

INTERFACIAL PHENOMENA AT BOUNDARIES OF MOLTEN ELECTROLYTE-CARBON ELECTRODE-LIQUID METAL IN ALUMINIUM ELECTROLYSIS CELL(PART I)^①

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ABSTRACT Some important interfacial phenomena in aluminium electrolysis, such as wettability of anode and cathode, initiation of anode effect and metal dissolution in molten electrolyte have been dealt with. They have significant influences on the energy consumption and current efficiency in aluminium production. The primary reason for the initiation of anode effect may be the anodic repulsion to the molten electrolyte, and the direct reason may be due to an electrostatic attraction of gases by the anode at high anodic potential.

Key words aluminium electrolysis molten electrolyte carbon electrodes

1 WETTABILITY OF CARBON ANODE AND CARBON CATHODE BY MOLTEN ELECTROLYTE

The wettability of carbon electrodes by molten salts is quite different when the electrodes are polarized than when they are not, because of the variation of the surface state of the electrodes, as well as the ionic concentration of the liquid layer adjacent to the electrodes during the electrolysis process. The laboratory microelectrolysis cell is shown in Fig. 1.

When the carbon plate was cathodically polarized, the molten drops gradually spread out on the carbon plate after several minutes of electrolysis, and tended to separate from the anode. This caused an interruption in electrolysis. However, the spread molten drops often collected together automatically and touched the anode again, then the electrolysis resumed (Fig. 2).

When the carbon plate was anodically polarized, good wettability of the carbon rod (now it was cathode) by the molten drop was observed. The wettability of the carbon anode due to the evolution of gases became poor, then the electrolyte even coalesced into a globe. At this mo-

ment, an anode effect occurred (Fig. 3 and 4). Sometimes, most of the melt adhered to the cathode (carbon rod) and separated from the carbon plate anode. These phenomena were cor-

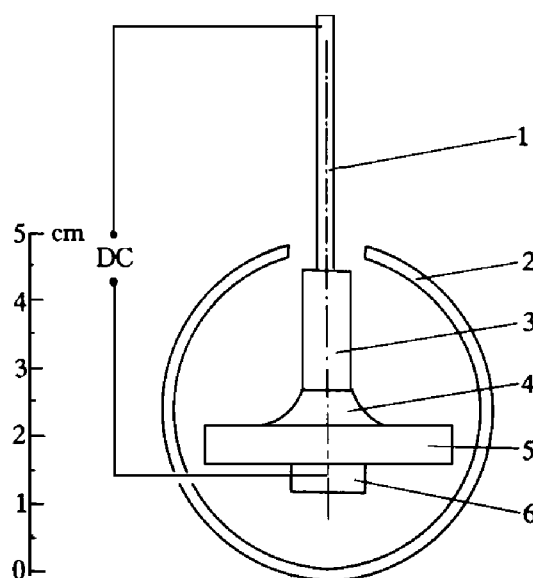


Fig. 1 Schematic diagram of the microelectrolysis cell

1—Ni-Cr wire conductor; 2—stainless steel tube (dia 45 mm, l 600 mm); 3—carbon rod (dia 8 mm); 4—molten electrolyte; 5—carbon plate (δ 5 mm); 6—steel support

