

Numerical simulation study of the effect of anodic bubble behavior in aluminum electrolysis cell

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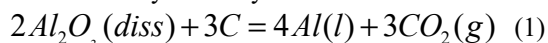
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Abstract: During the aluminum electrolysis process aluminum is produced at the cathode and CO₂ gas bubbles are generated on the anode and released. The bubbles reduce the active surface area of the anode, which increases energy consumption. They also cause the liquid aluminum to fluctuate and oxidize again. The study of anodic bubble behavior is important to reduce power consumption and improve current efficiency. In this paper, the phase field, laminar flow and tertiary current distribution modules in COMSOL Multiphysics are applied to simulate the growth and motion patterns of anodic bubble in the electrolytic cell to visualize and analyze the behavior of anode bubble.

1. Introduction

Aluminum electrolysis uses molten NaF-AlF₃ based fluoride as the electrolyte, alumina as the raw material, carbon block as the anode, and liquid aluminum as the cathode, which undergoes an electrochemical reaction at the temperatures of 930°C-950°C. Aluminum is produced at the cathode and CO₂ gas bubbles are generated at the anode [1].

Gas is produced by the oxidation of oxygen ions in the electrolyte to oxygen atoms by losing electrons on the surface of the anode, which then combine with carbon atoms of the anode to produce CO₂ bubble and release [2]. Equation (1) is the total reaction for the production of metallic aluminum by electrolysis of alumina.



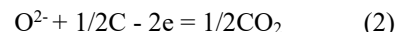
The study of anode bubble behavior is one of the research hotspots in the field of aluminum electrolysis in recent decades, which is divided into two types of methods: experimental observation [2-4] and computer numerical simulation [5-7]. In this paper, we use the phase field method to trace the gas-liquid interface, coupled with the electrochemical reaction process, electrolyte mass transfer process, gas and electrolyte flow, to visualize the anodic bubble behavior and explore the effect of them on the anode current and the stirring effect on the electrolyte.

2. Modeling

2.1. Control equations

The process of oxygen ions losing electrons on the anode surface to generate oxygen atoms and then reacting with carbon to generate carbon dioxide is very complex. For

the sake of simplicity, the reaction equation (2) is used in this paper.



The corresponding Butler-Volmer equation is:

$$j = j_0 \cdot \left\{ \exp \left[\frac{\alpha_a z F}{RT} (E - E_{eq}) \right] - \exp \left[-\frac{\alpha_c z F}{RT} (E - E_{eq}) \right] \right\} \quad (3)$$

Where j is the current density of electrode, A/m²; j_0 is the exchange current density, A/m²; E is the electrode potential; E_{eq} is the equilibrium potential; T is the thermodynamic temperature; z is the number of electrons involved in the electrode reaction; F is Faraday constant; R is the gas constant; α_a is anode transfer coefficient; α_c is the cathode transfer coefficient.

The amount of carbon dioxide produced by reaction (2) is determined by multiplying the current density expressed in equation (3) by the electrode area, and the current efficiency of carbon dioxide formation is set to 100%, thus the amount of carbon dioxide generated is calculated according to equation (4).

$$m_{co_2} = k_{co_2} I \quad (4)$$

Where k_{co_2} is the electrochemical equivalent and I is the anode current, which is equal to the product of current density and electrode area.

The laminar flow interface is used to calculate the velocity and pressure fields of a fluid in the laminar flow regime. The governing equations for fluid flow (Navier-Stokes equations) are shown below:

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho(\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot [-p\mathbf{I} + \mathbf{K}] + \mathbf{F} + \rho \mathbf{g} \quad (5)$$

Where ρ is the fluid density (kg/m³), \mathbf{u} is the fluid velocity (m/s), p denotes pressure (Pa), \mathbf{g} is the gravity vector (m/s²), and \mathbf{F} denotes the surface tension acting at the interface between the electrolyte and carbon dioxide.

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Tracing the diffusion interface of immiscible two phases using phase field method, The Cahn-Hilliard equation for the phase field is as follows:

$$\frac{\partial \phi}{\partial t} + \mathbf{u} \cdot \nabla \phi = \nabla \cdot \frac{\gamma \lambda}{\varepsilon^2} \nabla \psi \quad (6)$$

$$\psi = -\nabla \cdot \varepsilon^2 \nabla \phi + (\phi^2 - 1) \phi + \left(\frac{\varepsilon^2}{\lambda} \right) \frac{\partial f_{ext}}{\partial \phi} \quad (7)$$

Where λ is the mixing energy density (N); ε (m) is the interfacial thickness parameter to evaluate the thickness of the phase interface; σ is the surface tension coefficient and takes the value of 0.132 N/m. γ is the mobility ($\text{m}^3 \cdot \text{s}/\text{kg}$), which determines the time scale of diffusion; χ is the migration adjustment parameter, which determines the time scale of Cahn-Hilliard diffusion; ψ is the phase field assistant variable; f_{ext} is the external free energy.

