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Pilot study of mechanism of property-modified anode in aluminum electrolysis①

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Abstract: On the basis of serial laboratory research and industrial test, the mechanism of saving energy and reducing carbon consumption of property-modified prebaked anode in aluminum electrolysis was discussed. It is considered that the anodic over voltage is affected by the concentration of carbon monoxide surrounding anode. The property-modified prebaked anode can restrain the production of carbon monoxide. The reason of reducing carbon consumption was also analyzed, the result shows that besides physical action, chemical action also exists in the process where additives change the reaction rate of anodes.

Key words: aluminum electrolysis; prebaked anode; additive
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1 INTRODUCTION

Aluminum metallurgy adopts the method of high temperature melt salt electrolysis developed one hundred years ago. In the process of research and development in this field, physical chemistry, electrochemistry, material science, roboticized technology and so on were combined with aluminum metallurgy techniques, making the basic principle of the Hall-Heroult process being more deeply realized by people. Further more, this technology was developed constantly and became more and more perfect in order to further save energy, reduce raw material consumption and increase current efficiency.

In the researching field of aluminum electrolysis, carbon anode is important for its special status in production. The anodic performance affects not only the unit cost of aluminum electrolysis, but also the living circumstance, then the type of aluminum electrolysis cell was transformed from Söderberg cell to prebaked anode cell[1, 2]. Moreover, the research of new type anode such as inert anode is put in forth[3-5]. Of course, anodic performance-modifying is still important before inert anode can not be used in industrial production.

The technology of anodic additive can effectively improve the physical, chemical and electrochemical performance of the anode. Remarkable economic coefficient and social benefits had been obtained when this technology was used in Söderberg cells ten years ago. As the Söderberg cells were translated into prebaked-anode ones, the research of anode additive technology was still one of the focuses to which researchers paid attention.

The authors has finished the laboratory study and industrial test of property-modified prebaked anode in aluminum electrolysis, and obtained good results. In this article, some data obtained from laboratory study and industrial test were combined to conjecture the mechanism of the additives.

2 ENERGY SAVING OF PROPERTY-MODIFIED ANODE

The reason why this type of anode has effect on reducing anodic overvoltage is as follows[6, 7].

Property-modified materials will create corresponding compounds after being baked at high temperature. Because their chemical computation, valent state, electronical structure and surface state are different, each shows special function of electro-physics and electro-catalysis. They all distribute on the surface or infiltrate into interior of electrode and create more active center by any possibility. According to the theoretics of modern electrochemistry, the anodic reaction process of aluminum electrolysis can be divided into five steps:

$$O^{2-} \rightarrow O_{(ad)} + 2e \quad (1)$$

$$O_{(ad)} + xC \rightarrow C_xO \quad (2)$$

$$O^{2-} + C_xO \rightarrow C_xO \cdot O_{(ad)} + 2e \quad (3)$$

$$C_xO \cdot O_{(ad)} \rightarrow CO_{2(ad)} + (x-1)C \quad (4)$$

$$CO_{2(ad)} \rightarrow CO_2 \quad (5)$$

Because the ions to discharge increase when the current density becomes large, but the intrinsic active

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centers are not enough, the ions containing oxygen in molten electrolyte will be forced to discharge in the place with lower activity, therefore the intermediate compound (C_xO) will be created. Just because of the creation of intermediate compound, it must need additional energy for reactions (2) and (4) to process slowly, so the overvoltage will be created. When some catalyzers with certain characteristic are imported from the outside of electrode, the active center distributing on the surface of electrode will increase, therefore, the creation of C_xO will be restrained effectively. On the other hand, the catalyzers are propitious to the adsorption and discharge of the ions containing oxygen, and can accelerate the exchange and transfer of electron, so the decomposing rate of C_xO will be accelerated. As a result, the anodic overvoltage is reduced.

In reactions (1)−(5), if the value of x is 1, the C_xO will exist in the form of CO, for the same reason, it also need additional energy to create CO and decompose $CO \cdot O_{(ad)}$. The overvoltage will be created due to the additional energy and change with the content of carbon monoxide in molten salt.

