High Temperature Corrosion of Prebaked Anode Steel-structure for Aluminium Reduction

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Abstract. The industrial production of primary aluminium in Hall-Héroult electrolysis cells, where alumina (Al₂O₃) is dissolved in a molten fluoride-containing electrolyte consisting mainly of cryolite (Na₃AlF₆) at about 960°C. In a modern aluminium electrolysis cell several prebaked carbon anodes are dipped into the electrolyte, and oxide ions from the dissolution of alumina are discharged electrolytically onto the anodes as an intermediate product. Anode steel-structure is an important part of prebaked carbon anode type cells, which is an assembly unit for connection of carbon anode and aluminium guide rod. Anode steel-structure is always used in a bad environment of high acid and high temperature for a long time. Therefore, the anode steel-structure can just be used in a limited time because of the corrosion of acid. Furthermore, liquid aluminium can be polluted by corrosion layer, which results in the decrease of the quality of aluminium ingots. Thus, it is very important to find out the corrosion mechanism of the anode steel-structure. So this paper will investigate the anticorrosion mechanism of high-temperature corrosion of prebaked anode steel-structure for aluminium reduction.

1. Introduction
Aluminum is one of the most commonly used metallic elements. Due to its high corrosion resistance and mechanical strength to mass ratio, aluminum alloys are used as a major structural material in aircrafts, buildings, machinery parts, beverage cans, and food wraps.

Aluminum production is accomplished in two processes: the Bayer process for refining bauxite ore to obtain aluminum oxide, or alumina, and the Hall–Héroult electrolytic process for smelting the alumina dissolved in cryolite to produce pure aluminum metal. Molten electrolytic process is the only method of primary aluminum production. The raw material in the Hall–Héroult process are consumed according to the stoichiometric ratio predicted. This consumption theoretically amounts to 1.89 kg of Al₂O₃ per kg Al produced and it should then react with 0.33 kg of carbon producing 1.22 kg of carbon dioxide. In practice the typical values are 1.93 kg of Al₂O₃ per kg and 0.40-0.45 kg C per kg Al, which produces about 1.5 kg of CO₂ [1].

With the economical development, the society need more and more aluminum. Aluminum production consumes a lot of energy. In 2016, aluminum production consumed more than 420 billion kW·h in China, produced 3.9 million tons of carbon dioxide. So energy saving is one of the important work of China's aluminum industry.

Steel stub is the main structure of prebaked carbon anode in aluminium electrolysis production, connect between the carbon and bus, carrying large current, the current density to up to 10A/cm². The conductance of steel stub directly affects the current efficiency and the direct current consumption in
In the production of primary aluminum process, the gas carbon dioxide, carbon monoxide (CO), carbon tetrafluoride (CF₄), dicarbon hexafluoride (C₂F₆) and the molten cryolite-alumina salt electrolyte will corrosion anode steel stub, lead the conductive area of steel stub decreases, the current distribution of aluminum electrolytic cell is not reasonable, increase cell voltage, affect the current efficiency, and lead to fracture of anode carbon block. Due to the high temperature corrosion of anode steel structure, when the average current efficiency is 90%, if cell voltage increase 5mV, the direct current consumption in aluminum electrolysis production will increase 17 W·h per kg Al. An annual output of 300 thousand tons of electrolytic aluminum plant will increase power consumption by 500 million kW·h per year.

Therefore, the research of high temperature molten salt corrosion protection mechanism of prebaked anode steel structure is important, will reduce and inhibit the high temperature corrosion, reduce cell voltage, improve current efficiency, reduce the consumption of aluminum electrolysis production.

2. Component and Assembly of Prebaked Anode Steel-structure

In this paper, high temperature corrosion mechanism of prebaked anode steel structure in a 400kA pot is studied. Steel stub of prebaked anode is steel casting, which chemical compositions are given in Table 1.

| Component | C  | Si  | Mn  | S   | P   | Ni  | Cr  | Cu  | Mo  | V   |
|-----------|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| w/%       | 0.25 | 0.60 | 1.00 | 0.035 | 0.035 | 0.40 | 0.35 | 0.40 | 0.15 | 0.05 |

Improve current efficiency and reduce energy consumption will require the pots to maintain good heat balance, and prevent prebaked anode oxidation, alumina and solid aluminum electrolyte mixture are used to cover the prebaked anode (Figure 1). Therefore, the steel beam that not covered by the mixture material is easily corroded by high temperature mixed gas, while the stub covered by the mixture material can be corroded by the molten salt and high temperature mixture gas.

2.1 Analysis of High Temperature Corrosion Morphology

In the production of primary aluminum process, the high temperature gas will corrosion steel beam of prebaked anode. At the girder of the stub, appeared obvious high temperature oxidation (Figure 2), some red-filmed corrosion products layer having 0.5cm or less thickness are observed. Which are hard and dense iron oxides (FeO, Fe₂O₃ and Fe₃O₄) [2-4].

![Figure 1 Cover Morphology of Prebaked Anode and Steel Structure](image-url)
2.2 Analysis of High Temperature Corrosion Mechanism
In the process of aluminum electrolysis, CO₂, CO, HF, SO₂, asphalt gas and other mixed gases are produced. The temperature of mixed gas is about 150 °C, main components are shown in Table 2.

During the production process, the temperature of the steel beam is about 200 ~ 300 °C, and the mixed gas can react with the steel beam of the anode structure, will corrosion the steel beam.