2.2. Model building

In this paper, the electrolytic cell is simulated for electrolytic reaction at 950°C. The electrolytic cell has the inner diameter of 40 mm, the depth of 60 mm, the melt depth of 50 mm, and the anode working electrode diameter of 10 mm, which is inserted into the melt 10 mm.

3. Results

3.1. Bubble shape

Gas is generated at the horizontal surface of the anode by the electrochemical reaction, growing bubble that attach to the anode surface. When the bubble size is small, the surface tension at the gas-liquid interface plays a major role, so the bubble shape tends to be close to a regular semicircle. As the reaction proceeds, gas is continuously generated and the bubble gradually grows. At the same time, the buoyancy force gradually increases and presses the bubble toward the anode surface in a flattened shape. The simulation results showed that the bubble would not be detached immediately when they approached the anode edge, but would be longitudinally thickened by shaking from side to side at the horizontal surface of the anode and released immediately when they reached the electrode edge. The shape changes of the bubble growing at the horizontal surface of the anode and releasing along the side wall of the electrode are shown in Figure 1, which is consistent with the experiment observed by Stanic et al [8].

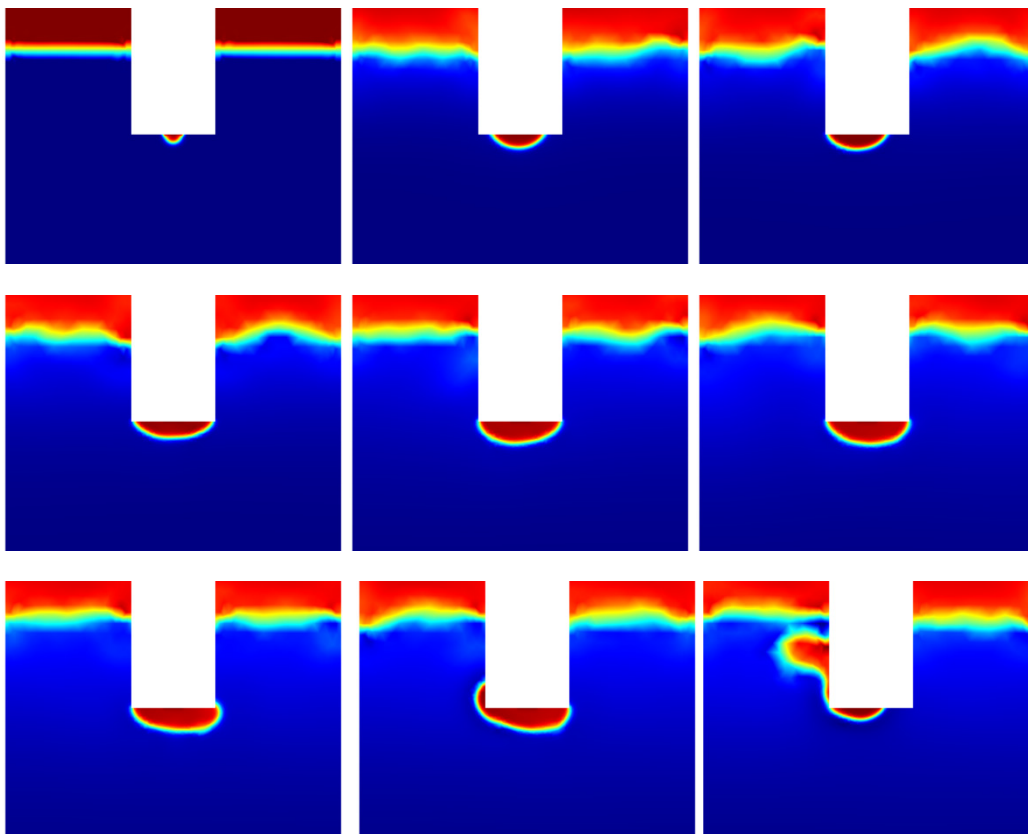


Fig 1 Phenomena of gas evolution

3.2. Variation of anode current caused by bubble

In the three times current distribution module, the anode electrode surface is set, the electrode phase potential is selected as potential, and the input constant external

potential is 1.3 V. Simulating the application of a stable electrode potential to the working electrode, the curves of the current density on the anode surface and the bubble coverage on the anode surface with time were obtained as shown in Fig 2.

