Effect of Fe-Cr-Al sublayer on the efficiency of aluminum oxide protective coating in a molten lead flow

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Abstract. In this work we investigated the possibility of increasing the efficiency of aluminum oxide protective coating on EP-823 steel by applying a sublayer consisted of aluminum and steel components before the coating deposition. It is shown that Fe-Cr-Al sublayer is able to prevent the steel corrosion in a molten lead flow in the case of damage of the oxide coating. In addition, the sublayer reduces the risk of delamination of aluminum oxide and slows down the transport of iron atoms from the steel towards the surface.

1. Introduction
Fuel cladding tubes of a nuclear reactor with a heavy liquid metal coolant are made of stainless steel which dissolves in a flow of lead or lead-bismuth eutectic (LBE) with an oxygen content \( C_O \sim (10^{-8} - 10^{-7}) \text{ wt.}\% \) and intensively oxidizes in this ambient at \( C_O > 10^{-6} \text{ wt.}\% \) [1-3]. Both of these scenarios cause the destruction of the cladding tubes and reduce the lifetime of the fuel elements as well as the fuel burnup level. One of the promising approaches to protecting steels from liquid metal corrosion is formation of alumina-based coating on a steel’s surface by plasma methods [4, 5], sol-gel methods [6, 7], or pulsed laser deposition technique [8, 9]. Numerous corrosion tests of aluminum oxide coatings have demonstrated that they are able to prevent both dissolution and rapid oxidation of steels in a molten lead or LBE [4-9]. However, the efficiency of these coatings is limited by the lack of self-healing ability in the case of damage, which is very likely because of the difference in lattice parameters and thermal expansion coefficients of aluminum oxide and steel, as well as the brittleness of the oxide [8, 9].

The aim of this work is to investigate the possibility of increasing the efficiency of aluminum oxide protective coating by formation of a sublayer consisting of Fe, Cr and Al on the steel’s surface before the coating deposition. The first results (500 hours) of corrosion testing of steel samples with and without Fe-Cr-Al sublayer and aluminum oxide coating are reported in this paper.

2. Experimental
Samples of ferrite-martensitic steel EP-823 (16Cr12MoWSVNbB) were cut from a tube (diameter 9.8 mm, wall thickness 0.5 mm) in the form of quaternary segments 8 mm long. Before the experiments, the samples were rinsed in an ultrasonic alcohol bath and dried.

Both Fe-Cr-Al sublayers and aluminum oxide coatings were deposited on the samples in plasma of gas discharge ignited between hot cathode and anode. Before deposition, the surface of each sample
was treated with ions of argon plasma to improve the adhesion of the deposited material to the substrate. Fe-Cr-Al sublayers were formed on the samples by deposition of atoms sputtered from steel and aluminum targets in argon plasma. During the deposition, the flux of atoms from steel targets gradually decreased, while the flux of Al atoms increased. Aluminum oxide coatings were grown on the samples by means of sputtering the aluminum targets in Ar + 7 at.% O₂ plasma. Thicknesses of both aluminum oxide coating and Fe-Cr-Al sublayer were ≈ 2 μm. The samples of the following types were prepared: (1) steel with aluminum oxide coating without Fe-Cr-Al sublayer, (2) steel with Fe-Cr-Al sublayer and aluminum oxide coating, and (3) steel with Fe-Cr-Al sublayer without coating.

Bare steel sample and the coated samples of all types were exposed to a molten lead flow in a rotary type test stand. The stand has a chamber consisted of a vertically located quartz tube (diameter 100 mm, length 970 mm, wall thickness 3 mm) and end flanges. Inside the chamber there is a quartz crucible (diameter 65 mm, length 170 mm, wall thickness 3 mm) filled with lead (about 3.6 kg) and mounted on a manipulator which allows to move it vertically. Heating and melting of lead were carried out using an inductor coiled around the chamber. The lead temperature was measured with a W-Re thermocouple. Based on this data, the heating power was regulated. The samples were mounted on the outer side surface of a cylindrical molybdenum holder attached to the shaft of an electric motor and located inside the chamber above the crucible.

Before testing, the stand was evacuated to \( P = 10^{-2} \) Torr by a scroll pump. Then, argon was fed into the stand up to atmospheric pressure. The lead was melted in a quartz crucible inside the stand and heated up to \( T = 600^\circ\text{C} \). After that, the molybdenum holder with the samples was immersed into the lead melt and rotationally driven with a frequency corresponding to their linear velocity \( v \approx 1 \) m/s relative to the melt. The corrosion test was carried out at these severe conditions (\( T = 600^\circ\text{C} \), \( v \approx 1 \) m/s) in an automatic mode for 500 hours, after which the samples were removed from the stand.

