High-temperature gas corrosion of cast-iron sections of the EcoSöderberg cell collecting bell

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Abstract. Investigations of the structure, chemical, mineralogical and phase composition of corrosion products of cast-iron sections of the EcoSöderberg cell collecting bell were carried out. Structural features of the scale were established using electron microscopy. The mechanism of corrosion products formation in the form of loose scale was proposed and scientifically substantiated.

1. Introduction

The gas collecting bell is one of the important structural elements of electrolysis cells. At the Russian aluminum-producing enterprises it is made from cast-iron sections. The transition to a new, more efficient design of the gas collecting bell [1] led to a significant change in the conditions of its service. In particular, the temperature of gases in the central domes of the gas removal system rises to 800 °C and the temperatures of the cast-iron sections of the gas collecting bell to 600–620 °C. Together with the general tendency to increase the sulfur content in the coke used in aluminum production, an increase in temperature led to the intensification of high-temperature gas corrosion of the cast-iron sections of the gas collecting bell, reducing their durability and service life.

Anode gases, in relation to VCh cast iron (high-strength with spherical graphite), from which sections of the gas collecting bell are made, are quite aggressive, since they contain intensifying high-temperature gas corrosion fluorine compounds (HF, ≤300 mg/nm³), elemental sulfur, sulfur oxides (up to 240 – 270 mg/nm³) and vanadium, resinous substances, the main sources of which are cryolite Na₃AlF₆, products of electrolyte evaporation, anode mass. According to [2], in the general case, during the electrolysis of aluminum, the dust-gas mixture may contain gaseous components: HF, CF₄, C₂F₆, SiF₄, SO₂, SO₃, H₂S, CS₂, COS, CO₂, CO, resinous substances and solid particles: C (carbon black), Al₂O₃, Na₃AlF₆, Na₃Al₃F₁₄, K₂NaAlF₆, AlF₃, CaF₂, MgF₂.

The corrosion resistance of the sections largely depends on the structure, chemical and phase composition of the corrosion products (scale) formed on the surface of cast iron. If in the process of operation there is no destruction of the scale layer, then oxidation (metal loss) obeys the square root law.

At the initial stage, when the metal surface is not oxidized, scale formation occurs intensively, almost linearly. Further, with an increase in the operating time, the thickness of the scale increases, it...
prevents the flow of diffusion processes to a greater extent, and the intensity of scale formation decreases.

In real conditions, the destruction of the scale layer can occur, caused by various factors, which leads to a deviation of the time dependence of the burn from the square root law. It is characteristic that after the destruction of the scale layer or the violation of its continuity, intensification of fumes occurs. The most dangerous from the point of view of metal loss is catastrophic oxidation [3].

It occurs in the cases when, during the operation of the section, the scale is removed from the surface of cast iron or practically does not have a protective effect in terms of reducing the intensity of diffusion processes. In such cases, the dependence of oxidation on time obeys an almost linear law and there is no effect of slowing down scale formation.

In this regard, the study of the structure, chemical and phase composition of the corrosion products of the cast-iron sections of the gas collecting bell of aluminum electrolytic cells EcoSöderberg is relevant and of great scientific and practical importance.

2. Methods of research

In the work the study on the structure, chemical, mineralogical and phase composition of VCh cast iron corrosion products selected from the inner surface of the gas collecting bell sections after operation was performed. Investigations (X-ray phase, chemical, spectral analyzes and optical microscopy) were carried out in the collective use center “Material Science” of Siberian State Industrial University.

The microstructure and chemical composition of the corrosion products were investigated using a scanning electron microscope (SEM, TESCAN VEGA 3) and electron microprobe analysis (EMPA, OXFORD AZtec) at MISiS National Research Technological University.

