CORROSION MECHANISM OF SnO_2–BASED INERT ANODES①

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ABSTRACT

According to the extent of their damage in cryolite melts, the corrosion of SnO_2–based inert anodes can be divided into three types: slight corrosion, marked corrosion and catastrophic corrosion. The conditions under which these three types take place and their mechanisms are different. Our work shows that depletion of oxygen containing ions in melts, high density, electrolyte penetration into the electrode and intergranular corrosion contribute greatly to marked corrosion and catastrophic corrosion and that the reduction reaction by aluminium only attacks the electrode slightly.

Key words: SnO_2–based inert anodes corrosion corrosion mechanism aluminium eletrolysis

1 INTRODUCTION

The corrosion resistance of the inert anode is one of its most important performance, because it is not only related to its service time, but also to the metal quality. It can be said that the corrosion resistance of an inert anode is one of the key factors, which determines whether if it can be used in Hall-Heroult cell for aluminium production.

Some work has been done on what influences the corrosion rate of inert anodes. However only several hypotheses on the corrosion mechanisms were proposed, and fewer experimental studies have been conducted[1–8]. Obviously, the further study of this topic will be helpful for understanding the corrosion mechanisms and improving the performance of inert anode, as well as for adjusting the operaton parameters to extend their service times. Based on the available literature, we did several supplemented experiments to further investigate the corrosion mechanisms of the SnO_2–based inert anode.

2 POSSIBLE CAUSES OF CORROSION OF THE SnO_2–BASED INERT ANODES

Based on available experimental results and thermodynamic calculations, several possible corrosion mechanisms for SnO_2–based inert anodes in molten cryolite melts were proposed.

2.1 *Reductive Reaction*

Because tin has a greater positive electrode potential than dissolved aluminium, sodium and aluminium monofluoride, the tin oxide tends to be reduced. These reactions can be expressed as follows:

$$SnO_2 + 4/3Al = Sn + 2/3Al_2O_3 \qquad (1)$$

$$\Delta G^{\circ}_{950℃} = -534.76\ kJ$$

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$$SnO_2 + 2AlF = Sn + 2/3Al_2O_3 + 2/3AlF_3 \qquad (2)$$

$$\Delta G^{o}_{950℃} = -395.13\ kJ$$

$$SnO_2 + 4Na = Sn + 2Na_2O \qquad (3)$$

$$\Delta G^{o}_{950℃} = -163.35\ kJ$$

If there are no kinetic obstacles, the above reactions are autokinetic. Static corrosion tests[7, 8] indicated that the electrode corrosion rate in the presence of aluminium is 6~ 65 times as fast as that in the absence of aluminium. It is also thought that the anodic polarization and the oxygen bubbles evolved by anodic reactions around the anode could inhibit the approach of aluminium and other reducing species dissolved in the bath to the anode surface. Therefore the corrosion rate would be slower. A set of experiments have been carried out to verify the above hypothesis. The results are shown in Table 1. The SnO_2− based anodes in this study were of the same composition and similar properties.

Table 1 The corrosion rate of the SnO_2−based electrodes under different conditions

Test No	Experimental conditions	Electrolyte compositions	Corrosion rate* / $g \cdot cm^{-2} \cdot h^{-1}$
1	no Al, no polarization, no Ar bubble	C. R. 2.8, $Al_2O_3$8%, CaF_2 4%, MgF_2 4%, 960℃	9.183×10^{-4}
2	Al present, no polarization, Ar bubble	C. R. 2.8, $Al_2O_3$8%, CaF_2 4%, MgF_2 4%, 960℃	2.165×10^{-3}
3**	Al persent, polarization, Ar bubble	C. R. 2.8, $Al_2O_3$8%, CaF_2 4%, MgF_2 4%, 960℃	4.942×10^{-3}
4	Electrolysis, $D_{anode} = 1A/cm^2$, Duration of runs, 4 h	C. R. 2.8, $Al_2O_3$8%, CaF_2 4%, MgF_2 4%, 960℃	7.795×10^{-3}
5	Electrolysis, $D_{anode} = 2A/cm^2$, Duration of runs, 4 h	C. R. 2.4, LiF8%, CaF_2 4%, MgF_2 4%, Al_2O_3 4%	1.278×10^{-2}

* The corrosion rate was measured according to the method in ref [6], and the data listed above are the average value of several experimental results.

* * So-called polarization means switching on the DC supply, but the anode potential is less than the oxygen evolution potential in the case where the current approaches zero.

