

### Experimental study of stability chromite–periclase and periclase–carbon refractories

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The comparative study of stability of chromite-periclase (Cr–Per) refractory (HPTU mark) and periclase-carbon (MgO–C) refractory (PU-9 mark) were carried out under laboratory conditions. These refractories applied in furnaces RNB 5500 of nickel plant ZF OAO “Norilsk Nickel” in the manufacture of non-ferrous metals. Slag, crushed with metal (nickel), were placed to crucibles made from the respective refractories. The samples were heated to a temperature of 1500 or 1600 °C, maintained for 12 hours and were quenched. After the experiments, samples were examined under optical and electron microscopes. The chemical composition of all phases was studied by electron-probe energy dispersive microanalyzer based on scanning electron microscope Jeol JSM-6480LV (spectrometer INCA-Energy 350) of Department of Petrology, Moscow State University.

The start composition of chromite-periclase (Cr–Per) refractory consists of 64% of the periclase (Per), from 25% chrome spinel (Spl), from 7% monticellit (Mont) and 4% olivine (Ol). Periclase-carbon (MgO–C) refractory consists of ~ 80–85% of the periclase, 5% monticellit and dicalcium silicate and 10–15% carbon (data Mol.%). Studies under the electron microscope showed that both types of refractory material as a result of the experiments assume a zonal structure. There is a sharp contrast to the resulting zoning in Cr–Per and MgO–C refractories at the border with molten slag and metal, expressed as a width of reaction zones, their structure, phase and chemical composition. In chromite-periclase refractory width of macroscopically visible reaction zone is about 5–6 mm, in periclase-carbon – less than 1 mm. Column interaction of Cr–Per refractory with the molten slag and nickel allocated 5 zones with a total width of 30 mm. The boundary of the first two zones established by the detection of Ni in the refractory in the amount of the 0.1–0.2 per cent. Throughout I and II zones in the refractory the content of SiO<sub>2</sub> (5 wt.%) and FeO (7%) increases and MgO (17%) and Cr<sub>2</sub>O<sub>3</sub> (6%) decreases. In this case, Per and chrome Spl corrode, the content of monticellit decreases and the number of olivine increases (from 4 to 12%). Ni enters into the composition of periclase first in small and then in significant quantities (up to 0.25 form. unit), and Fe - up to 0.13 form. unit. Chrome spinel grains are surrounded by rims of more aluminous and ferrous spinels, emerging and re-formed crystals of Spl. Periclase formed intergrowths with Spl, containing in addition to Cr – Al, Fe and Ni. The boundary between zones II and III clearly break off by changing the paragenesis phases: periclase disappears, the association Per + Spl + Mont + Ol is replaced by a Spl + Ol + Glass, in which spinel greatly predominates. Glass is present in an amount of about 10% and is formed in the space between the crystals of spinel. Among the newly-formed spinels of zone III crystals with a high content of Al [(Mg<sub>0,95</sub>Ni<sub>0,09</sub>Co<sub>0,02</sub>)<sub>1,06</sub>(Al<sub>1,20</sub>Fe<sub>0,18</sub>Cr<sub>0,63</sub>)<sub>2,01</sub>O<sub>4</sub>] with rims of more ferrous spinels, containing Ni and Co [(Mg<sub>0,83</sub>Ni<sub>0,19</sub>Co<sub>0,04</sub>)<sub>1,06</sub>(Al<sub>0,50</sub>Fe<sub>0,97</sub>Cr<sub>0,37</sub>)<sub>1,84</sub>O<sub>4</sub>], are dominated. Ni appears also in the olivine, and the ratio of Ni / (Mg + Ni) from 0.03 to 0.22 increases in zone III. Phases paragenesis in IV zone differs from one in zone III: decrease in the number of Ol (7%) and glass (up to 5%), even greater predominance of spinel and a change of its composition. The ratio of Ni/(Mg + Ni) in olivine increases to 0,36. Spinels form zonal crystals of two types: the first type, the center of the grains make up chrome-alumina spinel, the border - less than alumina, but more of nickel spinel, in the second type of reverse situation is observed. Crystals of both spinel types overgrow with phase corresponding bunsenit NiO with small amount of Mg (up to 0.1 fu) and the impurities Al, Fe, Cr and Co. The composition of the glass which is formed in the refractory conform to phonolites (SiO<sub>2</sub> – 56.2%, Al<sub>2</sub>O<sub>3</sub> – 19.5%, MgO – 1.0%, CaO – 1.8%, Na<sub>2</sub>O – 4, and 7%, K<sub>2</sub>O – 11.8%

$\text{Cr}_2\text{O}_3$  – 0.3%,  $\text{NiO}$  – 1.0%,  $\text{CoO}$  – 0.3%). Fine crystals of clinopyroxene are contained in the glass. There are fundamental changes of the phase composition in the V zone. It consists of bunsenit with a small amount (about 10 mol.%) of spinels. There is bunsenit solid solution with other components, which consist of 86–90 wt. %  $\text{NiO}$ , 4–8%  $\text{MgO}$ , 2–3%  $\text{FeO}$  and  $\text{Cr}_2\text{O}_3$ . Thus, at the interaction of metallurgical melts with chromite-periclase refractory intense interdiffusion of components is observed leading to the removal of Mg and Cr from it, and introduction of Al, Fe, Ni and Co from melts. This process causes the corrosion in the refractories, leading to its destruction.

Zone of the active interaction between periclase-carbon ( $\text{MgO-C}$ ) refractory and the molten slag and metal are very small and amounts to 0.5–1 mm unlike chromite-periclase. Throughout the column (from the bottom of the crucible to melt), the chemical composition of the refractory remains practically unchanged for all components. Neither of silica from the slag nor nickel from molten metal are introduced. The phase composition of refractories varies significantly only in the immediate vicinity (1–0.5 mm) to the molten slag: along with monticellit and calcium silicates- olivine and  $\text{MgAl}$ -spinel appears. Both these phases have also crystallized in the slag. None of the studied phase does contain Ni. It is obvious that such indifference in periclase-carbon ( $\text{MgO-C}$ ) refractory to aggressive metallurgical melts associated with the presence of carbon in its composition. Carbon prevents the diffusion of the components of slag and nickel melt in the refractory, acting as an antioxidant. It is likely that it forms a graphite film on the boundary of the periclase grains of refractory and the melt, preventing the passage of the mutual diffusion of components.

According to the studying result of the composition and structure of refractories should be concluded that periclase-carbon ( $\text{MgO-C}$ ) refractories are much more resistant to slag and nickel melts at high-temperature conditions of experiment compared with chromite-periclase refractories. Hence  $\text{MgO-C}$  refractories are more efficient at their use in commercial production of nickel.