Magnesium Technology 2011
Edited by: Wim H. Sillekens, Sean R. Agnew, Neale R. Neelameggham, and Suveen N. Mathaudhu
TMS (The Minerals, Metals & Materials Society), 2011

Effect of KCl on Liquidus of LiF-MgF_2 Molten Salts

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Keywords: Molten salt; Liquidus temperature; Cooling curve; Electrolyte

Abstract

Liquidus temperature of KCl-LiF-MgF_2 molten salts was determined based on cooling curve. The method of cooling curve was reliable and accurate. Experimental accuracy has been measured by the determined liquidus temperature of KCl. The measured value of KCl liquidus temperature of 769.27 ° C is near and comparable to the documented value 769.5 ° C. The difference value is 0.23 ° C, and the relative error was 0.03%. The results show that effect of KCl on liquidus of molten salt MgF_2-LiF electrolyte was great. The liquidus temperatures lowered with increasing of content of KCl in electrolyte. The liquidus temperature could be reduced 20 ° C with content of KCl in electrolyte increased to 50wt%. The experiments showed that the compound addition of KCl into LiF-MgF_2 electrolyte not only reduced the liquidus temperature of electrolyte effectively, but also decreased the aluminum-magnesium production cost and increased the economic benefits.

Introduction

As the lightest of all the commonly used metals, magnesium is very attractive for applications in transportation. It also has other advantageous features, such as good ductility, better damping characteristics than other metals and excellent castability. So, it has been widely used for aerospace industry, car manufacture, electronic technology, precise machines and so on. As the secondary element of aluminum alloy, increasing use of magnesium has been about 10-15% every year. Al-Mg alloys are widely used in construction and ship building industry[1-3].

However, the high cost of preparation of magnesium and magnesium alloys is a main factor to prevent them from wider use. For many years, many researchers[4-8] hope to prepare magnesium or its alloys in cell directly from magnesium oxide, and their focus is to cut down the loss of energy, shorten the process of the preparation and reduce the loss of metal oxidation. Preparation of Al-Mg alloys from MgO by molten salt electrolysis method is very popular in this research field. Some studies have attained exciting results. Aluminum-magnesium alloys could be prepared in 200 ampere with 20w%MgF_2-30w%LiF-50w%KCl as electrolyte, liquid aluminum as cathode, graphite as anode and magnesium oxide as raw material. The electrolytic process was stable, range of variation for cell voltage was narrow. The difference between the highest cell voltage and the lowest cell voltage was in 0.6V. Content of magnesium in alloy was not even because of construction of cell, the highest and the lowest were 20 w %, 6w%, respectively. The content of magnesium in alloys was 8.56 w% after refusion, and current efficiency was about 82%[9-14].

Liquidus temperature is one of important properties of electrolyte[15-17]. If liquidus temperature of electrolyte can be decreased, the electrolysis temperature can be reduced correspondingly. Thus, it has many advantages for low temperature electrolysis, such as to reduce energy consumption, decrease volatilization of electrolyte and increase current efficiency.

In this paper, the effect of KCl on liquidus of LiF-MgF_2 molten salts was studied by the cooling curve method. With increasing of KCl content in different electrolytes liquidus of the electrolytes were measured.

Experiment

Experimental apparatus and agents

KCl (Analytic agent), LiF (Analytic agent), MgF_2 (Analytic agent), all regents were dried at 400 °C for 2 hours to remove the water before experiments. Resistance furnace(2kw);Temperature controller(DWK-702); Thermal couple.

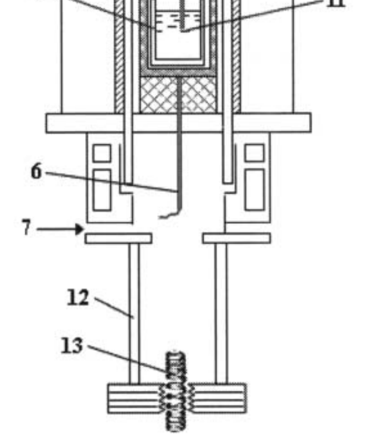

Figure 1. Experimental installation to measure liquidus of molten salt

1-Potential difference meter; 2-Thermal couple; 3- Alundum tube; 4-Heater; 5-Platinum crucible; 6- Thermal couple; 7-Pipe for argon; 8-Cooling water; 9-Resistance furnace; 10-Steel crucible; 11-Platinum ball; 12-Supporter; 13-Elevater;

Experimental process

Firstly, thermocouple was calibrated, and its accuracy was attained. Secondly, experimental system was measured, and accuracy of the method was determined. Amounts of dried KCl was fed into alundum tube container, KCl was melted in resistance furnace. The thermocouple was dipped into KCl molten salt. The temperature of furnace decreased slowly. A cooling curve could be shown on computer, and liquidus temperature of KCl could be estimated from the curve. The experimental results were compared with documented value. Thirdly, liquidus temperatures of electrolytes with different composition were measured by this method.

