CORROSION OF REFRACTORY MATERIALS IN IRON-CONTAINING MELTS

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Translated from Steklo i Keramika, Nos. 1 - 2, pp. 18 - 21, January – February, 1996.

The corrosion resistance of various refractory materials in an iron-containing glass melt is investigated. It is established that an increase in the melt temperature and iron concentration insubstantially affects the corrosion rate in KhATs-30 refractory but noticeably influences the rate of destruction of BK-33 refractory. The KhATs-30 and Kor-95 refractories are shown to possess much higher corrosion resistance than the other investigated refractories.

At present, a great number of glass ceramic materials with high physicomechanical properties have been synthesized with the use of waste from nonferrous metallurgy, the mining industry, ash and slag from steam power plants [1]. Though the potential range of application of these materials is rather wide, they are not produced on an industrial scale yet. One of the causes of this situation is the presence of a large amount of iron oxides (5 - 15%) in their composition. The presence of iron oxides substantially affects the processes of glass melting and shaping, decreases the thermal conductivity of melts, and intensifies their aggressive action on the refractories and electrodes when the processes are conducted in electric furnaces or in the case of additional electric heating.

The aim of the present work was to investigate corrosion of various kinds of refractories used in the glass industry in iron-containing melts.

The chemical and mineralogical compositions of the refractories are presented in Tables 1 and 2.

The investigated melt had the following composition (here and below, by weight): 50% SiO₂, 18% Al₂O₃, 22% CaO, 10% MgO, plus 0.3% Cr₂O₃, 2.5% Na₂O, and 5 - 15% Fe₂O₃ above 100%.

The corrosion resistance of the refractories was studied as a function of the temperature of the melt (1350 - 1450°C), the holding time (3 - 6 h), the depth of immersion in the melt (5 - 25 mm), and the content of iron oxides in the composition of the liquid glass (5 - 15%).

The corrosion resistance was determined by a static method by holding the specimens in a crucible with the melt. The specimens were bars 10 x 10 x 70 mm in size. The corrosion rate was calculated with the formula

\[
K = \frac{24}{\alpha \cdot \tau} \sum_{n=1}^{n} \Delta \delta_{m},
\]

where \( K \) is the corrosion rate, mm/day; \( \alpha \) is a parameter taking
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into account the attack from two opposite sides; $\tau$ is the holding time, h; $n$ is the number of cross sections in which the measurements were conducted; $\Delta \delta_m$ is the difference between the mean thicknesses of the specimen before and after the tests.

The corrosion process was investigated by the methods of petrography, x-ray spectral microscopic analysis (XSMA), x-ray phase analysis (XPA), and scanning electron microscopy (SEM).

The results of the investigation (Table 3) show that the highest corrosion resistance in iron-containing melts is exhibited by KhATs-30 and Kor-95 refractories and the lowest one is typical of molten quartz and BK-33. The corrosion resistance of Kor-95 and KhATs-30 exceeds that of molten quartz by a factor of 11 - 14.

In the investigation of the effect of the depth of immersion of the specimens in liquid glass on their corrosion (Table 4), we established that the corrodbility of refractories from molten quartz, KhATs-30, and Kor-95 is virtually independent of the depth of immersion in the liquid glass, whereas for ZS-1300 and BK-33 refractories, the effects of the surface and deep layers of the melt were different. With the depth of immersion, the corrosion rate of the ZS-1300 refractory decreases by almost a factor of 2. On the contrary, in BK-33 refractory, it increases almost three-fold. It is interesting that the changes in the corrosion rates of KhATs-30 and Kor-95 with the depth of immersion in the melt also have different tendencies, i.e., a certain increase in the first case and a certain decrease in the second.

A study of the effect of iron oxides on the corrodbility of KhATs-30 refractory showed that with an increase in the content of iron ions in the liquid glass, the corrosion increases to a certain degree. For example, the corrosion rate of KhATs-30 was 1.10 mm/day with 5% FeO, 1.19 mm/day with 10% FeO, and 1.29 mm/day with 15% FeO.

In order to determine the dependence between the corrosion rate and the melt temperature, we tested KhATs-30 refractory as the most stable and BK-33 refractory as least stable. We found out (Fig. 1) that an increase in the temperature of the melt virtually does not affect the corrosion rate in KhATs-30 (an insubstantial increase), whereas BK-33 refractory is destroyed 4 times faster.

In comparing the curves reflecting the effect of different parameters (the depth of immersion of the refractory in the melt, the content of iron oxide in the liquid glass, the temperature of the liquid glass) on the corrosion rate of KhATs-30 and BK-33, we noted the similar behavior of the curves. An increase in the parameters causes an increase in the corrosion rates of both refractories, but the intensity of the effect is different. For another pair of refractories, i.e., Kor-95 and ZS-1300, the dependence of the corrosion rate on the mentioned parameters has the opposite nature.

An analysis of the data obtained shows that the changes in the parameters affect the viscosity of the melt. This seems to be connected in the first place with the degree of oxidation of the iron. Indeed, according to the data from electron paramagnetic resonance, the surface layers of the melt are enriched with $\text{Fe}^{3+}$ and the lower layers are enriched with $\text{Fe}^{2+}$. It is known [2] that $\text{Fe}^{2+}$ considerably decreases the viscosity of the glass melt and has higher diffusivity than $\text{Fe}^{3+}$. An increase in the temperature decreases the viscosity of the melt by itself and also leads to a decrease in the degree of oxidation of the element with a variable valence.

Thus, the corrosion rate in KhATs-30 and BK-33 refractories depends on the viscosity of the melt (with a decrease in the viscosity, the corrosion rate increases), which is characteristic of the diffusion mechanism of dissolution of refractories [3]. The absence of such a dependence in Kor-95 and ZS-1300 (which are acid refractories) indicates predominance of the chemical interaction between the refractory and the melt over the diffusion process.

The data from XSMA, XPA, SEM, and petrography allow us to judge the nature of the interaction between the investigated refractories and the melt.

<table>
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<th>TABLE 4</th>
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<tbody>
<tr>
<td><strong>Refractory</strong></td>
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<tr>
<td>KhATs-30</td>
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<td>Kor-95</td>
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<td>ZS-1300</td>
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<td>BK-33</td>
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<td>Molten quartz</td>
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* At a temperature of 1450°C.