

# ZnFe<sub>2</sub>O<sub>4</sub> 基材料在 NaF-AlF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> 熔盐中的腐蚀

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**摘要:** 采用锌铁尖晶石材料作为铝电解惰性阳极, 考察了这种阳极在 NaF-AlF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> 熔盐中的腐蚀行为, 阳极电流密度为 0~2.5 A/cm<sup>2</sup>. 实验结果表明, 锌铁尖晶石材料在阳极极化条件下的 NaF-AlF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> 熔盐中具有很好的耐腐蚀性能. 在低电流密度下, 阳极材料的腐蚀速度随电流密度的增大而增大, 最高的腐蚀速度出现于 0.5~0.75 A/cm<sup>2</sup>. 此后, 腐蚀速度随电流密度的增大而降低. 实验证明, 高阳极电流密度(>1.5 A/cm<sup>2</sup>)、熔盐电解质中保持高 Al<sub>2</sub>O<sub>3</sub> 含量和低 NaF/AlF<sub>3</sub> 摩尔比, 对降低阳极材料的腐蚀速度有利, 这也将是惰性阳极应用的重要条件.

**关键词:** 锌铁尖晶石 尖晶石材料 铝电解 惰性阳极

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## 1 Introduction

Spinel structural material is known very corrosion resistant in molten salts. In the research work of inert anode for aluminum electrolysis, many investigations were focused on the substitution of carbon anode, which would be consumed in the electrolysis processes, with spinel structural oxide compounds. NiFe<sub>2</sub>O<sub>4</sub>-based and CoFe<sub>2</sub>O<sub>4</sub>-based materials were employed<sup>[1-4]</sup>, but it was found that the positive metals, such as Fe, Co, Ni could be electrodeposited on the cathode. This would not only cause corrosion of the anodes, but also contaminate the raw aluminum<sup>[3,4]</sup>.

The authors had developed the ZnFe<sub>2</sub>O<sub>4</sub>-based inert anode<sup>[5,6]</sup>, and the previous work proved that zinc ferrite was the most promising material<sup>[6]</sup>. In the present paper, a systematic investigation on the corrosion behavior of zinc ferrite in molten NaF-AlF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> has been carried out.

## 2 Experiments

### 2.1 Synthesis of ZnFe<sub>2</sub>O<sub>4</sub>

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$\text{Fe}_2\text{O}_3$  and  $\text{ZnO}$  powders, corresponding to stoichiometric composition were mixed in a ball mill for more than 72 h. The weight ratio of the ball to the mixed powder was 2:1. The powder was then sintered in the oxygen-rich atmosphere to synthesize  $\text{ZnFe}_2\text{O}_4$ . The partial pressure of oxygen was just a little higher than one atmospheric pressure. The sintered powder was characterized by X-ray ( $\text{CuK}\alpha$ ), the diffraction patterns is shown in Fig. 1.

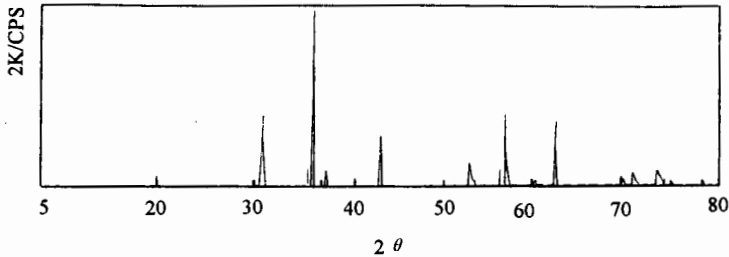


Fig.1 X-Ray patterns of synthesized  $\text{ZnFe}_2\text{O}_4$

## 2.2 Anode samples

The  $\text{ZnFe}_2\text{O}_4$  powder was pressed (320MPa) into a cylinder shape and then sintered at  $1450^\circ\text{C}$  for 30 h to produce anode samples, the partial pressure of oxygen was controlled at 56 kPa.

