PRODUCTION AND EQUIPMENT

PROPERTIES AND STRUCTURE OF MAGNESIA MODIFIERS
FOR CONVERTER SLAGS


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Recently with the aim of increasing the stability of converter linings there has been extensive use of a new class of synthetic magnesia modifiers that are added directly to the converter melt during steel melting. The chemical composition of modifiers and method for their preparation are provided. The basis of the magnesia modifiers is MgO oxide and its compounds. Modifier properties (density, open porosity) are studied in relation to a change in specimen heating and the mineral composition of modifiers of different chemical composition, and the change in the structure of modifier specimens during heating is examined. The mechanism of modifier dissolution in molten slag is suggested.

Processing iron in an oxygen converter is accompanied by formation of slag saturated with a considerable amount of iron oxides that have a negative effect on the converter lining. The corrosive nature of slag with respect to the converter lining, and in fact the amount of MgO passing from the lining into the molten slag in a unit of time is considerable at the start of blowing, it decreases during the decarburizing period and increases towards the end of blowing as a result of an increase in the solubility of refractory MgO in the iron slag [1].

The wear mechanism of periclase-carbon refractories is accompanied by the following processes:

- liquid-phase decarburization of the lining surface layer by iron oxides and free oxygen;
- infiltration of slag into the decarburized layer;
- reaction between the refractory and slag that leads to transfer of MgO into the slag.

Thus wear of periclase-carbon refractories of the converter lining is explained by the fact that iron oxide reacting with the refractory at high temperature during blowing of the metal (above 1600°C) by the reaction

\[ C + 2(FeO) = CO_2 + [Fe] \]

forms pores through which there is penetration of slag into the decarburized layer.

Wear rate \( v, \text{ kg/sec,} \) of the lining is generally described by the equation [2]:

\[ v = \frac{F(C_1 - C_2)}{\delta \left( \frac{1}{D_2} + \frac{1}{D_1D_2} \right)} \]

where \( F \) is lining contact area with the slag, \( m^2; \) \( C_1 \) and \( C_2 \) are the concentration of the diffusing component into the refractory and slag respectively, \( \text{kg/m}^3; \) \( \delta \) is diffusion boundary layer effective thickness, \( m; \) \( D_1 \) and \( D_2 \) are the diffusion coefficients in the refractory and slag respectively, \( m^2/\text{sec}. \)

It follows from Eq. (1) that the lining wear rate is directly proportional to the concentration of the diffusing component into the solid and liquid phases, i.e. it depends on the concentration of iron and magnesium oxides in the slag. Therefore a reduction in the corrosive action of high iron slag on the lining may be provided by introducing magnesium-containing materials into the melt.

As applied to the solubility of periclase refractory in converter slag Eq. (1) may be replaced by the expression [3]:

\[ \frac{dn}{d\tau} = (DF/\delta)(n_s - n), \]

where \( dn/d\tau \) is magnesium oxide dissolution rate; \( \tau \) is time; \( D \) is MgO diffusion coefficient in the slag; \( F \) is slag’ refractory reaction surface; \( \delta \) is diffusion layer thickness at the in-
The actual concentration of MgO in the slag.

With MgO concentration difference $n_t - n$ between the concentrations of MgO with saturation $n_t$ and the actual MgO concentration in the slag $n$ decreases and the dissolution rate $dn/dt$ is reduced. In the case when $n > n_t$, the slag is supersaturated with MgO and refractory dissolution rate in the slag slows down. With an MgO concentration in the slag above the saturation limit magnesium oxide starts to separate from the slag. In accordance with Raoult's law in a slag saturated with MgO the activity of MgO equals 1 and it equals the refractory MgO activity. This means that a slag saturated with this oxide may be considered as equivalent in respect to the refractory and according to chemical equilibrium theory dissolution of periclase refractory into the slag theoretically ceases.

The relationship, reflecting the balance of magnesium oxide in converter slags, is represented by the equation [3]:

$$\Delta M_{\text{MgO}} = CW_{\text{slag}} - W_{\text{MgO}}$$

where $\Delta M_{\text{MgO}}$ is loss of magnesium oxide with lining wear per melt, ton; $C$ is magnesium oxide concentration in the slag, %; $W_{\text{slag}}$ is the amount of slag, ton per melt; $W_{\text{MgO}}$ is the addition of magnesia materials per melt, ton.

