

Al₂O₃-Na₃AlF₆ MAN-MADE LEDGE COMPOSITES FOR ALUMINUM ELECTROLYSIS CELLS

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Abstract

Man-made Al₂O₃-Na₃AlF₆ composite ledge for aluminum reduction cell was developed because of the disadvantages of traditional self-forming ledge and the composite material was prepared by pressureless liquid-phase sintering under air atmosphere. The effect of Na₃AlF₆ mass fraction on the relative density, compressive strength, high-temperature stability and microstructure of Al₂O₃-Na₃AlF₆ composites was investigated. The results show that with the increasing of Na₃AlF₆ mass fraction from 0 to 15 wt%, the relative density increases from 62.05 % to 67.19 %, the compressive strength increases from 9.74 MPa to 17.81 MPa, and the high-temperature stability of composites under 1100 °C gradually becomes worse. However, compared to traditional self-forming ledge, Al₂O₃-Na₃AlF₆ composites have more excellent high-temperature stability. Such results indicate that Al₂O₃-Na₃AlF₆ composite is a promising man-made ledge for aluminum reduction cell.

Introduction

As is known to all, the newly built cells would experience an adjustment period (about 3 months) after baking and start-up. The adjustment period is the transition from abnormal operation after start-up to normal operation of cell. During the period, the operating temperature, cell voltage, CR ratio and electrolyte level adjust from high level to normal operating standard gradually, and the frozen electrolyte layer (ledge) is also formed [1, 2]. The self-formed ledge on the sidewall is vital for the aluminum reduction cell. It not only prolongs the service life of cell, but also helps to obtain higher current efficiency [3]. However, the self-formation of ledge in traditional cells causes other problems. Firstly, the high temperature, high cell voltage and high CR ratio would lower current efficiency [4] and increase power consumption significantly. Secondly, Na penetration of cathode and thermal stress concentration that caused by high temperature and high CR ratio [5] would increase cathode expansion and shorten cathode lining life. Thirdly, the profile of self-forming ledge would be difficult to be controlled during adjustment period after start-up because of a mismatch between cell heat preservation instruction design, pots temperature and electrolyte system. Lastly, non-regular ledge profile would influence cell's stability and lower current efficiency significantly and it is difficult to adjust the self-forming ledge profile during abnormal operation.

In order to overcome the disadvantages of the self-forming ledge of traditional cell during the adjustment period, man-made ledge cells have been proposed recently. The cell's man-made ledge was built along shell using man-made ledge materials to form ideal profile before baking and start-up. In this case, the newly built cells don't need to experience the long time adjustment period to self-form ledge. By optimizing man-made ledge materials performance or designing reasonable heat balance, man-made ledge can be permanently fixed in the cell from start-up to cell

matures. Compared with traditional cell, man-made ledge cell has followed advantages: (1) lower the energy consumption from start-up to normal operation; (2) lesser Na penetration of cathode caused by high temperature and high CR ratio during adjustment period, and prolong cathode lining life; (3) the difficulty of profile adjustment for the self-forming ledge of traditional cell because of its high stability can be solved; (4) the regular ledge profile of man-made ledge cell is more favorable and controllable for improving stability and current efficiency.

The man-made ledge materials are necessary for development and application of man-made ledge cell and need to have following properties: low electrical conductivity, excellent high-temperature stability, good strength and excellent chemical stability in the electrolyte melt and metal. Al₂O₃ material has some excellent properties such as high melting point, excellent mechanical strength and high electrical resistivity [6]; the liquid temperature of Na₃AlF₆-Al₂O₃ system is only about 960°C [7], which may lower the sintering temperature significantly due to liquid-sintering [8]; in addition, both Na₃AlF₆ and Al₂O₃ are electrolyte composition. Synthesizing these factors aforementioned, Al₂O₃-Na₃AlF₆ system is chosen to be man-made ledge materials system. The traditional self-forming ledge is mainly composed of Na₃AlF₆ with small amounts of α -Al₂O₃ [1]. Although the traditional self-forming ledge has good chemical stability and compatibility with metal and electrolyte melt, high-temperature stability of the traditional ledge is relatively poor because of high Na₃AlF₆ content. For this, man-made ledge materials are prepared by using Na₃AlF₆ as sintering additive and Al₂O₃ as matrix.

In this study, Al₂O₃-Na₃AlF₆ composites were prepared by pressureless liquid-phase sintering under air atmosphere. The effects of cryolite (Na₃AlF₆) mass fraction on bulk density, relative density, compressive strength, high-temperature stability and microstructure of Al₂O₃-Na₃AlF₆ composites were investigated. In addition, the high-temperature stability of self-forming ledge materials also was tested to obtain the optimal component of man-made ledge materials.