## 2.3 Corrosion experiments

Corrosion experiments were carried out in a specially designed graphite crucible which was set in an electric furnace in argon atmosphere. The  $\text{NaF-AlF}_3\text{-Al}_2\text{O}_3$  molten salt contained in the crucible was used as electrolyte. The bottom of the crucible was used as cathode to conduct the experiments. The area of the cathode was much bigger than the area of the anode. In the atmosphere of argon, experiments were taken at  $950^\circ\text{C}$  for 6~8 h. The samples were then taken out and put into the boiling solution of 30%  $\text{AlCl}_3$  to leach the electrolyte adhered on it.

## 3 Results and discussions

The corrosion rate of the anode was calculated from the weight loss of the sample, experiment results are shown in Fig. 2 to Fig. 4.

In Fig. 2, corrosion rates of the anode were determined at different mole ratio of  $\text{NaF/AlF}_3$  when  $C(\text{Al}_2\text{O}_3) = 3\%$ . In Fig. 3, corrosion rates of the anode were also determined at different alumina content when  $\text{NaF/AlF}_3 = 2.8$ . The two figures showed the same results that the corrosion rate was variable with the anodic current density. The biggest corrosion rate appeared in the range of  $0.5\sim 0.75 \text{ A/cm}^2$ . The corrosion rate went down after that peak value.

In Fig. 4, the molten salts were saturated with alumina. Curve B showed the corrosion rate of the anode without anodic polarization. When the electrolyte was saturated with alumina and the anode was anodic polarized, the corrosion rate decreased with the increasing of the anodic current density and

increased with the increasing of NaF/AlF<sub>3</sub> in the molten salts. The corrosion rates in curve E ( $i_A = 1.5 \text{ A/cm}^2$ ), F ( $i_A = 2.0 \text{ A/cm}^2$ ) and G ( $i_A = 2.5 \text{ A/cm}^2$ ) were almost the same value. This means that the corrosion rate would not be affected by the anodic current density or by the mole ratio of NaF/AlF<sub>3</sub> when the electrolyte was saturated with alumina and the current density on the anode ( $i_A$ ) was higher than  $1.5 \text{ A/cm}^2$ .

From the results of Fig. 2 to Fig. 4, we concluded that high anodic current density ( $>1.5 \text{ A/cm}^2$ ), high alumina concentration and low mole ratio of NaF/AlF<sub>3</sub> in the molten salts would be the most important conditions for the inert anode.

Temperature certainly affected the corrosion reactions. The temperature of  $950^\circ\text{C}$  was chosen because it is the practical temperature in aluminum industry. There were at least four kinds of corrosion reactions of the oxide compound in the molten salts when it was anodically polarized. These four kinds of reactions could be used to explain the results of the corrosion experiments mentioned above.

(1) Replacement reaction



$$\Delta G_T = \Delta G_T^0 + RT \ln \left[ \frac{a_{\text{Al}_2\text{O}_3}^n a_{\text{MeO}}^6}{a_{\text{Al}}^{2n} a_{\text{MeO}}^{2n}} \right] \quad (a - \text{activity}) \quad (1)$$

When the pure oxide is chosen as the standard state,  $a_{\text{MeO}} = 1$ . If the molten salts is saturated with alumina, there comes another approximation,  $\gamma_{\text{Al}_2\text{O}_3} = 1$  ( $\gamma$ -activity coefficient).

