DISSOLUTION KINETICS OF MGO-CAO AND MGO-CR2O3 (MAG-CHROME) REFRACTORIES IN SECONDARY STEEL SLAG AND THE BINARY PHASE DIAGRAMS

*MgO-CaO Phase Diagram*

The above figure shows the phase diagram of MgO-CaO binary system. The solid solubility at high temperatures leads to formation of a high temperature bond in dolomite refractories.

*MgO-Cr2O3 System (MgO-MgCr2O4 Phase Diagram)*
The only intermediate compound which exists in the binary system MgO-Cr₂O₃ is Magchrome spinel (MgO.Cr₂O₃ or MgCr₂O₄). From the above phase diagram of Magnesite-Magchrome spinel (MgO-MgCr₂O₄) binary system it can be observed that for steel plant refractories direct bonding between magnesia-chrome phase is formed when these two are heated together at temperatures above 1600°C as a result of the partial solubility of the constituents.

**Dissolution Kinetics of Refractory Oxides**

Refractories are non-metallic materials used for the lining of kilns and furnaces required for high temperature operations in several metallurgical and non-metallurgical industries such as iron & steel, aluminium, copper, glass, cement, petrochemicals etc.

**Dissolution of solid oxides** in liquid slag is governed mainly by –

1. Chemical reaction at the slag / refractory interface,
2. Transport or diffusion of reacting species.

In the second case, rate of dissolution can be expressed in terms of Nernst equation:

\[
J = D \frac{(C_s - C_m)}{\partial}
\]

Where, \(D\) is the diffusion coefficient (m² s⁻¹), \(C_m\) and \(C_s\) are, respectively, concentration and saturation solubility of refractory in slag (g m⁻³), and \(\partial\) is the effective boundary layer thickness (m). Increasing \(D\) or decreasing \(\partial\) (i.e. increasing \(D/\partial\)) result in increase of dissolution rate, \(J\). Moreover, it is also clear from the above equation that the value of \((C_s - C_m)\) strongly influences the dissolution rate. If slag is saturated with refractory oxide then \(J = 0\). Naturally, to minimize the rate of dissolution, it is necessary to minimize \((C_s - C_m)\). For example, with increasing MgO
content in the slag, the corrosion of the periclase phase in Mag-Chrome refractories will decrease. If \( C_m = 0 \), then the value of \((C_s - C_m)\) reaches a maximum and thus, so does the dissolution rate.

Dissolution kinetics of MgO-CaO and Magnesite-chrome refractories in secondary steel slag was studied by Chen Zhaoyou Wu Xuezhen Ye Fangbao at Luoyang Institute of Refractories Research by means of the rotating cylinder method. Materials investigated include four MgO-CaO samples (MgO content: 40 to 93%) and two magnesite-chrome samples (co-clinkered and semi-rebonded). The experiments were carried out in Argon atmosphere at different temperatures (1600-1750°C) and revolution speeds (200 to 500 rpm) using synthetic slags similar to VOD and AOD slags with different basicities (0.6-2.68). Based on their experimental results the mechanism and kinetics of the dissolution process are discussed. The conclusions drawn are as follows:

1. Erosion resistance of magnesite-chrome (MgO-Cr\(_2\)O\(_3\)) refractories is better than that of MgO-CaO materials.
2. When the content of MgO is about 60-80%, slag dissolution resistance of MgO-CaO samples will be comparatively higher. When basicity of slag is 1.0, the dissolution rate of magnesite-chrome refractories (i.e. Mag-Chrome, MgO-Cr\(_2\)O\(_3\)) is much lower than that of MgO-CaO.
3. With increase of basicity of slag, the dissolution rate of magnesite-chrome increases, whereas that of MgO-CaO decreases.
4. For the increase of temperature of 100°C at one time, the dissolution rate of MgO-CaO increases by 2-3 times while that of magnesite-chrome increases 5-6 times. Dissolution activation energy for MgO-CaO refractory is 70 kcal/mol and that for magnesite-chrome is 110 kcal/mol. The diffusion coefficient of MgO in the slag is \(3.7 \times 10^{-5}\) cm\(^2\)/s.
5. \(M_2S\) is formed by magnesite-chrome with acid slag in the reaction zone while \(C_2S\) is formed by MgO-CaO with basic slag in the reaction zone.
6. The process of dissolution of MgO-CaO refractories in slag is controlled by the diffusion mechanism.