Experimental

Preparation of Al₂O₃-Na₃AlF₆ composites

The following raw materials were used in this study: Na₃AlF₆ (99.9%), α -Al₂O₃ (mean particle size 32.1 μ m, 99%). Both of Na₃AlF₆ and Al₂O₃ were pre-processed for 48 hours under 120°C before being used.

The α -Al₂O₃ powder and Na₃AlF₆ powder, together with 1% PVA as a binder, were mixed with ethanol in a ZrO₂ ball mill for 2 h. Then the mixture was dried in air at 100°C for about 8 h, and sieved through a 40-mesh screen. The powder mixtures were compacted into cylindrical samples of 20 mm diameter by cold uniaxial pressing at 200 MPa. The samples were heat-treated at

600°C for 6h under N₂ to decompose the PVA. The heat-treated samples were sintered in a temperature controlled furnace under air at heating rate of 4°C/min up to 1100°C for 2h.

Performance tests

The bulk densities of the sintered samples were determined by their weight-to-volume ratio. The theoretical densities of sintered samples were calculated using the true density values of 3.97 and 3.11 g/cm³ for α -Al₂O₃ and Na₃AlF₆, respectively. Weights of specimens were measured before and after sintering to calculate the sintering weight loss. The phase analysis was conducted with an X-ray diffractometer using Cu K α radiation. The compressive strength of composites materials was determined according to ISO 12985 -2:2000. The microstructure of fracture surfaces for the sintered composites was observed by scanning electron microscopy (SEM). The high-temperature stability was determined according to the change of shape, dimension and weight between before and after high-temperature testing, and the testing device is shown in Figure 1. Although the electrolysis bath temperature is normally close to 950°C, the local temperature in the cell would reach 1100°C during the start-up period. In order to guarantee the reliability of composites, the testing temperature was determined to be 1100°C (testing time 6h).

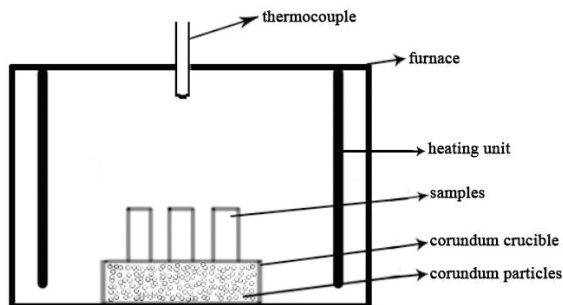


Figure 1. The high-temperature stability testing device

Results and discussion

The relative density and compressive strength of Al₂O₃-Na₃AlF₆ composites

The effect of cryolite (Na₃AlF₆) mass fraction on the relative density (RD) and compressive strength (CS) of Al₂O₃-Na₃AlF₆ composites was shown in Figure 2. When the Na₃AlF₆ mass fraction increases from 0 to 15wt.%, the relative density of composites increased from 62.05% to 67.19%, the compressive strength of the composites increased from 9.74 MPa to 17.81 MPa. That is to say, the influence of Na₃AlF₆ mass fraction on the relative density and compressive strength of composites showed the similar trend. The relative density and compressive strength of composites were low, and the maximum values were only 67.19% and 17.81 MPa respectively.

In general, densification during liquid-phase sintering can be divided into three distinct stages: (i) rearrangement of solid particles after the formation of a liquid phase; (ii) solution-precipitation of the solid grains through the liquid phase; and (iii) coalescence or solid-phase sintering, where only the first two stages are dependent on the presence of a liquid phase [9-11]. When other conditions are consistent, the high liquid phase

content could promote grain rearrangement and solution-precipitation, so with the increase of Na₃AlF₆ mass fraction, the relative densities and compressive strength of the composites would increase.

It is well known that the mechanical properties of ceramic materials can be enhanced with the increase of relative density [12]. The pores of ceramic materials not only reduce the load area but also cause stress concentration around the pore so that the load capacity of the materials would be weakened. This is the reason why the influence of Na₃AlF₆ content on the relative densities and compressive strength of composites showed the same trend.