Table 2 emission of components in the flue gas of aluminum electrolysis (kilogram / ton-aluminum)

| component | HF  | CO₂ | CO  | SO₂ | CF₄ | dust |
|-----------|-----|-----|-----|-----|-----|------|
| w/%       | 9~15| 1000| 300 | 5~15| 2   | 20~100 |

By thermodynamic calculation under normal production conditions, the above reaction can occur:

\[
4Fe + 3O_2 = 2Fe_2O_3
\]

\[
3Fe + 2O_2 = Fe_3O_4
\]

\[
4Fe + 3SO_2 = 2Fe_2O_3 + 3S
\]

\[
3Fe + 2SO_2 = Fe_2O_3 + 2S
\]

\[
4Fe_2O_3 + O_2 = 6Fe_2O_3
\]

\[
3Fe + 2CO_2 = Fe_3O_4 + 2C
\]

\[
4Fe + 3CO_2 = 2Fe_2O_3 + 3C
\]

\[
2Fe + 3CO = Fe_3O_4 + 3C
\]

\[
3Fe + 4CO = Fe_2O_4 + 4C
\]

From the above reaction analysis, it is known that the high temperature gas corrosion of the steel beam mainly generates Fe₂O₃ and Fe₃O₄, and corrosion product is mainly Fe₂O₃, shows filmed corrosion products layer.

3. Analysis of High Temperature Corrosion Mechanism of Vertical Column

3.1 Analysis of High Temperature Corrosion Morphology
In the industrial production of primary aluminum process, the temperature of the steel column is about 400°C~ 600°C. At the vertical column of the steel, which corrosion by the molten electrolyte, and reduce the diameter of the steel, descend the conductance (Figure 3).

The macroscopic appearance of the corrosion products and the delamination products of the steel column is shown in Figure 4. Part of them appear brown red, and some white spots in the middle part.
Some are yellow brown with obvious layered structure.

Figure 3 High Temperature Corrosion Macroscopic Morphology

Figure 4 Macro Morphology of High Temperature Corrosion Layered Peeling Products

In order to study the high-temperature corrosion mechanism of the columns, the corrosion products are analyzed by SEM-EDX. Figure 5 and table 3 show the steel column suffers corrosion at the surface. The oxide layers are extension spall, consist of the mixed F, O, Na and Fe, etc. So high temperature corrosion of the steel column is the molten cryolite-alumina salt corrosion.
Table 3 Content of Main Elements of High Temperature Corrosion Products (%)

|       | C     | O     | F     | Na    | Al    | S     | Mn    | K     | Ca    | Fe    | Totals |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|
| 6a    | 1.36  | 31.36 | 23.49 | 12.33 | 21.43 | 2.67  | 0     | 0.14  | 2.10  | 5.11  | 100    |
| 6b    | 0.94  | 25.35 | 26.18 | 18.15 | 15.54 | 4.24  | 0     | 0     | 0.66  | 8.94  | 100    |
| 6c    | 0     | 14.11 | 43.23 | 11.56 | 6.72  | 0     | 0.27  | 0.19  | 0.38  | 23.54 | 100    |
| 6d    | 0     | 10.71 | 49.55 | 14.66 | 8.85  | 0.22  | 0     | 0.28  | 0.31  | 15.41 | 100    |

3.2. Analysis of High Temperature Corrosion Mechanism

In the process of primary aluminum production, the steel column is covered the mixed material of alumina and aluminum solid electrolyte. Because of raw materials (alumina, carbon anode, fluoride salts) sources of diversity, and aluminum electrolyte composition is very complex [5-6]. The typical electrolyte components of the 400kA aluminum electrolysis are shown in Table 4.

Table 4 Chemical Composition of Aluminum Electrolyte System

| component | Al₂O₃ | AlF₃ | NaF | LiF | MgF₂ | KF | CaF₂ |
|-----------|-------|------|-----|-----|------|----|------|
| w/%,      | 2.77  | 40.41| 49.32| 0.79| 0.85 | 1.42| 4.44 |

In production conditions, the steel column can react with the high temperature mixture gas, and generate Fe₂O₃ and Fe₃O₄. By thermodynamic calculation, the cast carbon steel can also react with the fluoride (MFₓ) in the molten salt system of aluminum electrolyte as follows:

\[ Fe + MF_x \rightarrow FeF_3 + M \]  (10)

\[ Fe + MF_x + O_2 \rightarrow FeF_3 + M_2O_x \]  (11)

From the above reaction analysis, we can know that the high temperature gas and the molten salt electrolyte will corroision anode steel column, produced Fe₂O₃, Fe₃O₄ and FeF₃, so that the columns of the steel column are continuously corroded and thinned.

4. Conclusion

Aluminum alloys are used as a major structural material in aircrafts, buildings, machinery parts, beverage cans, and food wraps, and the Hall–Héroult electrolytic process for smelting the alumina dissolved in cryolite to produce pure aluminum metal.

In the production of primary aluminum process, the high temperature gas will corrosion steel beam of prebaked anode, produced some red-filmed corrosion products layer, which are hard and dense iron oxides (FeO, Fe₂O₃ and Fe₃O₄).

The high temperature gas and the molten salt electrolyte will corrosion anode steel column, produced Fe₂O₃, Fe₃O₄ and FeF₃, so that the columns of the steel column are continuously corroded and thinned.
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