The concentration of Me (Fe or Zn) and Al in the molten salts is very low, this means that the activity of the metals in the electrolyte equals approximately to its concentration,  $a_{\text{Me}} \approx C_{\text{Me}}$ , and

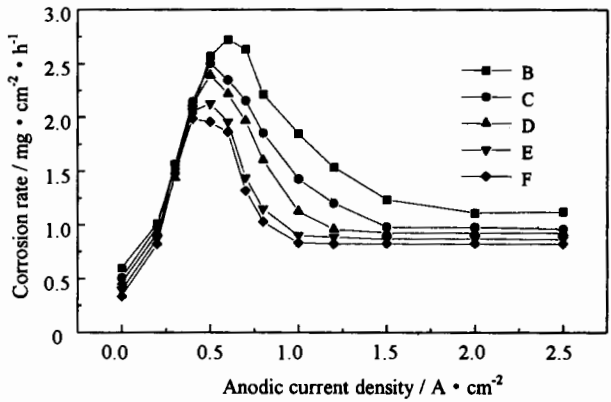


Fig. 2 Corrosion rate of zinc ferrite samples in molten salts with different ratio of NaF/AlF<sub>3</sub>  
C(Al<sub>2</sub>O<sub>3</sub>) = 3%, NaF/AlF<sub>3</sub> (mole ratio): B - 2.8, C - 2.4, D - 2.2, E - 2.0, F - 1.8

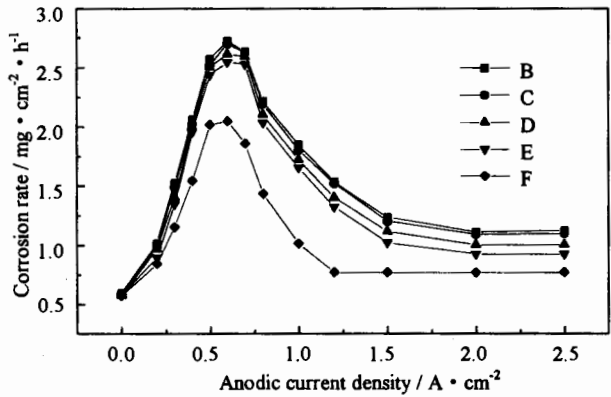


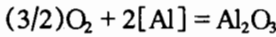
Fig. 3 Corrosion rate of zinc ferrite samples in molten salts with different alumina content  
NaF/AlF<sub>3</sub> (mole ratio): 2.8%, Al<sub>2</sub>O<sub>3</sub>: B - 3%, C - 4%, D - 5%, E - 6%, F - saturated

$a_{Al} \approx C_{Al}$  ( $C_{Me}$ ,  $C_{Al}$ -concentration of Me and Al in the molten salts).

If the reaction is in equilibrium ( $\Delta G_T = 0$ ), the equation (2) can be derived from (1):

$$\ln C_{Me} = (n/3)\ln C_{Al} + \Delta G_T^0/6RT \quad (2)$$

The content of the dissolved aluminum in the anode region may be decreased by oxygen produced on the anode:

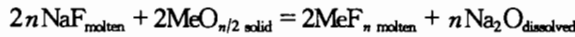
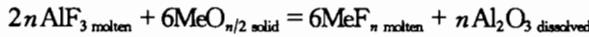


In order to decrease aluminum concentration in the molten salts, the

alumina content in the melts should be kept at high level. This was proved in Fig. 2 and Fig. 3.

(2) Exchanges between  $O^{-2}$  and  $F^{-2}$

When the anode is immersed in the molten salts, the exchanges of  $O^{2-}$  and  $F^{2-}$  is inevitable:



From the equations above, we conclude that by increasing the concentration of  $Al_2O_3$  and decreasing the mole ratio of  $NaF/AlF_3$ , the corrosion rate is decreased, that are also shown in Fig. 2 to Fig. 3.

(3) Dissolution of the oxide compound

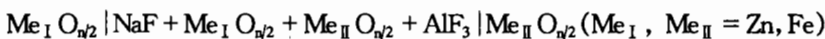
The oxide compound dissolves in the molten salts, but it is difficult to identify this dissolution from other kinds of corrosion. The rate of the dissolution is affected by the composition of the molten salts and also affected by the intensity of the current on the anode.

It is clearly that by increasing alumina content in the molten salts, the dissolution rate of the anode would be decreased.