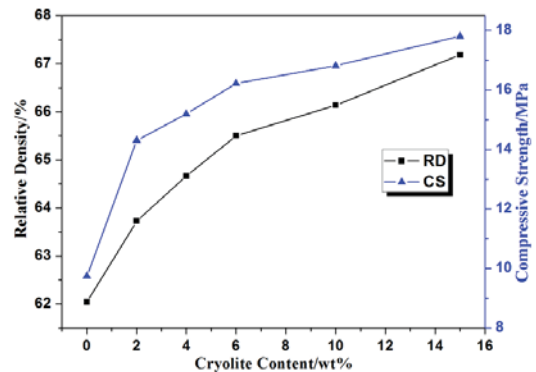


Figure 2. The effect of cryolite content on the relative densities and compressive strength of Al₂O₃-Na₃AlF₆ composites

Three aspects can cause the low densification of the composites. Firstly, the particle size of α -Al₂O₃ (the average particle size 32.1 μ m) is too large to ensure rearrangement of the solid grains through the liquid phase. Secondly, α -Al₂O₃ is extremely difficult to be dissolved into Na₃AlF₆ melt so that solution-precipitation process would be suppressed. Lastly, the porosity of composites would increase because of vaporization of Na₃AlF₆ melt, the effect of Na₃AlF₆ mass fraction on the sintering weight loss is shown in Figure 3. It can be seen from the figure 3 that adding Na₃AlF₆ can effectively increase the sintering weight loss of Al₂O₃-Na₃AlF₆ composites. When the Na₃AlF₆ mass fraction increases from 0 to 15wt.%, sintering weight loss of composites increased from 0 to 0.9%.

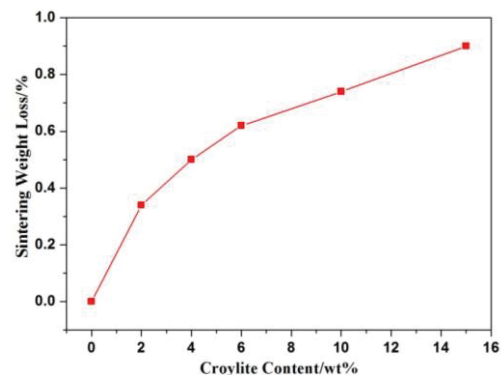


Figure 3. The effect of cryolite content on the sintering weight loss of Al₂O₃-Na₃AlF₆ composites

The microstructure of Al₂O₃-Na₃AlF₆ composites

Figure 4 shows the SEM images of fracture surfaces of the $\text{Al}_2\text{O}_3\text{-Na}_3\text{AlF}_6$ composites. From Figures (a), (b) and (c) many pores and fine alumina can be seen in the composites with low Na_3AlF_6 content, and sintering degree is relatively low. When Na_3AlF_6 content increases to 15wt.%, pores and fine alumina inside the composites reduced considerably with grain coarsening and densification, as shown in Figure (d).

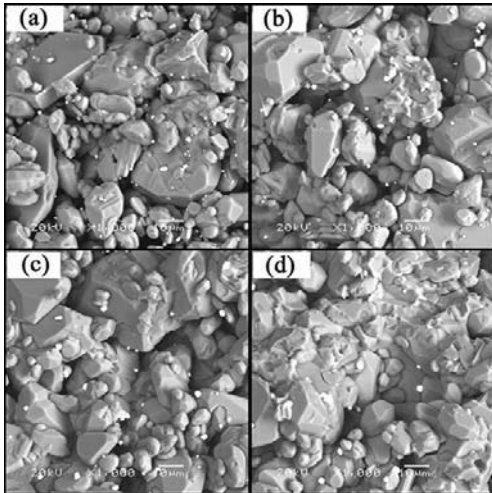


Figure 4. SEM micrographs of fracture surfaces of $\text{Al}_2\text{O}_3\text{-Na}_3\text{AlF}_6$ composites with (a) 0wt.% Na_3AlF_6 , (b) 2wt.% Na_3AlF_6 , (c) 6wt.% Na_3AlF_6 , (d) 15wt.% Na_3AlF_6 (1000 times magnification)

The fine alumina can be dissolved in Na_3AlF_6 melt and precipitate on coarse grained alumina gradually during sintering process. The pores can be filled by the liquid phase fluidity and solution-precipitation of alumina, and the densification degree is improved. However, if the Na_3AlF_6 mass fraction is too low, this process will not happen because of the lack in liquid phase. This makes grain coarsening and densification hard to achieve. With the increase of Na_3AlF_6 content the high liquid content can more effectively improve transport rates responsible for grain coarsening and densification than the low liquid content. The element distribution of 15wt.% Na_3AlF_6 composites is shown in Figure 5. It can be seen that F and Na concentrate in the densification area circled in red from the Figure 5, which demonstrates Na_3AlF_6 play a decisive role in sintering of the composites.

