2% for Novoselits kaolins. There are sharp changes at 1100°C. In specimens fired at 1100°C in air the content of insoluble residues equals 3-4%, while in reducing conditions it reaches 39% for Novoselits kaolin and 46% for Polozhe kaolin. The maximum amount of insoluble residues is attained at 1400-1500°C. With further temperature rise to 1600°C there is a reduction in the residue content, which is due to some solution of mullite in the melt.

The densification of the specimens commences at 1000°C from the moment when liquid phase appears. The fastest reduction in porosity and increase in apparent density occur up to 1400°C (Fig. 3). The closed porosity is increased from a temperature of 1200°C, and at 1600°C reaches 6%. This is accompanied by a continuous increase in the amount of liquid phase and change in its composition. At 1500°C the Novoselits kaolin forms 61% mullite, while in the Polozhe it is 58%. The equilibrium of the mullite with the melt also depends on the kaolin’s content of impurities and their composition.

In reducing conditions the equilibrium temperature of the melt containing mullite is lower than in the oxidizing medium. These results show that the main mullite-forming processes and densification of the refractory occur when the material is heated to a certain temperature. Holding the specimens at high temperatures (1500°C) increases the porosity and reduces the apparent density owing to the rise in the volume of the pores (Fig. 4), which embrittles the refractory. These processes occur in the same way in specimens of both kaolins. However, with the Polozhe in reducing conditions the amount of mullite is increased more slowly, which is explained by the high content of liquid phase and its low viscosity. This causes partial solution of the mullite. Our experiments stress the importance of the cooling cycle after firing of the refractories.

Different cooling rates were investigated in order to establish the effect of the cooling cycle on changes in the properties and phase compositions of the refractories made from the two types of kaolin. After firing in the two gaseous media at 1500°C and holding at maximum temperatures for 2 h, the specimens were cooled slowly at 2.5°C/min, and rapidly at 5.6°C/min.

Figure 5a shows that the specimens fired in oxidizing conditions during cooling from 1500 to 1200°C undergo certain changes. The sharpest fall in porosity during cooling occurs from 1500 to 1400°C, i.e., when there is rather a high liquid-phase content. The slower the cooling, the more effectively does the phase composition change, and hence the properties. The most rapid changes occur in the Polozhe specimens fired in reducing conditions (Fig. 5b). During rapid cooling from 1500 to 1300°C the apparent density dropped from 2.35 to 2.29 g/cm\textsuperscript{3}. In all cases, with a reduction in the cooling rate from 5.6 to 2.5°C/min there is a rise in the apparent density by 0.05-0.07 g/cm\textsuperscript{3} for Polozhe kaolin and 0.04-0.05 g/cm\textsuperscript{3} for Novoselits kaolin specimens (see Fig. 5a-d).