Under the condition of constant voltage, the anode active surface area of bubble shielding gradually increases, which makes the anode current gradually decrease [9]. When the bubble coverage reaches the peak, the anode current density reaches the valley. Gas is detached from the bottom surface of the anode, the bubble coverage on the working surface of anode instantaneously decreases to

the valley, and the anode current instantaneously increases to the peak, and then changes periodically. The time from nucleation to detachment of the big bubble is about 1.3s. The maximum peak of current density is 0.89A/cm² and the minimum valley is 0.47A/cm². The bubble release frequency is 0.75Hz.

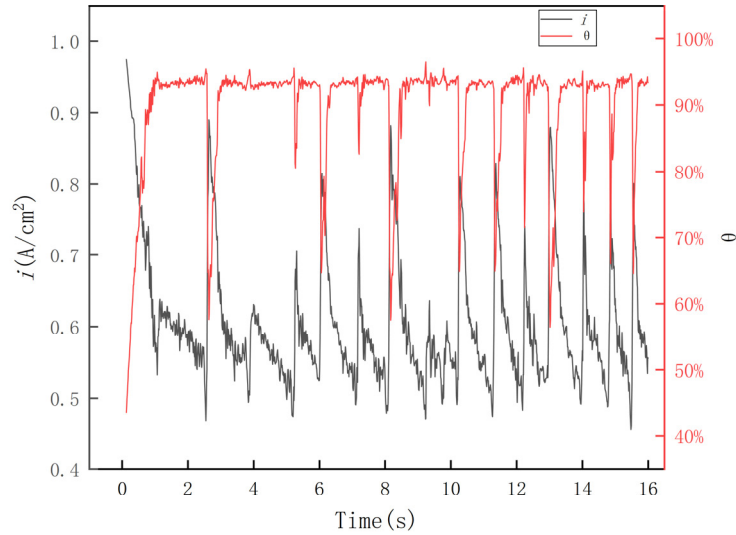


Fig 2 Variation of anode current density and bubble coverage

3.3. Variation of anode potential caused by bubbles

The constant current density of 0.4 A/cm² is input in the model. The anode potential variation are shown in Figure

3. Anodic bubble contributes to an increase in cell voltage by covering the anode surface and reducing the active surface area. The anode potential increases with the increase of bubble coverage [9], and the potential fluctuation caused by the anodic bubble is between 70 and 140 mV.

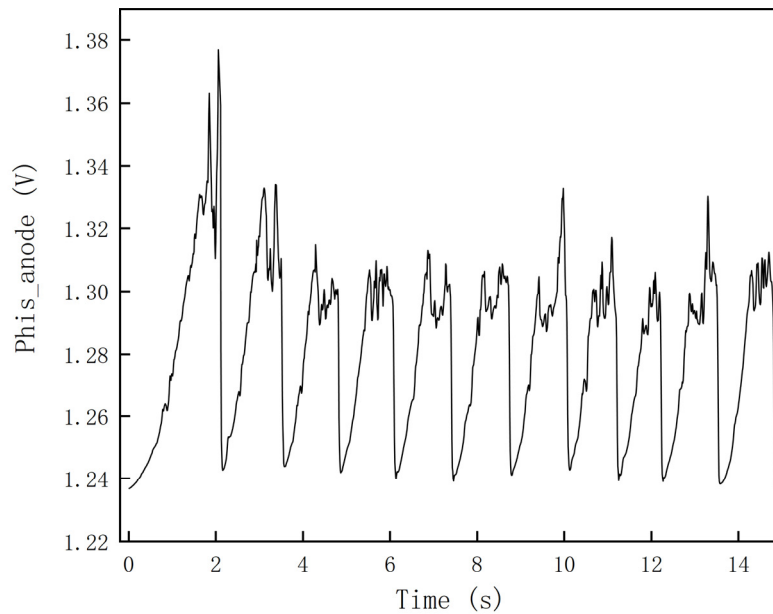


Fig 3 Variation of anode potential

4. Conclusion

The characteristics of bubble shape changes and their caused anode potential and current density changes during the bubble behavior of aluminum electrolytic anode were obtained by computer numerical simulation experiments. As the bubble nucleate, grow and coalesce to form bubble film, the bubble coverage on the working surface of anode gradually increases. Under the condition of constant voltage, the anode active surface area gradually reduce, which make the anode current gradually decrease. As the gas is released, the bubble coverage on the working surface of anode decreases instantaneously, causing the anode current to increase instantaneously, followed by a periodic variation. Under the condition of constant current, the anode potential increases with the increase of bubble coverage. The presence of anode bubble increases the electrolyte resistance, anode overvoltage, and makes the electrolysis energy consumption increase. The future direction can be focused on the combination of mass transfer on the gas-liquid interface and electrolyte flow.

Acknowledgements

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