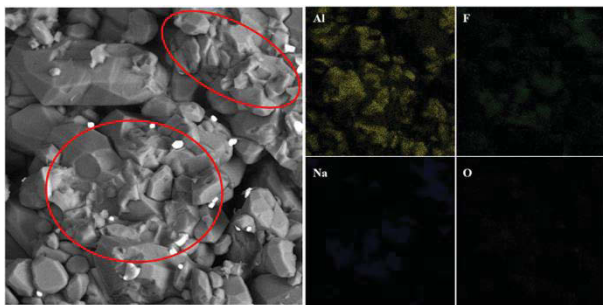


Figure 5. The element distribution of 15wt.% Na_3AlF_6 composites (1000 times magnification)

The high-temperature stability of $\text{Al}_2\text{O}_3\text{-Na}_3\text{AlF}_6$ composites and self-forming ledge materials

The photo of the composites with different Na_3AlF_6 content before and after high-temperature test is shown in Figure 6. The high-temperature stability of composites under 1100 °C gradually becomes worse and worse when the Na_3AlF_6 mass fraction increased from 0 to 15wt.%. When Na_3AlF_6 content increased to 6wt.% or higher, high-temperature environment caused the large crack in the composites and volume expansion of the composites result in failure of the composites.

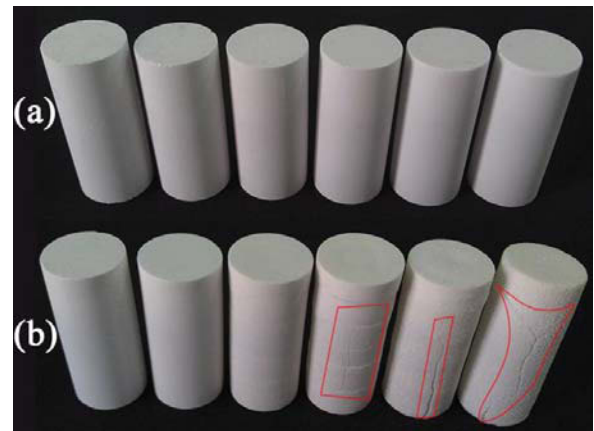


Figure 6. The photo of the composites before (a) and after (b) high-temperature stability test

* From left to right on the photo, the Na_3AlF_6 content are in order, 0 wt.%, 2 wt.%, 4 wt.%, 6 wt.%, 10 wt.% and 15 wt.%

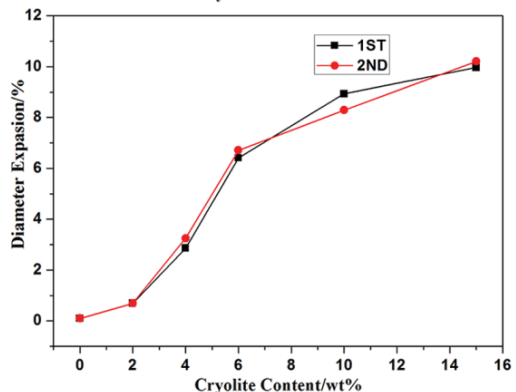
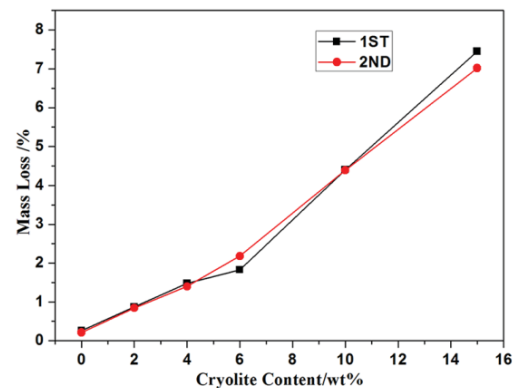


Figure 7. The effect of Na_3AlF_6 content on the mass loss and diameter expansion of $\text{Al}_2\text{O}_3\text{-Na}_3\text{AlF}_6$ composites after test “1ST” and “2ND” present 2 times test results

High temperature Na_3AlF_6 molten liquid is volatile. Vapor pressure of Na_3AlF_6 melt reached 1.83 KPa under 1100 °C according to Kvande's research results [13]. This means that vaporization of melt would cause the mass loss and volume expansion for $\text{Al}_2\text{O}_3\text{-Na}_3\text{AlF}_6$ composites at high temperature, the effect of Na_3AlF_6 content on the mass loss and diameter expansion of $\text{Al}_2\text{O}_3\text{-Na}_3\text{AlF}_6$ composites is shown in Figure 7. When the Na_3AlF_6 mass fraction increases from 0 to 15wt.%, the mass loss increased from 0 to above 7%, the diameter expansion increased from 0 to about 10%. The vaporization of melt forced the pore to grow up result in volume expansion. Then the large pore would be connected to form a channel leading to formation of large crack. The mismatch of expansion between different parts of the composites might also be a major cause of the big crack.