During the test, the gas analytical method was used to measure current efficiency. The contents of carbon monoxide, carbon dioxide and oxygen in testing and contrasting cells were measured as shown in Table 1. The results show that the concentration of carbon monoxide in testing cells are generally lower than those in the contrasting ones. The relationship between anodic overvoltage and the concentration of carbon monoxide were also studied in laboratory. The results show that both the anodic overvoltage contrast anodes (U7) and property-modified anodes (M7) increase during electrolysis, but the difference is that the property-modified anodes have better effect in resisting carbon monoxide than the contrasting ones. For example, when the current density is 0.75 A/cm^2, the dispersion of overvoltage between contrasting anode(U7) and property-modified anode(M7) increases from 23 V(without bubbling CO) to 57 V(bubbling CO).

Table 1 Contents of carbon monoxide, carbon dioxide and oxygen in testing and contrast cells (mass fraction, %)

Time	Type of cell	CO_2	O_2	CO
1	Testing cells	80.1	1.6	16.2
	Contrasting cells	79.0	1.5	17.5
2	Testing cells	79.7	1.6	18.7
	Contrasting cells	77.6	1.6	20.8
3	Testing cells	78.8	1.8	18.4
	Contrasting cells	74.5	1.3	20.2
4	Testing cells	76.6	1.2	18.2
	Contrasting cells	75.8	1.8	18.9
5	Testing cells	74.9	1.8	18.0
	Contrasting cells	78.7	1.8	19.4
	Average of testing cells	78.0	1.6	17.9
	Average of contrast cells	77.1	1.6	19.4

3 REASON FOR REDUCING CARBON CONSUMPTION OF PROPERTY-MODIFIED ANODE

In the precondition of which physical performance of carbon anodes is determinated, the consumption rate of carbon anode in the process of electrolysis is influenced to a large degree by inorganic impurities contained in anode, such as V_2O_5, Fe_2O_3, Na_2CO_3. Two general mechanisms have been proposed so far to account for the diversified catalytic effects of these impurities during carbon oxidation reaction. This theories can be broadly classified as oxygen-transfer mechanism and electron-transfer mechanism.

The electron-transfer mechanism was used by Barton, Harrison and Sykes to explain the factor of influencing anode consumption rate. This theory assumes a redistribution of π-electrons, a weakening of the C—C bonds at the edge site of the carbon basal plane, and an increase in C—O bond strength when the catalyzed oxidation reaction occurs. The chemisorption of oxygen is controlled by electrons distributing on a double electrical layer on the carbon surface. Impurities which influence the kinetics of carbon oxidation can be divided into three classes: 1) electron donors, such as alkali metals, which form positive ions on the carbon surface, decrease the potential energy barrier to oxygen chemisorption, and accelerate carbon oxidation; 2) electron acceptors, such as halogens, which form negative ions at the surface, increase the potential energy barrier, and act as oxidation inhibitors; 3) transition metals, which accept electrons into their unfilled d-bands and thereby produce active sites on carbon surface and increase the rate of oxidation. This kind of explaination accords with the result obtained by adding additives containing fluorin to anode, the fluorin forms negative ions on the surface of anode, which increases the potential energy barrier to oxygen chemisorption, restrain carbon oxidation, and finally, gains the ends of reducing anode consumption.

The oxygen-transfer mechanism was applied by Walker[10] to explain carbon oxidation. The theory considers that, as the carriers of oxygen on the surface of carbon, additives react as catalysis or anti-catalysis in the process of carbon oxidation:

$$2M_2O + O_2 = 2M_2O_2 \quad (6)$$

$$2M_2O_2 + C = 2M_2O + CO_2 \quad (7)$$

Therefore, M_2O express additives with catalysis or anti-catalysis.

This catalysis exists in two aspects, one is catalyzing the baking process of anodes, the other is catalyzing oxidation reaction of anode. In the process of baking, the additives react with anode and form another substance, or embed into the carbolic crystal lattice directly and form layer-compound. The new substance reacts as catalysis (or anti-catalysis) in the process of carbonization of pitch.