Table 1 shows that the corrosion rate in the presence of Al is four times larger than in the absence of Al and that the anodic polarization does not decrease the corrosion rate, and that under the same conditions, the corrosion rate markedly increases with the current density. It will be necessary to further verify whether the oxygen bubbles evolved from anodic reaction can decrease the corrosion rate. However, the corrosion of anodes by the reductive reaction is slight($10^{-3} g/cm^2 \cdot h^{-1}$) and is affected by mass transfer.

2.2 *Fluorination*

The SnO_2−based anodes were fluorinated in the cryolite melt possibly as follows:

$$SnO_2 + 4/3AlF_3 = SnF_4 + 2/3Al_2O_3 \qquad (4)$$

$$\Delta G^{o}_{950℃} = 115.6\ KJ$$

The equilibrium constant can be expressed as

$$K = \frac{a_{SnF_4} \cdot a^{2/3}_{Al_2O_3}}{a^{4/3}_{AlF_3}} = 1.155 \times 10^{-5}$$

Assuming $a_{SnF_4} = 1$, i. e. SnF_4 is satuarted in melt, when the cryolitic ratio is 2.2, $a_{AlF_3} = 1.827 \times 10^{-3}$, then

$$a_{Al_2O_3} = 1.31 \times 10^{-13}$$

According to Dewing formula, we have

$$a_{Al_2O_3} = (C/C_s)^{2.77}$$

If $C_s = 0.045$, then

$$C_{Al_2O_3} = 1.006 \times 10^{-6}$$

which indicates that only when the concentration of alumina is lower than 1.006×10^{-6}, can the fluorination be automatic and attain equilibrium at once with little alumina production. However, when the electrode is anodized and electrolyzed, especially with a high current density, an utterly different situation occurs. As the oxgencontaining ions are continuously consumed in electrolysis and depleted in the melt layer near the anode, it is possible that the concentration of alumina near the anode could attain or be lower than 1.006×10^{-6}. Then the above reaction would proceed continuously, and the reaction could be read as follows:

$$SnO_2+4F^{-}-4e=SnF_4+O_2\uparrow \qquad (5)$$

or

$$SnO_2+4/3AlF_3=4/3Al+O_2\uparrow+SnF_4 \qquad (6)$$

$$\Delta G^{\circ}_{950℃}=974.1\ kJ$$

The standard electromotive force for the reaction is

$$E^{\circ}=-2.52\ V$$

At a current density of $1A/cm^2$, the over potential for O_2 evolution at the SnO_2–based anodes is about 0.1 V. Hence the actual decom- position voltage above is about 2.62 V, while the actual decomposition voltage of alumina is about 2.3 V. The potential difference between them is about 0.32 V, which can be easily attained. According to the calculation, when the concentration of alumina is lower than 1.75×10^{-5}, the decomposition voltage can also attain 2.62 V, under which circumstances Al_2O_3 and SnO_2 would simultaneously decompose. The SnO_2–based inert anodes would quickly be subjected to damage, which explains why the static corrosion rate of the SnO_2–based electrode is very small. Once electrolysis began, the corrosion rate increased abruptly as the current density increased. Recently, the steady state polarization curves and the corrosion experiment in pure cryolite for the SnO_2–based anodes made by Xiao Haiming *et al*[9] verified the above hypotheses.

Some of the SnF_4 produced from reaction (5) was evapoated, and the rest reacted with alumina to produce SnO_2 again.

$$SnF_4+2/3Al_2O_3=SnO_2+4/3Al_3 \qquad (7)$$

$$\Delta G^{\circ}_{950℃}=-115.6\ kJ$$

The SnO_2 precipitated from the above reaction was needle-like, which can be seen in the corresponding SEM photos. Otherwise, SnF_4 reacted with NaF to SnF_5 as

$$SnF_4+NaF=Na_2SnF_5$$

$$\Delta G^{\circ}_{950℃}=-1{,}652.9\ kJ$$

2. 3 *Wetting and Penetration of Electrolyte in to Electrodes*

The microstructure of the SnO_2–based electrode is clearly shown in Fig. 1. The cracks among particles are about 0.3~ 1 μ, which makes penetration by electrolytes possible.

The penetration of electrode by electrolytes is closely related to wet ability. The wetting angle of the electrolyte to the SnO_2–based anodes was determined in different Al_2O_3 concentrations, as shown in Fig. 2.

Fig. 1 SEM morphology of the SnO_2–based electrode

Fig.2 shows that the wetting of the SnO_2–based electrode by cryolite-alumina melts is excellent. Whatever the Al_2O_3 concentration is, the melts can wet the whole electrode at quite high speed.

