EFFECT OF ADMIXTURES OF OXYGEN ON THE OXIDATION OF IRON AND Fe–Cr ALLOYS IN LEAD MELTS

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We study the process of oxidation of Armco iron and Fe–16Cr and Fe–16Cr–1Al model alloys held in lead melts with different concentrations of oxygen for 1000h at 650°C. It was discovered that the intensity of oxidation, the structure, and phase composition of oxide layers are determined by the activity of oxygen in the liquid metal. By the methods of layer-by-layer X-ray diffraction analysis and microscopic X-ray diffraction analysis, it was shown that, for low concentrations of oxygen in lead \( (C_0 \leq 10^{-6} \text{ wt.\%}) \), a thin (1–5 μm) oxide \([\text{magnetite (Fe}_2\text{O}_4]\) film is formed on the surface of iron. If alloys are held under the same conditions, then we also observe an increase in the concentration of chromium in the subsurface layers. For higher concentrations of oxygen (up to \( 10^{-3} \text{ wt.\%} \)), a film of magnetite (with inclusions of pure lead) is formed on the surface of unalloyed iron. In alloys, under the layer of magnetite, we detect the formation of oxide layers with the same composition as a solid solution of \( \text{Fe}_3\text{O}_4 \) and \( \text{FeCr}_2\text{O}_4 \) and the structure of spinel. These layers efficiently suppress the process of penetration of lead but do not completely terminate the process of diffusion of oxygen into the bulk of the material, which eventually leads to the internal oxidation of alloy.

Admixtures of oxygen in liquid metals and metal eutectics significantly increase the rate of corrosion fracture of numerous structural materials based on iron \([1, 2]\). At the same time, systematized data about the influence of the concentration of oxygen on the corrosion resistance of iron and its alloys in high-density liquid-metal heat carriers are absent in the literature. The preliminary analysis of the kinetics of corrosion processes for Armco iron and Fe–Cr–Al alloys demonstrates that the intensity of corrosion in lead melts for saturating concentrations of oxygen of about \((6–8) \cdot 10^{-3} \text{ wt.\%}\) is very high \([3]\). The actual concentrations of oxygen in sealed heat-transfer loops with lead melt used as a heat carrier are much lower \((10^{-5}–10^{-6} \text{ wt.\%})\). Thermodynamical estimates demonstrate that the reaction of oxidation of iron may take place in a fairly broad range of concentrations, from \( 10^{-3} \) to \( 5 \cdot 10^{-7} \text{ wt.\%} \) (Table 1). In more diluted Pb–O solutions, one can expect the formation of oxides of some alloying elements (Cr, Al, Si, etc.).

Table 1. Free Energy of the Formation of Some Oxides and Pb–O Solutions at a Temperature of 650°C

<table>
<thead>
<tr>
<th>Oxide</th>
<th>( \Delta G ), kJ/g-atom</th>
<th>Pb–O solution, ( C_0 ), wt.%</th>
<th>( \Delta G ), kJ/g-atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbO</td>
<td>-123.930</td>
<td>( 10^{-3} )</td>
<td>-137.348</td>
</tr>
<tr>
<td>FeO</td>
<td>-202.930</td>
<td>( 10^{-4} )</td>
<td>-155.030</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>-293.886</td>
<td>( 10^{-5} )</td>
<td>-172.670</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-461.905</td>
<td>( 10^{-6} )</td>
<td>-190.352</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>-197.265</td>
<td>( 10^{-7} )</td>
<td>-208.033</td>
</tr>
</tbody>
</table>

The role of admixtures of oxygen in the process of oxidation of Armco iron and Fe-16Cr and Fe-16Cr-1Al model alloys was studied by the ampoule method under static conditions at a temperature of 650°C. To prevent the process of mass transfer, we used ampoules made of Armco iron or 20Kh13 steel.

Melts with various concentrations of oxygen were obtained by filling the ampoules with Sch-00-grade lead melt in two different modes (Table 2).

In the first case, lead was melted, poured into ampoules, and sealed in a pressure chamber filled with argon at 350°C. According to the formula

\[
\log C_{\text{max}} = 4.67 - \frac{5350}{T},
\]

this method of filling the ampoules guarantee the initial concentration of oxygen in the melt of about \(9 \cdot 10^{-6}\) wt.%. However, in the course of high-temperature holding, it may decrease due to the oxidation of the surfaces of the specimens and the ampoule. As soon as the ampoules are cooled, some samples of rapidly cooled lead are subjected to direct analysis for oxygen by the method of vacuum melting in a special device supplied by the Leco Corporation. The concentration of oxygen found to be lower than the limit of sensitivity of this device (\(10^{-5}\) wt.%) (Table 2).

In the second case, a powder of lead oxide was placed in ampoules with specimens prior to adding the melt. The amount of PbO was calculated from the condition of maintenance of the reaction of dissociation and establishment of the equilibrium \(\text{Pb} \leftrightarrow \text{Pb}[\text{O}]\) on the interface of lead oxide and the melt at fixed temperature and pressure for 1000 h. The experimentally measured value of the concentration of oxygen in the melt was equal to \(10^{-5}\) wt.% in good agreement with the data of numerical analysis (Table 1).

The procedures of metallographic and microscopic X-ray spectral analyses of specimens held in the melts included the analyses of the character of corrosion damage and the distribution of alloying elements and lead in the oxide film and suboxide layers. The corrosion losses were evaluated by measuring the decrement of the cross section of a specimen along the boundary of the region of penetration of a melt.

The phase composition of the surface layers of flat specimens was determined by the method of X-ray diffraction analysis performed in FeKα-radiation with a DRON-3 diffractometer. To reveal changes in the phase composition and structure occurring in the depth of the specimens, we applied layer-by-layer recording, i.e., the surface layers were consecutively abraded with microabrasive paper and the resulting cold-work hardening was removed by slight heating.

It was discovered that the kinetics of formation of surface oxide layers and the degree of corrosion damage to alloys essentially depend on the concentration of oxygen in the melts.

For low concentrations of oxygen, a very thin oxide film is formed on the surface of specimens of Armco iron for 1000 h. This conclusion is made on the basis of the analysis of diffraction spectra where the intensity of lines of \(\text{Fe}_3\text{O}_4\) oxide is extremely low against the background of the lines of the matrix of \(\alpha\)-Fe and liquid lead. The data of metallographic analysis demonstrate that oxide films are continuous but their thickness varies within the range 1–5 μm. As follows from the data of layer-by-layer phase and microscopic X-ray spectral analyses, lead is observed both on the oxide–matrix interface and in the suboxide layer, along grain boundaries, to a depth of up to 10 μm.