Before and after the corrosion test, the surface of each sample was analyzed by scanning electron microscope (SEM) Tescan Vega 3 and X-ray energy dispersive spectrometer (EDX) INCA-xAct (Oxford Instruments).

3. Results and discussion

3.1. Bare steel

Surface analysis of the bare steel sample exposed to a molten lead flow revealed that this sample was severely damaged, mainly from the lead flow side (Figure 1). A significant part of the sample was completely removed during the corrosion test. Huge cavities and small pits are clearly visible on the surface as well.

![Figure 1. SEM image of the bare steel sample after the corrosion test in a molten lead flow (600°C, 500 hours).](image-url)
The EDX results showed (Table 1) that the interaction of the bare steel sample with molten lead caused the increase of the oxygen concentration on most of the sample’s surface from ≈ 3 at.% to ≈ 70 at.%. Obviously, the steel was oxidized by oxygen dissolved in the lead melt. Also, elemental analysis of the surface allowed to distinguish the two types of regions on it. The first type is almost entirely composed of iron oxide, while the second type contains more chromium than iron. This observation can be interpreted taking into account that the oxide layer grown on the surface of ferrite-martensitic steel in an oxygen-saturated lead or LBE melt is known to have a two-layer structure: an external loose magnetite (Fe$_3$O$_4$) layer and an internal Cr spinel (Fe(Fe$_{1-x}$Cr$_x$)$_2$O$_4$) layer [10, 11]. The reason why we can observe the Cr-enriched surface regions is, apparently, the fragmental removal of the magnetite layer by the lead flow, which was previously observed by other researchers [11]. The sequential formation and washout of magnetite may explain the observed character of steel destruction in the lead flow.

**Table 1.** The surface composition of the bare steel sample before and after the corrosion test in a molten lead flow (600°C, 500 hours).

|                  | O, at.% | Fe, at.% | Cr, at.% |
|------------------|---------|----------|----------|
| **Before testing**       | 2.7     | 80.7     | 12.6     |
| **After testing (region 1)** | 69.7     | 27.3     | 1.8      |
| **After testing (region 2)** | 72.1     | 7.1      | 17.7     |

3.2. *Steel with aluminum oxide coating without Fe-Cr-Al sublayer*

Aluminum oxide coating deposited on the steel sample successfully protected a major part of its surface from corrosion in a molten lead flow. However, in some areas, where, presumably, a delamination of the coating occurred during the test, a number of cavities are observed, indicating a corrosion attack on the steel (Figure 2).

**Figure 2.** SEM image of the steel sample with aluminum oxide coating without a sublayer after the corrosion test in a molten lead flow (600°C, 500 hours).

The EDX results of the undamaged surface area before and after the corrosion test are presented in Table 2. According to these results, the oxygen concentration in the surface layer of the coated sample was initially low (10 at.%). After the test, this value increased, but to a lower level (≈45 at.%) than that of the bare steel (≈70 at.%). Thus, aluminum oxide succeeded to mitigate the oxidation of steel in lead. Another point that can be seen in Table 2 is that the Fe/Al ratio in the surface layer of the sample
increased from 0.1 to 0.7 during the test. This change in the surface composition indicates that a significant amount of steel components (primarily iron atoms) diffused from the steel into the coating.

Table 2. The surface composition of the steel sample with aluminum oxide coating without a sublayer before and after the corrosion test in a molten lead flow (600°C, 500 hours).

|                     | O, at.% | Fe, at.% | Cr, at.% | Al, at.% | Fe/Al |
|---------------------|---------|----------|----------|----------|-------|
| Before testing      | 10.0    | 7.5      | 1.5      | 81.0     | 0.1   |
| After testing       | 44.7    | 20.7     | 3.6      | 31.0     | 0.7   |

3.3. Steel with Fe-Cr-Al sublayer and aluminum oxide coating

When the Fe-Cr-Al sublayer was deposited onto the steel prior to aluminum oxide coating, then neither defects nor corrosion traces were observed on the sample’s surface after the exposure to a molten lead flow. Surface morphology did not change as well (Figure 3). One may assume that the sublayer reduces the level of stresses in the oxide coating arising from different lattice parameters and thermal expansion coefficients of the coating and the substrate. As a result, the risk of the coating cracking or delamination decreases.