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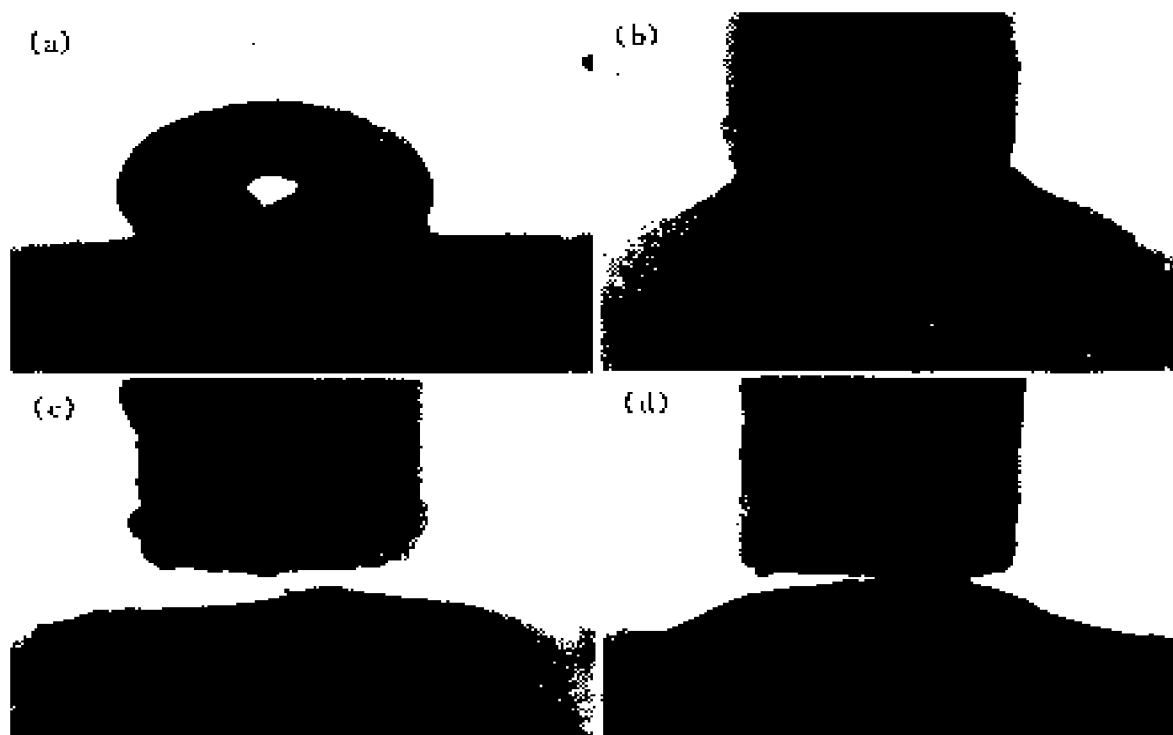


Fig. 2 Wetting phenomena of carbon electrodes

carbon rod anode, carbon plate cathode, CR= 2.75, Al_2O_3 = 5.5% (in mass), 1 000 °C;

after melting (a), electrolysis started (b), electrolyte spread

on the cathode plate and separated from the anode rod (c),

electrolyte collected and touched the anode again (d)

sistent with that in the previous case.

When a platinum wire loop was used instead of carbon as an anode or a cathode, similar phenomena were observed. The wettability of platinum by the molten cryolite-alumina electrolyte was originally very good, but when it was used as anode and a carbon plate as cathode, after a D. C. was applied, the molten electrolyte would be repulsed by the anode and separated from it, due to an evolution of oxygen gas on it. After a while the electrolyte would touch the anode again. There appeared a cyclic process of electrolysis-repulsion-electrolysis. When platinum wire loop was used as cathode and the carbon plate as anode, the electrolyte would be attracted by the cathode, and an anode effect was observed on the anode carbon plate. The Pt loop would shake vigorously.

So both carbon and platinum electrodes showed the same behaviour of repulsing the electrolyte when being anodically polarized, this

phenomenon is called “Anodic Repulsion”; and attracting the electrolyte when being cathodically polarized, this phenomenon is called “Cathodic Attraction”^[1].

The anodic repulsion may be the primary reason for the anode effect, and the cathodic attraction may be the fundamental reason for the impregnation of molten electrolyte into the carbon cathode.

2 ANODE EFFECT

Some characteristics of the anode effect in aluminium electrolysis may be described briefly as follows:

(1) When an anode effect occurred in one cell, the cell voltage was with high frequency (about 10 000 to 20 000 Hz); the electric sparks were twinkled, they appeared first at some places, then at other places; the carbon anode and aluminium bus-bar were vibrated.