Excellent wetting of the SnO_2–based electrode by cryolite melts and capillary action made it possible for cryolite melts to penetrate the inside of the electrode and gradually fill in the cracks and holes among the SnO_2 particles, which resulted in a lack of ties among the particles and disintegration of tiny SnO_2 particles into the electrolyte. Under unfavorable conditions, such as low alumina concentration, high LiF concentration and high current density, the disintegration would proceed more quickly.

Then the electrode would disintegrate and disappear in a few minutes, so it was called catastrophic corrosion. The penetration of the electroed by the electrolyte resulted in the disintegration is shown in Fig. 3.

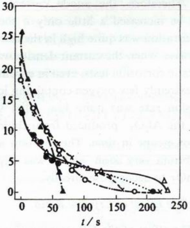

Fig. 2 The wetting angles (θ) of the SnO_2–based electrodes by cryolite-alumina melts as a function of time (t) at 1,012 ℃. Alumina concentration (wt.–%):

●—0.0; △—0.5; ○—1.0; ×—2.0; ▲—5.0.

The sample in Fig. 3 was made by the following procedures. After electrolysis ended, the electrode was not taken out but cooled with the furnace. Then, the electrode was fetched with electrolyte to be cut open vertically, and a SEM photo of the boundary between the electrode and electrolyte was taken. The white parts in Fig. 3 indicate the bulk and a piece of the SnO_2–based electrode, and the black are electrolyte. The disintegration of SnO_2 from the bulk electrode may be produced by reacting SnF_4 with Al_2O_3.

2.4 *Electrode Disintegration Due to the Selective First Solution of* CuO

Out of all the constituents of the SnO_2–based elecctrodes, only fluorination of CuO has a negetive standard Gibbs energy, i. e. the following reaction automatic.

$$2CuO + 4/3AlF_3 = 2CuF_2 + 2/3Al_2O_3 \quad (8)$$

$$\Delta G^{o}_{950℃} = -92.8\ kJ$$

The electrode sample in the SEM photo displays a marked depletion of Cu near the electrode surface[6]. The selective first solution of CuO enlarges the cracks and holes among the SnO_2 particles and finally causes disintegration of the electrode because the CuO was used as a binder in the SnO_2–based electrode.

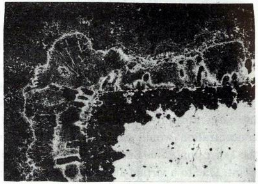

Fig. 3 The vertical section SEM morphology of the electrolyzed SnO_2–based electrode.

Electrolysis conditions: CR = 3; $C_{Al_2O_3}$ = 1wt.–%; i = 1A / cm²; T = 1,030 ℃; t = 4.25 h.

3 THE FACTORS INFLUENCING THE CORROSION RATE OF THE SnO_2–BASED INERT ANODES

3.1 *The Effect of* Al_2O_3 *Concentration*

The effect of Al_2O_3 Concentration on corrosion rate is shown in Fig. 4.

The curves in Fig. 4 can be divided into three sections. The Al_2O_3 concentration in section CD is more than 4% of saturation. Under that condition the corrosion rate of the electrode is very small, and a change in Al_2O_3 concentration has no remarkable effect on the corrosion rate, which indicates that only if there are enough oxygen-containing ions to be transfered close to the anode, the SnO_2–based electrode would be stable. Reduction increases the corrosion rate only a little as Al_2O_3 concentration

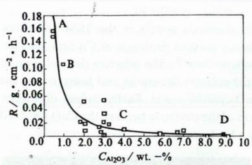

Fig. 4 The effect of Al_2O_3 concentration $C_{Al_2O_3}$ on corrosion rate R of SnO_2−based inert anodes. CR = 2.8, 1A / cm^2.

decreases. The Al_2O_3 concentration in section AB is lower than 1 % and the corrosion rate increases abruptly. A tiny change in Al_2O_3 concentration would cause strong effects on the corrosion rate. SnO_2 is unstable at that point. Due to a virtual absence of oxygen-containing ions, especially since the Al_2O_3 concentration in the diffusion layer near the electrode is lower than 10^{-6}, the flurorination and even slight decomposition of SnO_2 would occur, and the oxygens are escaped almost from SnO_2. Section BC is a transition section. A change in the Al_2O_3 concentration would produce a marked effect. The decrease of the Al_2O_3 concentration not only preceeds the reduction, but also starts the flurorination of the electrode. In the mean time, one of the oxygen escaping from the anode reaction came from oxygen-containing ions in melts, and the other from SnO_2.

3. 2 *The Effect of Current Density*

The effect of current density of the corrosion rate is shown in Fig. 5.

