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RESEARCH OF CO-OPERATION FOR ALUMINIUM WITH CRYOLITE-ALUMINOUS ELECTROLYTE

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Solubility of aluminium and sodium in an electrolyte has been determined and as well as speed of aluminium losses at the expense of dissolution in an electrolyte has been defined by experiment. The mechanism of metal losses at the electrolysis of aluminium has been offered. Dependence between the metal losses and output on a current has been established.

Keywords: electrolyte, electrolysis, solubility of aluminium and sodium, mechanism of losses for aluminium, output on a current

One of reasons of cathode metal losses is partial dissolution of aluminium in an electrolyte. According to modern presentations [1], the process of dissolution for aluminium in a cryolite-aluminous electrolyte is carried out by the reactions of cooperation of aluminium with his fluoride with formation of sub-fluoride of aluminium and exchange of sodium fluoride and aluminium by fluorine. Sub-fluoride of aluminium and sodium are dissolute in an electrolyte is carried by convective streams to the anode, where oxidize dioxide of carbon on reactions:

$$3AlF + 3CO_2 \Leftrightarrow Al_2O_3 + AlF_3 + 3CO \; ; \tag{1}$$

$$3Na + 1{,}5CO_2 \Leftrightarrow 1{,}5Na_2O + 1{,}5CO \; . \tag{2}$$
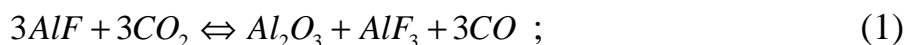
The size of different losses of cathode metal is estimated as follows [2]: dissolution of aluminium in an electrolyte – 5-8 %; renewal of sodium – 2-3 %; electronic conductivity – less than 2 %; renewal of admixtures – a less than 1 %. Loss of aluminium at a teem usually does not exceed 2 %.

Determination of mass for aluminium losses with an electrolyte does not give an idea of mechanism of process. More complete idea of physical and chemical processes, flowing in electrolysis bath, allows to get the results of researches for speed of metal losses.

Speed of dissolution of aluminium in a cryolite-aluminous electrolyte was determined with using kinetic curves of the declines of clean aluminium drop mass in contact with an electrolyte, and also on results the analysis of gas mixture, got after propagation of carbon dioxide above fusion «electrolyte - metal». Experiments realizated in the interval of temperatures 970-1050 °C in the atmosphere of carbon dioxide at cryolite relation $CR = 2.0\text{-}2.8$.

Speed of mass aluminium losses $V_{l,Al}$ was expected on a formula:

$$V_{l,Al} = \frac{\Delta m}{S \cdot \tau} \; , \tag{3}$$

where Δm is the measured mass loss for drop of aluminium; S is a surface of drop, $S = 20.6 \cdot 10^{-4}$ м^2; τ it is time of fusion soaking in the atmosphere of carbon dioxide

($\tau = 1$ hour, at the relation of mass of drop and electrolyte 3.0 made and with $CR = 2,5$.

Metal losses are the result of the parallel flowing of three processes: dissolutions of aluminium in an electrolyte; disparaging of metallic aluminium in an electrolyte, and also oxidizations of aluminium and foods of his dissolution in an electrolyte at the expense of anodic gases.

By-turn, the process of dissolution includes the reactions of formation of aluminium sub-fluoride and metallic sodium at the border of division «metal - electrolyte», molecular diffusion and convective transfer for foods of these reactions to the anode, and also their oxidization by carbon dioxide of anodic gases.

The process of disparaging of metallic aluminium, except for formation of suspension of metal, foresees the convective transfer of metallic fog drops and their oxidization on an anode by carbon dioxide with the receipt of aluminium dioxide (Al_2O_3). Finally, the process of oxidization at the expense of anodic gases is included disparaging of gas phase on an anode, convective transfer of anodic gas bubbles and oxidization of aluminium and foods of his dissolution by carbon dioxide with the receipt of Al_2O_3, CO and C.

A transport stage - molecular diffusion and convective transfer of colution and metallic aluminium to the anode – is limiting stage and it presented in all processes. Applying the first law of Fik to the transfer of metal, get expression for the aluminium losses:

$$\Delta m = \frac{D \cdot (C_0 - C)}{S} , \qquad (4)$$

where D is a coefficient of diffusion for colution aluminium; C_0 and C are accordingly concentration of aluminium on a border «metal - electrolyte» and on outer side of diffusive layer; S is a thickness of diffusive layer.

From equation (4) it is follows that the metal losses increase with the increase of temperature process and speed of electrolyte circulation.

Accepting, that the basic aluminium losses are related with his dissolution in an electrolyte and transporting from a cathode to the anode, it is possible to write down equation for the stream of solution aluminium $p*$:

$$p* = K_S \cdot (C* - C_p) \cdot S = \frac{D}{S_N} \cdot (C* - C_p) \cdot S , \qquad (5)$$

where K_S is a constant of mass transfer speed; $C*$ is solubility of aluminium in an electrolyte; C_p is a concentration of aluminium, soluting in an electrolyte; S is an area of metal; D is a coefficient of aluminium diffusion in an electrolyte; S_N is a thickness of diffusive layer of Nernst.

A constant of mass transfer speed K_S is the function for conditions of convection on an interphase border and it can be expected on an empiric formula [3]:

$$K_S = \frac{220}{J} \cdot D^{0,67} \cdot V^{0,83} \cdot \mu^{-0,5} \cdot \ell^{-0,17} \cdot d^{0,5} , \qquad (6)$$

where V is a speed of motion of border «metal - electrolyte»; μ it is dynamic viscidity; ℓ is distance between poles; d is a closeness of electrolyte.

From expressions (5) and (6) is follows, that for diminishing of metal losses it is necessary to limit the area of interphase a «metal - electrolyte», to decrease circulation of metal in bath and his dispergation, and also to take to the minimum solubility of metal in an electrolyte.

In general view dependence between the metal losses and output on a current it is possible to present expression:

$$B_C = 1 - \frac{\Delta m}{q \cdot j_K} \ , \tag{7}$$

where B_C is an output on a current; Δm are metal losses with one cm^2 of surface for cathode on one hour; q is an electrochemical equivalent of aluminium ($q = 0.3355 \cdot 10^{-3}$ kg/A·h.); j_K is a cathode closeness of current, $j_K = 0.7$ A/cm^2; q·is an amount of aluminium, appearing in theory.

Then get:

$$B_C = 1 - \frac{\Delta m}{0,0284} \ . \tag{14}$$

Using the experimental values of aluminium mass loss, and also a formula (14) is found $B_C = 0.85 = 85$ %, that corresponds to the real values of output on a current and specifies on possibility of application of this formula.

LIST OF LITERATURE

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