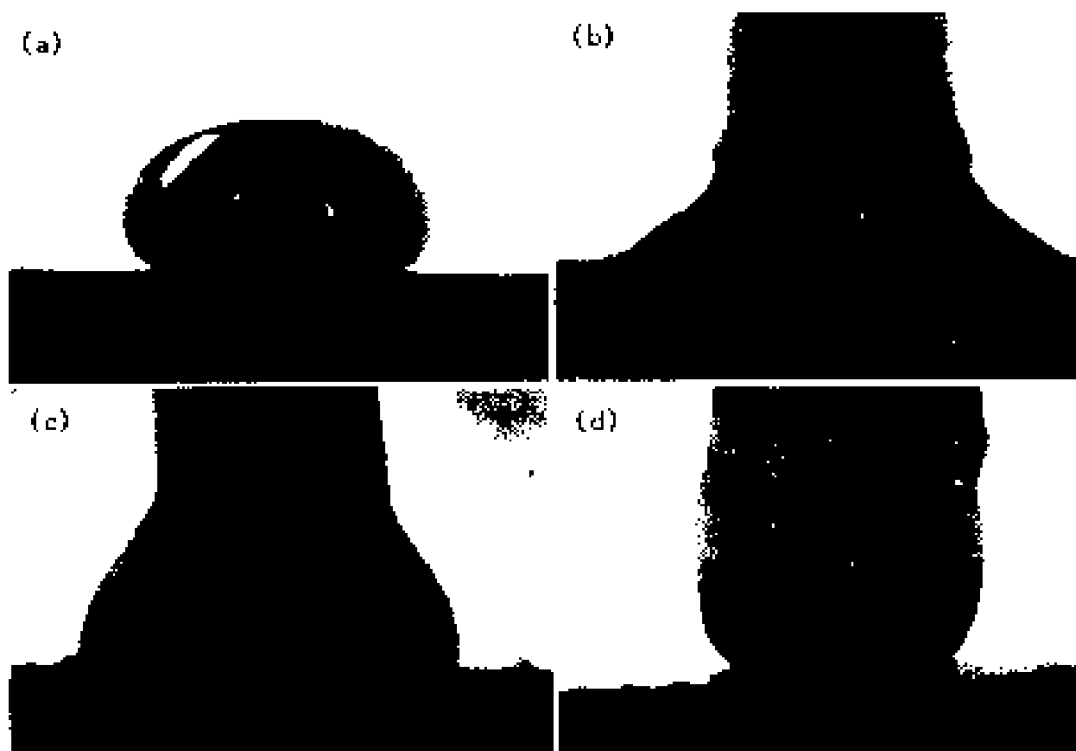
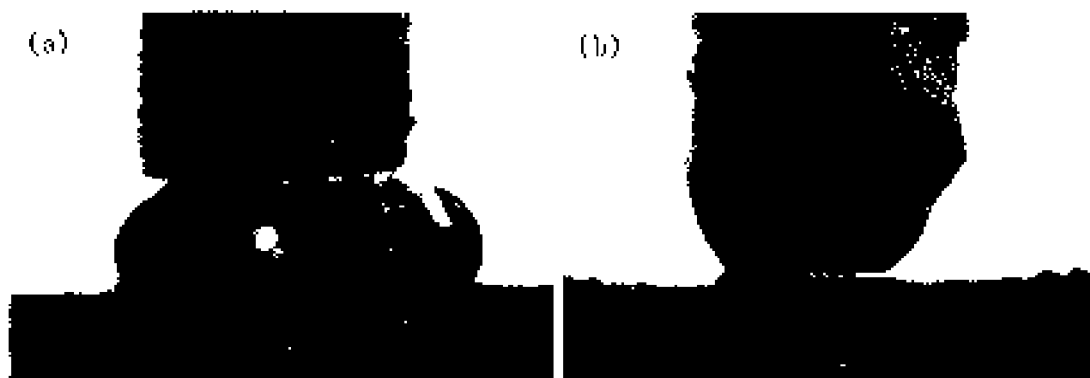