Both petrolic coke and pitch belong to the substance with many holes, the carbon anodes are with many holes (the hole rate of prebaked anode is 14%－18%). The reaction process of anode and carbon dioxide is the same as the model of gas-solid reaction with many-holed solid, the reaction process includes three steps: 1) mass-transfer of gas; 2) diffuseness of holes; 3) chemical reaction on the surface of solid. From the point of physical mechanism, pitch will go through four steps such as melting, decomposing, shrinking and coking and form loose-structure pitch coke in the process of being baked, additives are packed by pitch and disperse equally in interior of pitch, the holes of pitch are jammed by additives and the reaction of mass-transfer of gas is baffled, the activity reaction of pitch coking is depressed at the end. On the other hand, additives only bestrew on the surface of the petrolic coke, and the resistance of chemical reaction is increased, so the additives will have less influence on the activity of petrolic coke. According to the theory, the balance between pitch coking and activity of petrolic coke can be kept by adding additives to anodes, then the selective oxidation of anodes will be reduced and the consumption of carbon will be slowed down.

However, it is unable to explain the experimental result that the content of additives have influence on pitch carbonized. In laboratory study, when the content of additives increased, the reaction activity of carbonized pitch was not depressed gradually all the times. For example, one of the additive components (coded name AO) was added into pitch powder of 0－5% (mass fraction), the agravic rate of pitch carbonization was considered. Fig. 1 shows the relationship between reactive activity of CO_2 and the content of AO during pitch carbonization.

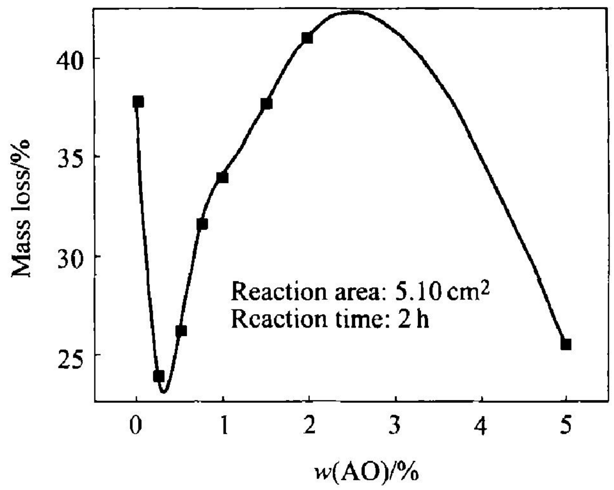

Fig. 1 Relationship between reactive activity of CO_2 and content of AO during pitch carbonization

Fig. 1 shows that the influence of AO on agravic rate of pitch carbonization presents certain rule with the increasing of additives. When the content is 0.2%－0.5%, the reactive activity of pitch carbonization reduces markedly and the mass loss becomes the least. Along with increasing content of AO, the agravic rate of pitch increases gradually, when the mass fraction of AO is 1.8%, the rate is accordant with that of the contrasting one (without containing AO). The reactive activity arrives the peak value when the content is 2.5%－3%, then it turns to go down with the continue increasing content, that's to say, when the content of AO exceeds a certain range, the mass loss of pitch carbonization will keep in a relatively balanceable range.

So it can be concluded that chemical effect also exists in the influence of additives on reaction activity of anode besides physical effect. Of course, deeper laboratory study should be done in order to prove whether the additives have influence on the pitch coking process or the carbon oxidation. Comparing the examining results between property-modified anodes and contrasting ones prepared in factory, we can discover that the surface structure of property-modified anodes is compact, the holes and protruding grain on the anodes reduce, and the quantity of brushing off (including naturally and forcibly) reduces markedly, comparing with the contrasting anodes.

In a word, it is difficult to deeply discuss the reaction mechanism of additives on pitch coking, petrolic coke and anode on the basis of present lab researching result, the successful experiment obtained in industrial test will be used to perfect mechanism research in lab, and the technique of additive may be more mature.

4 CONCLUSIONS

1) The value of anodic overvoltage is concerned with concentration of carbon monoxide formed around anode, the property-modified anode can effectively resist the production of carbon monoxide.

2) There exists chemical effect in the influence of additives on reaction activity of anode besides physical effect. It still need deeper lab study that additives

influence on either the pitch coking process or carbon oxidation.

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