3. Analysis of the research results

The analysis of the study results shows that the corrosion products mainly consist of iron oxides and alloying elements of cast iron, however, a number of samples are characterized by the presence of an increased content of C (up to 4.3%), Al (up to 4.2%), Na (up to 5.62 %), K (up to 3.08%), S (up to 3.32%). X-ray phase analysis confirmed the presence of iron oxides Fe$_3$O$_4$ – magnetite, Fe$_2$O$_3$ – hematite, revealed the presence of potassium, sodium, aluminum, fluorine-containing compounds Ka$_2$NaAlF$_6$ – elpazolite and Na$_2$MgAlF$_7$ – weberite.

The scale has a pronounced layered structure, contains a large number of defects in the form of pores and cracks (figure 1). The layers differ in chemical, phase composition and macrostructure (figure 2, table 1). All studied samples are characterized by cyclic alternation of relatively dense layers of iron oxides Fe$_2$O$_3$ and Fe$_3$O$_4$ and more porous interlayers between them.

![Defects in the microstructure of scale.](image)
The interlayers are characterized by a high content of C and F. Sulfur is distributed fairly evenly over the thickness of the scale. Carbon in the form of small graphite plates is found in scale. A distinctive feature of the investigated samples of scale is high defectiveness, friability, the presence of a large number of pore cracks, discontinuities, low adhesion to the oxidized surface of cast iron. This is a consequence of the content in the scale of various phases and compounds having different coefficients of thermal expansion.

The cyclic changes in the temperature of the section during operation lead to the appearance of structural and phase stresses in the scale contributing to its loosening. It is important that when the section temperature changes from 220 to 620 °C on the surface of cast iron in the scale at temperatures above 560 – 570 °C, a layer of wustite is formed, which decomposes into iron and magnetite at lower temperatures, the cyclicality of this process adversely affects the continuity and protective properties of scale. The source of carbon in the layers of scale is also a gas atmosphere, which as a result of the reaction of interaction of molten aluminum with CO:

\[ 4\text{Al} + 6\text{CO} = 2\text{Al}_2\text{O}_3 + 6\text{C} \]
\[ 2\text{CO} = \text{CO}_2 + \text{C} \]

as one of the products contains C in the form of graphite or soot forming coal foam [4].

**Table 1.** The composition of scale (wt.%).

| Spectrum name | C  | O  | F  | Na | Al | Si | S  | V  | Mn | Fe | Cu | Total |
|---------------|----|----|----|----|----|----|----|----|----|----|----|-------|
| Spectrum 64   | 8.51 | 31.2 | 3.06 | 0   | 0   | 0.19 | 1.6 | 0   | 0   | 54.98 | 0.47 | 100   |
| Spectrum 65   | 7.07 | 33.06 | 2.79 | 0.04 | 0   | 0.18 | 1.38 | 0   | 0.37 | 55.11 | 0   | 100   |
| Spectrum 66   | 8.2 | 30.41 | 5.1 | 0   | 0   | 0.13 | 1.91 | 0   | 0   | 54.25 | 0   | 100   |
| Spectrum 67   | 18.16 | 14.16 | 24.99 | 0 | 0.16 | 0.14 | 2.91 | 0.01 | 0   | 39.47 | 0   | 100   |
| Spectrum 68   | 9.74 | 28.18 | 9.62 | 0.03 | 0   | 0.12 | 1.21 | 0.03 | 0   | 51.06 | 0   | 100   |
| Spectrum 69   | 12.24 | 12.41 | 18.26 | 0   | 0   | 0.11 | 1.21 | 0   | 0   | 55.35 | 0.42 | 100   |
| Spectrum 70   | 8.91 | 32.1 | 3.07 | 0   | 0   | 0.07 | 1   | 0   | 0   | 54.22 | 0.64 | 100   |
| Spectrum 71   | 15.3 | 22.65 | 15.78 | 0   | 0   | 0.04 | 1.71 | 0   | 0   | 44.51 | 0   | 100   |
| Spectrum 72   | 10.91 | 11.36 | 32.01 | 0   | 0   | 0.09 | 2.01 | 0.04 | 0   | 43.52 | 0.05 | 100   |

The presence of carbon scale in the interlayers is associated, among other things, with parallel processes of decarburization of cast iron in a gaseous medium containing oxidizing and reducing components. According to the data of [5, 6], as a result of decarburization, the oxide film can partially recover, become loose and thin, its expansion and formation of growths filled with soot carbon are observed.