Fig. 3 Wetting phenomena of carbon electrodes

CR= 2.75, Al_2O_3 = 5.5% (in mass), 1000 °C, carbon rod-cathode, carbon plate-anode;
after melting (a), electrolysis started (b),
electrolysis was going on (c), electrolyte coalesced (d))



**Fig. 4 Anode effect occurred when carbon rod was anode (a),
and carbon plate was anode (b)**

(2) From measurement of voltage-time curves of industrial cells by oscillography, it revealed that according to the curve characteristics there are three stages in the anode effect: initiation stage, stable voltage stage and termination stage^[3] (see Fig. 5, for the normal electrolysis, ordinate 1 V per scale unit, abscissa 1 ms per scale unit; for the three stages of anode effect, ordinate 5 V per scale unit, abscissa 1 ms per

scale unit).

(3) The anode gas composition changed suddenly when an anode effect occurred. During normal electrolysis the anode gas usually consisted of 75% ~ 80% CO_2 and 20% ~ 25% CO. When an anode effect occurred, the gas composition changed to 25% CO_2 , 50% CO, 22.5% CF_4 and 2.5% C_2F_6 . This fact implies that there happens a change in anodic reaction from

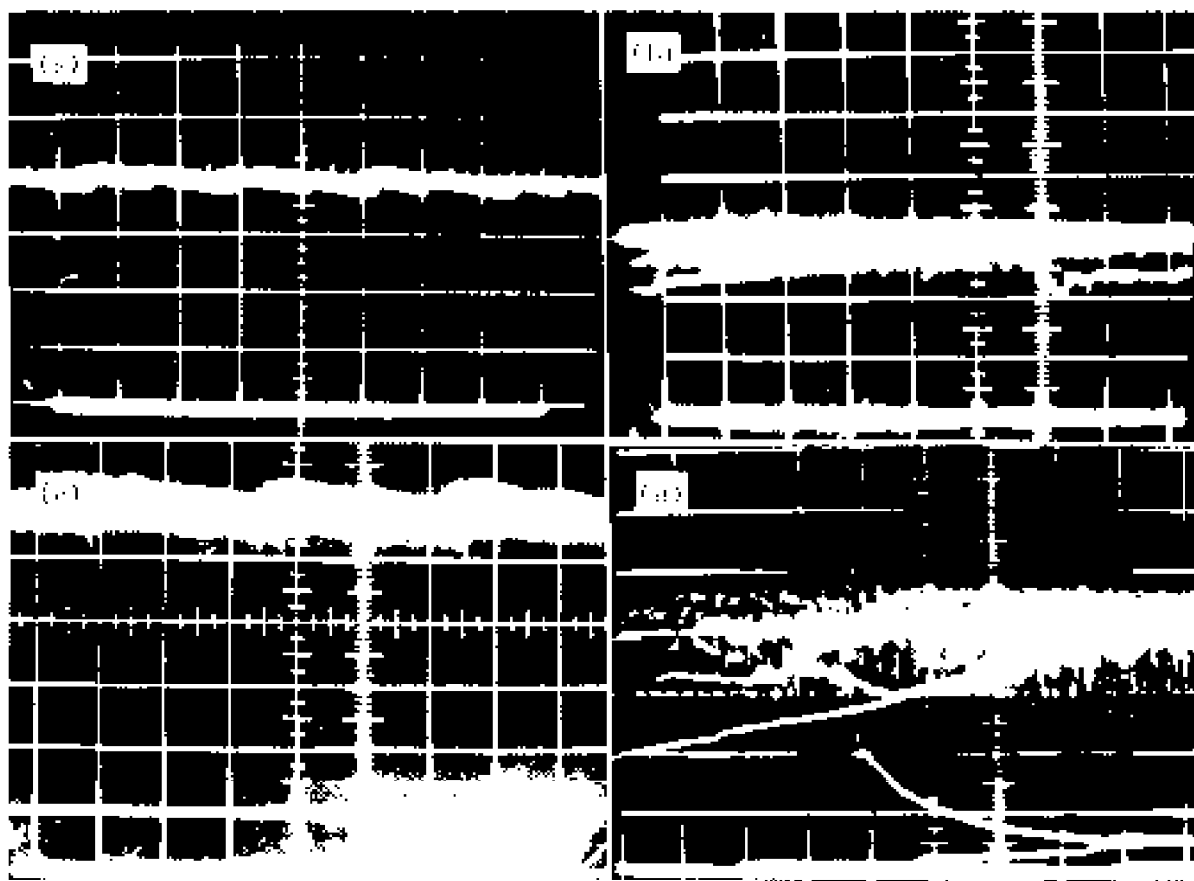


Fig. 5 Voltage waves during an anode effect in an industrial aluminium electrolysis cell with prebaked anodes operated at 130 kA

(a) —normal electrolysis; (b) —initiation stage of anode effect;
(c) —stable voltage stage of anode effect; (d) —termination stage of anode effect

the discharge of oxygen ions to co-discharge of oxygen and fluorine ions.

(4) During the anode effect, there was a jet action from the anode bottom surface when the cell voltage was over 20 V. From jet actions it was observed that there were minute gas bubbles injecting from the carbon anode into the molten bath, causing a violent stirring in the interpolar space. The jet action from the carbon anode was found in molten PbCl_2 as well as in molten cryolite-alumina salts. The reason for the jet action may be due to an expansion of anode gases at high temperature during anode effect. However, this jet action is harmful to current efficiency because the stirring action of these gas bubbles would cause much liquid metal on the cathode to be reoxidized (see Fig. 6).

It was found in a see-through cell that during normal electrolysis in cryolite-alumina melts the anode gas bubbles could leave the carbon an-