The first three samples were studied at a current density of $0 \sim 2A / cm^2$, and there were a minima at $0.5A / cm^2$ and $1A / cm^2$. Xiao Haiming studied the effect of current density to a greater extent. The above results together show that if the current density is larger than $1A / cm^2$, the corrosion rate increases abruptly as the current density increases. High current densities caused a greater depletion of oxygen-containing ions in the electrolyte near the electrode, and made SnO_2 fluordize or decompose. Therefore, the anode current density could be increased a little only if the Al_2O_3 concentration was quite high in the electrolyte. Otherwise, when the current density was zero, i. e. static corrosion tests, even in cryolite melts with extremly few oxygen-containing ions, the corrosion rate was quite low. That was because the Al_2O_3 produced from fluorination did not escape in time. The reaction attained equilibrium very soon, and it was impossible for SnO_2 to decompose directly.

3. 3 *The Effect of Cryolite Ratio*

The effect of the CR on corrosion rate of the SnO_2−based electrode is shown in Fig. 6.

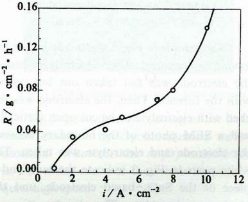

Fig. 5 The effect of the current (i) density on the corrosion rate (R) of the SnO_2−based electrodes

Reference resources: 1—Xue Jilai; 2—Wang Huazhang; 3—Cai Qifeng; 4—Xiao Haiming

The results in Fig. 6 show the corrosion rate increases as the CR decreases in acid electrolyte, when the CR decreases, the activity of AlF_3 increases, and the fluordination proceeds. In the meantime, a decrease in the CR reduce the solubility of Al_2O_3, limits the increase of oxygen-containing ions in melts and strengthens the penetration of electrolyte, so further studies are needed.

3. 4 *The Effect of LiF Concentration*

When the LiF concentration in the electrolyte is lower than 4 %, the corrosion rate of SnO_2– based electrodes is very slow, while at LiF concentrations greater than 8%, the corrosion rate increases abruptly[6].

4 CORROSION MECHANISMS OF SnO_2– BASED INERT ELECTRODES

The corrosion of the SnO_2–based elect-rode can be divided into three types: slight corrosion, serious corrosion and catastrophic corrosion. The differences among them are shown in Fig.7.

The three electrodes were of the same length before the experiment. Slight corrosion is visible in Fig. 7(a), and the corrosion rate is 0.0061 $g / cm^2 \cdot h$. Serious corrosion is in Fig. 7(c), where the corrosion rate is 0.03$g / cm^2 \cdot h$. Catastrophic corrosion is in illustrated Fig. 7(b), where the corrosion rate is 11 $g / cm^2 \cdot h$. The corrosion conditions and mechanisms of corrosions are different as shown in Table 2.

Table 2 The conditions and mechanisms of the three corrosions

	slight corrosion	Serious corrosion	Catastrophic Corrosion
Corrosion rate $/ g \cdot cm^{-2} \cdot h^{-1}$	0.001～0.01	0.01～0.1	0.1～10
Electrolysis conditions	Al_2O_3 conc.4% up to sat. C. R. 3±0.2 i<1A / cm^2 LiF<4%	Al_2O_3 1～4% C.R. <2.6 i:1～2A / cm^2 LiF 4～8%	Al_2O_3<1% C. R.<2.2 i>2A / cm^2 LiF >8%
Corrosion mechanism	Reduction	Reduction Fluorodization Penetration of electrolyte Corrosion between crystals	Penetration of electrolyte Corrosion between crystals Strong fluorodization Direct decomposition of SnO_2

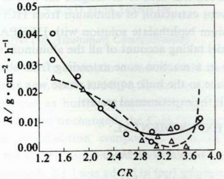

Fig. 6 The effect of the cryolite ratio (CR) on the corrosion rate (R) of the SnO_2–based anodes

Reference resources: △—Wang Huazhang

○—Xiao Haimig

The destruction due to catastrophic corrosion is very great and will be absolutely forbiden in industrial applications of inert anodes in the future. It must be stated that catastrophic corrosion can only occur when subjecting a SnO_2–based electrode to electrolysis and other conditions such as extremely low Al_2O_3 concentration or high LiF concentration, So far, it

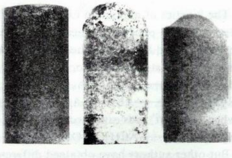
(a) (b) (c)

Fig. 7 The corrosion of the SnO_2–based electrode under different electrolysis conditions

(*To be continued on page* 20)