Elemental analysis revealed that the oxidation of the sample with the Fe-Cr-Al sublayer and aluminum oxide coating in molten lead proceeds to the same extent as in the case when the coating was deposited without the sublayer (Table 3). At the same time, the Fe/Al ratio in the surface region of the former sample increased significantly less (from 0.1 to 0.2). This means that the sublayer suppresses the diffusion of iron atoms from the steel into the coating.

Table 3. The surface composition of the steel sample with Fe-Cr-Al sublayer and aluminum oxide coating before and after the corrosion test in a molten lead flow (600°C, 500 hours).

|                     | O, at.% | Fe, at.% | Cr, at.% | Al, at.% | Fe/Al |
|---------------------|---------|----------|----------|----------|-------|
| Before testing      | 13.4    | 6.8      | 1.3      | 78.5     | 0.1   |
| After testing       | 52.8    | 6.9      | 1.7      | 38.5     | 0.2   |

3.4. Steel with Fe-Cr-Al sublayer without aluminum oxide coating

The results described above confirmed the previously reported information [4-9] on the resistance of aluminum oxide coating to liquid lead and LBE. In addition, we showed that Fe-Cr-Al sublayer
reduces the risk of the coating delamination. However, it is extremely important to establish whether the sublayer will protect the steel from corrosion if local destruction of the oxide coating does occur. For this reason, Fe-Cr-Al was deposited onto the steel sample without subsequent deposition of aluminum oxide and tested in a molten lead flow. After the corrosion test of this sample a number of tiny pores were found on the sample’s surface (Fig. 4). However, no pits, cavities or other corrosion traces were observed.

![Figure 4](image)

**Figure 4.** SEM image of the steel sample with Fe-Cr-Al sublayer without aluminum oxide coating before (a) and after (b) the corrosion test in a molten lead flow (600°C, 500 hours).

According to the EDX data (Table 4), after the interaction of the sample with a molten lead flow, the oxygen content in its surface layer increased from ≈5 at.% to ≈25 at.%. This value is significantly less than that of the bare steel sample, which means that the Fe-Cr-Al sublayer effectively protects the steel from oxidation. In contrast to the previously considered samples, the Fe/Al ratio in the surface layer of the steel coated only with a sublayer did not increase, but, on the contrary, decreased (from 4.5 to 3.6). This fact indicates that upon contact of the Fe-Cr-Al structure with the oxygen-containing lead, an oxide film enriched in aluminum oxide forms on the surface and prevents further oxidation of the steel. The predominant formation of an aluminum oxide layer on the surface of the Fe-Al mixed layer is known to be thermodynamically conditioned [12, 13].

|                  | O, at.% | Fe, at.% | Cr, at.% | Al, at.% | Fe/Al |
|------------------|---------|----------|----------|----------|-------|
| **Before testing** | 4.5     | 64.1     | 16.7     | 14.4     | 4.5   |
| **After testing** | 25.6    | 50.9     | 9.0      | 14.3     | 3.6   |

### 4. Conclusion

An experimental study of the effect of Fe-Cr-Al sublayer on the efficiency of aluminum oxide protective coating during 500 hours in a molten lead flow was carried out. It was found that, upon contact with the lead flow, bare steel undergoes severe destruction from the flow side and intense oxidation over the entire surface by oxygen dissolved in lead. Aluminum oxide coating deposited onto the steel without a sublayer generally prevents the corrosion of steel, however, corrosion damage is observed in some areas, where the coating is presumably delaminated. In addition, if the sublayer is absent, the components of the steel actively transfer into the oxide coating.

It was established that Fe-Cr-Al sublayer deposited onto the steel before aluminum oxide significantly slows down the diffusion of steel components into the coating, and also reduces the risk
of the coating cracking by decrease of the stress level in it. Moreover, what is most important, upon interaction with the lead flow, Fe-Cr-Al sublayer forms a surface oxide film enriched with aluminum oxide, which prevents corrosion of steel. This means that even if the aluminum oxide coating peels off before or during the contact with lead, the steel will be protected. Thus, the use of aluminum oxide protective coating with Fe-Cr-Al sublayer promises the increase of the lifetime of fuel elements and the fuel burnup level of reactors with a heavy liquid metal coolant.

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