It follows from Eq. (3) that with an increase in the amount of magnesia materials added and thereby an increase in MgO concentration in the slag there is a reduction in lining wear.

Normally natural materials are used as magnesia materials (in future modifiers): dolomite, dolomitized lime, magnesia, etc. Almost all of the large converter shops in the USA, Canada, Japan, China use calcined dolomite containing 30 – 40% MgO. Recently for these purposes modifiers have been used with a content up to 70% MgO. They are pressed periclase powder with a small amount of additions containing carbon or without it. In the metallurgical plants of Western Europe there is mainly use of dolomized lime and calcined dolomite. In the converter shops of the Ukraine and Kazakhstan dolomitized lime containing less than 15% MgO and calcined dolomite are mainly used. In OAO MK Azovstal' ferruginous dolomite is used containing 30 – 35% MgO and 2 – 5% Fe$_2$O$_3$. Before the end of the 1990s in the converter shops of Russia calcined dolomite was used, and from 2000 there has been extensive use of ferruginous dolomite (OAO MMK) and a lime-magnesia flux containing 29 – 33% MgO and 7 – 10% Fe$_2$O$_3$ (OAO Severostal', OAO NTMK, OAO ZSMK, OAO Mechel).

Use of natural materials as magnesia modifiers makes it possible to increase converter lining stability, to increase their productivity, to reduce the cost of steel as a result of reducing expenditure in lining maintenance and the amount of refractory consumed per ton of steel melted.

However, in spite of the presence of iron oxides in converter melt molten slag, that promote an increase in the solubility of these modifiers in the slag, nonetheless that dissolve poorly in the slag due to presence in them of refractory compounds (bicarbonate and tricalcium silicates, periclase), as a result of which there is heterogenization of molten slag and an increase in its viscosity. The behavior of a converter melt with this slag is accompanied by a slowdown in sulphur and phosphorus removal from the metal, a reduction in the output of finished steel, and an increase in thermal energy required to dissolve magnesia modifiers. With the aim of overcoming these drawbacks magnesia modifier compositions have been developed that are synthetic materials consisting of three or more components differing in chemical composition, physicochemical properties and designation [4 – 6].

A feature of the new magnesia modifiers is a higher content of magnesium and iron oxides, and carbon (Table 1). Each form of modified is prepared by its own technology.

The rate of modifier dissolution in a slag of the composition 40% CaO, 40% SiO$_2$ and 20% Al$_2$O$_3$ was determined in a Tamman furnace at 1600°C. Previously formed specimens in the shape of spheres was placed in the slag. Results are provided in Table 2 for a study of the specimen dissolution rate in the molten slag. Pellets of SMG-10S have the greatest dissolution rate since their dissolution promotes not only the liberation of volatiles from pellets but also more rapid reaction of it with slag iron oxides. Briquettes of FMBUZh dissolved in the slag more rapidly than FOM prepared by sintering the original materials.

The microstructure of modifier specimens was studied in an Axioplan optical microscope from Karl Zeiss and an XL-30 electron microscope from Philips. The phase composition of modifiers is presented in Table 3.

The main mineral is periclase in all modifiers. The microstructure of FOM is a nonuniform porous structure of periclase (Fig. 1). The main mass of sintered

<table>
<thead>
<tr>
<th>Modifier</th>
<th>MgO, wt. %</th>
<th>CaO, wt. %</th>
<th>Fe$_2$O$_3$, wt. %</th>
<th>SiO$_2$, wt. %</th>
<th>C, wt. %</th>
<th>$\Delta m_{\text{pen}}$, No</th>
<th>Production method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferruginous magnesia flux (FOM)</td>
<td>80–90</td>
<td>4–10</td>
<td>4–8</td>
<td>1–4</td>
<td>No</td>
<td>1–2</td>
<td>Rotary furnace (dry method)</td>
</tr>
<tr>
<td>Magnesia flux briquetted with carbon and iron oxides (FMBUZh)</td>
<td>75–80</td>
<td>3–7</td>
<td>4–8</td>
<td>1–4</td>
<td>4–8</td>
<td>2–3</td>
<td>Briquetting of original materials with binder</td>
</tr>
<tr>
<td>Self-distributing magnesia pellets (SMG-10S)</td>
<td>50–60</td>
<td>1–3</td>
<td>No</td>
<td>1–2</td>
<td>8–11</td>
<td>30–40</td>
<td>Pelletizing of original materials in a plate-like pelletizer</td>
</tr>
</tbody>
</table>