Figure 3 shows the proposed dynamics and mechanism of high-temperature gas corrosion of the cast-iron sections of the gas collecting bell. The initial state (figure 3 a) corresponds to the microvolume of the new section, the surface of which is not covered with scale. During operation,
under the influence of a temperature less than 570 °C and an oxidizing medium, a scale of hematite and magnetite forms on the surface of cast iron (figure 3 b).

Further, due to structural, phase, and thermal stresses, cracks, chips, and other discontinuities are formed in the mill scale (figure 3 c). The intensification of their formation is facilitated by the phenomena of cast iron growth, cyclical changes in the temperature of the section, and an increase in the thickness of the scale. Discontinuities open the contact of the surface of cast iron with the atmosphere.

The atmosphere, including solid particles, in particular carbon, for example in the form of soot or graphite, penetrates into the cavity in which these particles are deposited on its walls, and aggressive oxidizing gases form a new layer of hematite and magnetite on the surface of cast iron (figure 3 d), and magnetite surrounding the cavity is oxidized to hematite. In this case, the cavity itself with a different chemical and phase composition, when the section temperature changes, begins to play the role of a strong stress concentrator and the cracks formed in it serve as next channels for the penetration of the oxidizing atmosphere (figure 3 f).

Figure 3. Diagram of the dynamics and mechanism of high-temperature gas corrosion of cast-iron sections of gas collecting bell.

Thus, in the macrovolume, the formation of such cavities and discontinuities repeatedly leads to the formation of loose scale on the surface of the section. Under the influence of gravity and gas flows, partial collapse of loose scale occurs, which further intensifies scale formation.

The transition to a temperature range of more than 570 °C and further cooling are important. Under such conditions, a three-layer scale is formed containing wustite, which decomposes upon cooling. This process causes additional stresses that contribute to the violation of the protective properties of scale [7]. The presence of carbon in the cavities under certain conditions promotes the occurrence of reduction processes, for example, the restoration of hematite to magnetite.

Fluorine-containing and sulfur-containing components of the atmosphere are unconditional intensifiers of high-temperature gas corrosion and an increase in their content in gases in contact with the cast-iron sections of gas collecting bell leads to their more rapid destruction.

4. Conclusion
The study of the structure, chemical, mineralogical and phase composition of the corrosion products of the cast-iron sections of EcoSöderberg cell collecting bell was carried out. The mechanism of the
corrosion products formation in the form of loose scale was proposed and scientifically substantiated. At 
the first stage, during operation, under the influence of a temperature of less than 570 °C and an 
oxidizing medium, a layer of scale from hematite and magnetite is formed on the surface of cast iron. 
Further, cracks, chips, and other discontinuities are formed in the scale due to structural, phase and 
thermal stresses. The intensification of their formation is facilitated by the phenomena of cast iron 
growth, cyclical changes in the temperature of the section, and an increase in the thickness of the 
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Discontinuities open the contact of the cast iron surface with the atmosphere. The atmosphere, 
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formation of such cavities and discontinuities repeatedly leads to the formation of loose scale on the 
surface of the section.

Under the influence of gravity and gas flows, a partial collapse of the “fur coat” occurs, which 
further intensifies scale formation. Upon transition to a temperature zone of more than 570 °C and 
further cooling, a three-layer scale containing wustite is formed, which is destroyed upon cooling. This 
process causes additional stresses that contribute to the violation of the protective properties of the 
scale. The presence of carbon in the cavities under certain conditions promotes the occurrence of 
reduction processes, for example, the restoration of hematite to magnetite.

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