ELECTROWINNING OF LIQUID MAGNESIUM
BY USING A STACKED-TYPE BIPOLAR ELECTRODE CELL

Tatsuo Ishikawa, Toshio Narita, and Shoichi Konda

Department of Metallurgical Engineering
Faculty of Engineering, Hokkaido University
Kita-13, Nishi-8, Kita-ku, Sapporo 060, Japan

ABSTRACT

This paper describes the design and construction of a stacked-type bipolar electrode cell for electrowinning liquid magnesium from chloride melts. The laboratory-scale electrolysis was carried out with a bipolar electrode-type cell operated at 50 A current at about 750°C. During electrolysis the metallic particles of magnesium move to the melt surface together with gas bubbles of chlorine. The experimental results are discussed considering the collection of magnesium particles from chlorine gas and the circulation of chloride melt.

INTRODUCTION

Nearly half of the metallic magnesium produced in Japan today is being used as a reducing agent in a Kroll process for the titanium production. Magnesium dichloride as a reaction product in the titanium manufacturing process is used again as a raw material for electrowinning metallic magnesium. It is worth noting that the electric energy consumed in the magnesium process accounts for a large part of the total energy consumption in the titanium manufacturing process.

In order to achieve energy-saving during the electrowinning of aluminum we have developed over a period of ten years a stacked-type bipolar electrode cell and carried out laboratory-scale experiments in NaCl-MgCl₂ fused salts containing aluminum chloride.(1) In the course of the investigation we proposed a principle for the design of such stacked-type bipolar electrode cells in order to attain homogeneous melt circulation.(2)

In the present paper, the progress in design and construction of the stacked-type bipolar electrode cells for electrowinning liquid magnesium from mixtures of chloride melts is described. The results of laboratory-scale electrolysis using cells composed of four anode-cathode units are also presented. In the electrowinning process described above, metallic magnesium particles deposited on cathode surfaces move upward in the melts with chlorine gas bubbles evolved on anode surfaces. The experimental results are discussed taking into
account the separation of metal particles from the chlorine gas and the circulation of melts in the cells, and an optimum cell construction for high current efficiency is proposed.

EXPERIMENTAL MATERIALS AND PROCEDURES

Electrolytic cell and bipolar electrodes

A transparent quartz tube with an inner diameter of 95 mm and a length of 700 mm was used as the electrolysis cell. It was placed in an electric furnace which had a window for the observation of the inside of the cell during electrolysis. The electric furnace wound with nichrome wire was composed of two parts. The frozen salts at the bottom of the container was melted at the lower part and the fused salts were discharged after an experiment. An end cathode, an end anode, and three bipolar electrodes made of graphite were cylinders with thick walls and with a hole each in the center. The upper and lower surfaces of the columns function as a cathode and an anode, respectively, and they have an inclination of 30° to the horizontal. The thickness of the bipolar electrodes is 30 mm. Each electrode has six projections made of graphite on the side to fit in the center of the container. The five electrodes were separated by three alumina rods (3 mm in outer diameter) each placed between electrodes to construct the four anode-cathode units. The distance between electrodes was kept at 15 mm. Two graphite rods, 18 mm in diameter, were attached to the end anode and the end cathode each and one was used for measurements of bath voltage and the other was used for applying current. The rods to the cathode were covered with alumina tubes. All electrodes were supported at the bottom of the end anode by three alumina rods with a diameter of 15 mm and a length of 100 mm.

Determination of electrode sizes

Some preliminary experiments of magnesium electrowinning by using an anode-cathode pair cell showed that the sizes of chlorine gas bubbles were larger than that in aluminum electrowinning. It appears that it would be difficult to circulate the chloride melts in the cell, if the cell was designed according to the same design principle as for aluminum electrowinning. Accordingly for magnesium electrowinning, the cross-sectional area of the clearances between electrode peripheries and the container wall and the cross-sectional area of the center holes of electrodes were determined so as to enlarge such cross-sectional areas from the bottom to the top, keeping the ratio of both cross-sectional areas constant. The values of those sizes are presented in Table 1.

Preparation of melts and supplement of raw materials

A mixture of NaCl 90 m/o-BaCl_2 10 m/o was employed as a supporting electrolyte; the specific gravity of the melt is enough large to float metallic magnesium produced by electrolysis. Magnesium chloride as a
raw material was supplied into the cell during electrolysis continuously in a solid state and intermittently in a liquid state and its concentration was kept between 20 and 25 m/o. The cross section of the electrolytic cell with the feeder of solid magnesium chloride is presented schematically in Fig. 1.

A liquid mixture of MgCl₂ 25m/o–NaCl 75 m/o was added to the electrolysis cell, pre-heated at 700° C and pre-electrolysis was carried out at 30 A for 30 minutes, to remove impurities such as moisture. The BaCl₂ predried was added to make up the concentration of 10 m/o to NaCl. In order to supply magnesium chloride in a solid state anhydrous magnesium chloride was melted and solidified as small particles. These were added to the melt by using a rotary valve (see Fig. 1) at a fixed rate from the top of the cell under nitrogen carrier gas.