ode freely, but when the electric current density was raised to the critical value, the gas bubbles on the anode would be tightly pulled up and stuck on the whole anode surface to form a thin continuous film, at that time an anode effect occurred. The anode gases were already ionized and attracted electrostatically by the carbon anode. When the current was cut off, the gas film contracted all at once to form a single bubble which stayed on the undersurface of the anode.

From the above facts we can infer that the direct reason of anode effect may be related to the electrostatic attraction of ionized gas bubbles by the anode. This is due to the newly formed gases, such as CF_4 , C_2F_6 and CO , which are more easily polarized and can be attracted electrostatically by the anode at high potential. This gas film sticks firmly on the anode surface and penetrates into the pores and fissures of the carbon anode.

The above viewpoint may be confirmed by the appearance of electric sparks on the anode during the anode effect. In industrial cell, the



Fig. 6 Jet action from carbon anode during the anode effect in cryolite-alumina melts
(right —carbon anode;
left —carbon cathode)

carbon anode is very big. It may be 12 m^2 in one piece. During the anode effect, the gas film is not actually continuous, which may be in shape of a network. At the boundaries of gas bubbles there are some electrolyte. The electric sparks first appear at some locations, then they move to other places. So the electric sparks are twinkling. The occurrence of electric sparks means ionization of gas bubbles. When the electric charges of gas bubbles are neutralized in some p-

laces, there the electric sparks will disappear.

In industrial cells, for quenching the anode effect we usually make the anode and cathode short-circuited for a short time, i. e., by splashing the negatively charged liquid aluminium in the cell to the anode, so that the electric charges on the gas bubbles can be neutralized. This is a support for the electrostatic attraction theory.

Therefore, the primary reason for the initiation of anode effect may be the anodic repulsion to the molten electrolyte, and the direct reason may be due to an electrostatic attraction of gases by the anode at high anodic potential^[4, 5].

The anode effect also occurred on gold and platinum anodes in molten cryolite-alumina melts at very high current densities, the reason of its initiation may be explained as above stated.

When gases are evolved on cathode, there may appear cathode effect. Therefore, the gas evolution on electrodes is obviously the common reason of anode effect or cathode effect.

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