(4) Electrochemical corrosion

This kind of corrosion can be mentioned in two aspects.

1) When the anode is immersed in the molten salts, the corrosion cells will be constructed:



2) When the electrode is polarized, by-reactions will take place on the cathode:

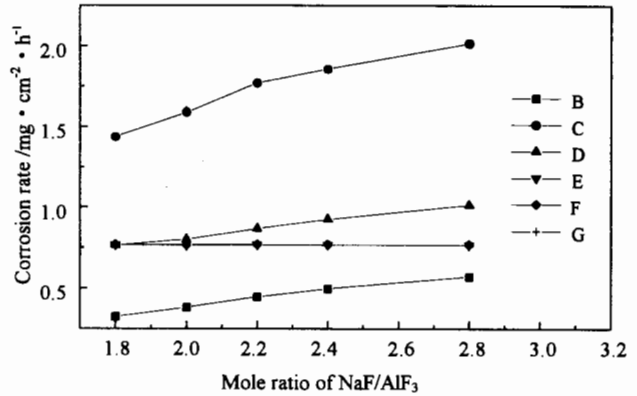


Fig. 4 Corrosion rate of zinc ferrite samples in alumina saturated molten salts  
 $Al_2O_3$ : saturated, Current density ( $A/cm^2$ ): B - 0, C - 0.5, D - 1.0, E - 1.5, F - 2.0, G - 2.5

These are reactions that can not be eliminated and they are related with the concentration of Me in the molten salts, which can be determined by equation (2). The results and discussions proved that the corrosion of the spinel materials is inevitable in the molten salts, but it can be decreased by (a) decreasing the mole ratio of  $\text{NaF}/\text{AlF}_3$  in the molten salts, (b) increasing the alumina content, and (c) increasing the current density on the anode. If the melt is saturated with alumina and the  $i_A$  is higher than  $1.5 \text{ A}/\text{cm}^2$ , the corrosion rate of the spinel anode decreased to a limited value (Fig. 4 curves E, F, G). So the high current density on the anode and the alumina saturated electrolyte may be the most important conditions for spinel materials when used as inert anode in aluminum electrolysis.

#### 4 Conclusion

Zinc ferrite materials was proved to be very corrosion resistant in  $\text{NaF-AlF}_3\text{-Al}_2\text{O}_3$  melts under the condition of anodic polarization. Anodic polarization would cause a remarkable increasing of corrosion rate when the anodic current density is low. The biggest corrosion rate appears in the range of  $0.5 \sim 0.75 \text{ A}/\text{cm}^2$ . The rate drops after that peak value, and decreases to a constant value with the increasing of anodic current density. High anodic current density ( $> 1.5 \text{ A}/\text{cm}^2$ ), high alumina concentration and low mole ratio of  $\text{NaF}/\text{AlF}_3$  would be the most important conditions for inert anode selection.

When the electrolyte is saturated with alumina and the anodic current density is higher than  $1.5 \text{ A}/\text{cm}^2$ , the corrosion rate would be decreased to the minimal value.

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## CORROSION OF ZINC FERRITE IN NaF-AlF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> MOLTEN SALTS

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**Abstract:** Zinc ferrite was used as inert anode materials for aluminum electrolysis. The corrosion behavior of zinc ferrite as investigated under the anodic current density of 0-2.5A/cm<sup>2</sup>. Experimental results prove that zinc ferrite materials is very corrosion resistant to molten NaF-AlF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> under the condition of anodic polarization. The biggest corrosion rate appears in the range of 0.5~0.75A/cm<sup>2</sup>. The corrosion rate will get down after that peak value. High anodic current density (>1.5 A/cm<sup>2</sup>), high alumina concentration and low mole ratio of NaF/AlF<sub>3</sub> in the molten salts would be the most important conditions for using inert anode.

**Key words:** zinc ferrite, spinel material, aluminum electrolysis, inert anode, corrosion in molten salts