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Gas-refractory interactions of basic refractories with sulfur-bearing gases produced in converter furnaces during extraction of Platinum Group Metals in non-ferrous industry.

ABSTRACT: The fundamental reaction mechanisms, when unused chrome-magnesite, magnesite-chrome and magnesite refractories are exposed to sulfur-bearing gas mixtures of SO_2-O_2, SO_2-N_2 and SO_2 at 700°C to 1350°C, were investigated. The investigations comprised chemical analyses, thermodynamic analyses and microstructural examination. The extent of the conversion reactions was measured as a function of temperature and reaction time. Six basic refractories were investigated and characterized using Scanning Electron Microscopy (SEM) and X-ray powder diffraction (XRPD) methods. The microstructural examination indicated that physical changes in the original microstructure of the refractory could possibly influence the reactions with sulfur-bearing gases and the chemical analyses of the product phases confirmed the formation of secondary sulfates within pores, along grain boundaries and cracks. The structural features in the original refractory were determined by technological processes employed during original firing in production. The factors attributed to the principal physical changes of the original microstructure were related to the diffusion processes, which affected the phase distribution, pore size distribution and grain size. The fundamental reactions involved in the pore size distribution and microstructure were attributed to the differential diffusion mechanism of individual components that resulted in the development of magnesia spinels.

The effects on the microstructure demonstrated that the reactions were limited to the grain boundary region due to the product layer formed as the reactions progressed. The chemical product analyses indicated that in the sulfates formed, the sulfation reactions were significantly affected by the equilibrium thermodynamics of the oxygen and sulfur dioxide gas combination in the products of $P_{SO_2} P_{O_2}^{1/2}$. The phase changes led to the dissolution of the refractory components and crystallization of MgO and CaO. This influenced the permeability of the sulfur-bearing gases that reacted to form $MgSO_4$ and $CaSO_4$ found as grain boundary and pore space fillings. Resistance to sulfur-bearing gas infiltration and sulfation in fine-grained direct bonded refractories were found to be better than that of the coarse-grained direct bonded refractories. The decreased sulfation of the fine-grained refractory was related to the restricted diffusion processes due to the stable magnesia spinel phases and retention of the closed pore structure at different temperatures. However, the dissolution and crystallization mechanism described in sulfation, demonstrated that $MgSO_4$, $CaSO_4$, $CaMg_3(SO_4)_3$ and compound mixtures of sulfate, silica, magnesia and sesquioxides (Fe_2O_3, Al_2O_3 and Cr_2O_3) were formed along the grain boundaries.