Accurate of system

The cooling curve of KCl was shown as figure 2, and the error analysis is shown in table 1:

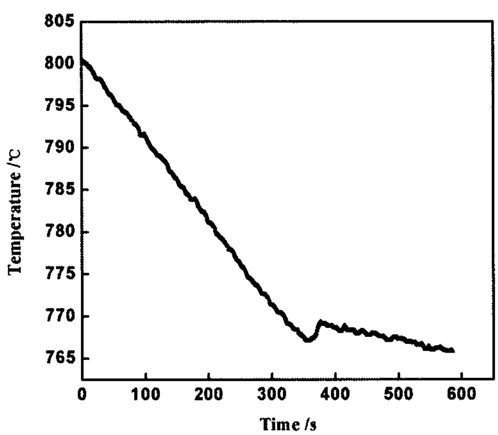

Figure 2. Cooling curve for potassium chloride

Table 1 Relative error analysis

Mass	Experimental value(° C)	Documental value(° C)	Error value(° C)	Relative error(%)
KCl	769.27	769.5	0.23	0.03

Figure 2 and table 1 can show that inflection liquidus temperature was clear, and the relative error was little, so the method was accurate.

Components of electrolyte were given as table 2:

Table 2 Components of electrolyte

Number	Components
1	0w%KCl-30w%LiF-70w%MgF_2
2	10w%KCl-30w%LiF-60w%MgF_2
3	20w%KCl-30w%LiF-50w%MgF_2
4	30w%KCl-30w%LiF-40w%MgF_2
5	40w%KCl-30w%LiF-30w%MgF_2
6	50w%KCl-30w%LiF-20w%MgF_2

Results and discussion

Experiments were carried out at different temperatures with different electrolytes. The results are shown as figure 3:

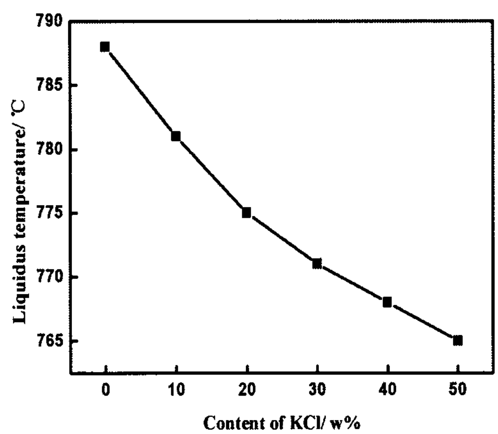

Figure 3 Relationship between content of KCl and liquidus temperature

Figure 3 shows that liquidus temperature decreased with content of KCl in electrolyte, the decreased value was about 20 ° C as content of KCl increased from 0w% to 50w%. After 20w% KCl in electrolyte, the decreased in values were reduced gradually. In other words, too much content of KCl in electrolyte had no contribution to decreasing liquidus temperature. The effect of KCl in electrolyte on liquidus temperature was clear if content of KCl was under 20%. In addition, increasing content of KCl and decreasing content of MgF_2 should be considered together for decreasing liquidus temperature. The decreased content of MgF_2 may have had some effects on decreasing liquidus temperature, not only liquidus temperature decreased by increasing of content KCl in electrolyte.

Conclusions

The method of cooling curve was accurate to measure liquidus temperature of electrolyte, and the relative error was 0.03%.

The effect of KCl on liquidus of molten salt was great for MgF_2-LiF electrolyte. The liquidus temperature could be reduced 20° C with increasing content of KCl in electrolyte from 0wt% to 50wt%. Increasing content of KCl and decreasing content of should be considered together for decreasing liquidus temperature. The decreased content of MgF_2 may have had some effects on decreasing liquidus temperature.

Acknowledgements

The authors wound like to acknowledge the financial supported by "The Education Department of Jiangxi Province (GJJ09513)", and express great thanks to Pr. Zhaowen Wang for his help in experiments.

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