The high-temperature stability of self-forming ledge material was also tested under the same condition, and the result of this test was shown in Figure 8. The self-forming ledge material for experiment was from industrial 300kA cells in China. From Figure 8, the traditional self-forming ledge materials had completely melted during the high-temperature test. Figure 9 shows that, the self-forming ledge materials are mainly composed of Na_3AlF_6 (about 95%) with a small amount of AlF_3 and Al. The melt point of Na_3AlF_6 is only about 1010°C, so it is impossible that the self-forming ledge materials have excellent high-temperature stability under 1100°C. Although the large crack formed when Na_3AlF_6 content increased to 6wt.% or higher, $\text{Al}_2\text{O}_3\text{-Na}_3\text{AlF}_6$ composites keep the original shape after test. In conclusion, $\text{Al}_2\text{O}_3\text{-Na}_3\text{AlF}_6$ composites have more excellent high-temperature stability than the traditional self-forming ledge materials.

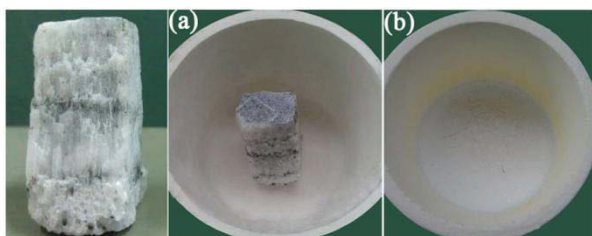


Figure 8. The photo of self-forming ledge materials before (a) and after (b) high-temperature stability test

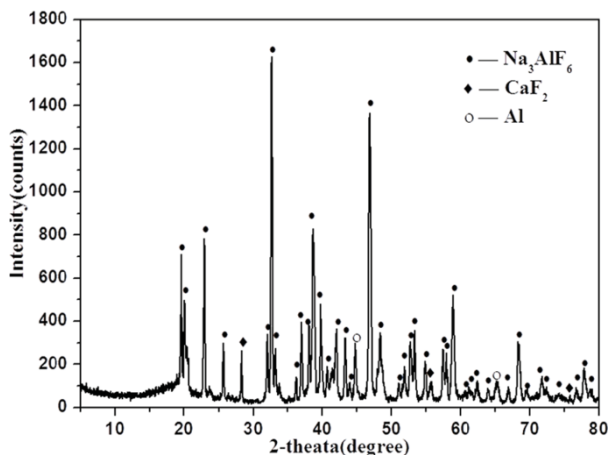


Figure 9. X-ray diffraction diagram of the traditional self-forming ledge material

Conclusion

The $\text{Al}_2\text{O}_3\text{-Na}_3\text{AlF}_6$ composites were chosen to prepare man-made ledge materials by pressureless liquid-phase sintering. The effects of Na_3AlF_6 content on the bulk density, relative density, compressive strength, microstructure, and high-temperature stability of $\text{Al}_2\text{O}_3\text{-Na}_3\text{AlF}_6$ composites were studied. In addition, the high-temperature stability of self-forming ledge materials also has been tested. The conclusions are listed as follows:

- (1). When the Na_3AlF_6 mass fraction increases from 0 to 15wt.%, the relative density of composites increased from 62.05% to 67.19%, the compressive strength of the composites increased from 9.74 MPa to 17.81 MPa. The influence of Na_3AlF_6 mass fraction on the relative density and compressive strength of composites showed the similar trend.
- (2). The SEM images of fracture surfaces of the $\text{Al}_2\text{O}_3\text{-Na}_3\text{AlF}_6$ composites show that pores and fine alumina inside the composites reduced with increasing of Na_3AlF_6 content, and Na_3AlF_6 concentrate in the densification area.
- (3). The high-temperature stability of composites under 1100 °C gradually becomes worse and worse with increasing of Na_3AlF_6 content. When Na_3AlF_6 content increased to 6wt.% or higher, high-temperature circumstance caused the large crack in the composites result in failure of the composites. Compared to traditional self-forming ledge, $\text{Al}_2\text{O}_3\text{-Na}_3\text{AlF}_6$ composites have more excellent high-temperature stability under 1100 °C.

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