Discharge of chlorine gas and sampling method of melts for chemical analysis

As shown in Fig. 1, the chlorine gas evolved during electrolysis was trapped into the 10 % sodium hydroxide solution by driven by the pumping action of an aspirator. The container of sodium hydroxide was replaced every 30 minutes and the amount of chlorine gas absorbed in it was determined by iodometry. From this the current efficiency for magnesium electrowinning was calculated.

In order to determine the concentration of MgCl₂ in the course of an experiment a small amount of the melt was taken at fixed time intervals, carefully, so as not to contain metallic magnesium. The samples were dissolved into twice-distilled water and the concentration of MgCl₂ was measured by ICP spectroscopy.

Electrolysis procedures

After addition of BaCl₂ to the melts electrolysis was carried out at a current of 50 A for seven hours. During the experiment applied current, bath voltage, and temperature were recorded by a computer system. In the course of electrolysis, the relation between current and voltage was determined at every 30 minutes by lowering current stepwise for short time. The replacement of the sodium hydroxide container and sampling of the melts were also carried out simultaneously. If necessary, liquid magnesium chloride prepared in other vessels was poured in 100 or 200 gram portions to the melts. After electrolysis for a given time, the frozen salts in the bottom of the container were melted to discharge the electrolyte.

RESULTS AND DISCUSSION

Calculation of net current efficiency from the relationship between current and voltage
As reported elsewhere (2), the current efficiency (gross current efficiency) in operation of a bipolar electrode cell is represented as a product of a cell efficiency, \( \eta_{\text{cell}} \), and a net current efficiency, \( \eta_{\text{net}} \). The former is determined in terms of dimensional factors of the bipolar electrode cell and the latter is concerned with electrochemical reactions and/or chemical reactions.

The cell efficiency is estimated by using the decomposition voltage, \( V_d \), and the relation between applied current, \( I_m \), and the bath voltage, \( V_b \), under the multi-working state of the cell; the slope, \( c' \), and the intercept on the ordinate, \( d' \), of the \( V_b-I_m \) relations are used for the calculations. In Fig.2, the procedure obtaining \( \eta_{\text{cell}} \) from the \( V_b-I_m \) relations is described. \( n \) is the number of the inter-spacing reaction zone between electrodes. \( \beta' \) is a constant corresponding to the resistance ratio and \( I_m^{SM} \) is the minimum applied current for electrodes to work in bipolar manner. Thus \( \eta_{\text{cell}} \) is given as a function of applied current.

Fig.3 shows an example of the \( V_b-I_m \) relations obtained during electrolysis and \( \eta_{\text{cell}} \) is calculated as 0.818 ' from \( c' \), \( d' \), and \( V_d \) given as 2.65 V. The values of \( \eta_{\text{net}} \) shown in the following figures were obtained by dividing the gross current efficiency by \( \eta_{\text{cell}} \); the gross current efficiency was determined from chemical analysis of evolved chlorine gas.

Results in a stacked funnel-type electrode cell

In the present experiments two kinds of bipolar electrode cells were investigated, one is a cell where funnel-type electrodes are stacked and the other, conical-type electrodes are stacked.

A vertical section of the funnel-type cell is schematically described in Fig.4. In this figure the arrows indicate the flow of the melts in the cell, and magnesium particles deposited on cathode surfaces also move upward through the periphery clearances with chlorine gas evolved on anode surfaces.

As shown in Fig.5, the net current efficiency remains in the range between 40 and 60 %, though it increases a little with time. During the experiments, it was observed that a lot of magnesium particles were caught in the descending flow of the melts through the center holes of the electrodes and were circulating in the system. Therefore the low current efficiency is attributed to the recombination of magnesium with chlorine and/or the electrochemical dissolution on anode surfaces. In order to reduce the descending flow rate of the melts, the diameters of the center holes were enlarged. Also, by supplying liquid MgCl\(_2\) to the melts the sizes of chlorine gas bubbles became smaller probably due to impurities like moisture, and it resulted in the increase in the circulation rate of the melts. The net current efficiency obtained in such experiments, as shown in Fig.6, has very small values.
As indicated in the previous paragraph, in order to achieve high current efficiency, it is required to lower the descending flow rate of the melt. For this purpose, a cell composed of conical-type electrodes (funnel-type electrodes stacked upside down) was constructed in which the descending flow passed through the periphery clearances.

The vertical section of the upper part of the cell is presented in Fig. 7. As shown in the figure, magnesium particles and chlorine gas come together in the center holes. An alumina tube attached to the top of the end cathode works as a guide for magnesium particles so as not to be caught by the descending flow at the periphery clearances. The magnesium particles floating on the melt surface settle as a ring around the inner wall of the container, as shown in the figure.

Fig. 8 shows the time variation in net current efficiency and the MgCl₂ concentration in the course of the electrolysis experiments at 700°C, using the cell shown in Fig. 7. During the experiments solid MgCl₂ was added continuously. For the first five hours of the electrolysis the level of the melts was kept at 5 cm above the top of the guiding alumina tube and for the next two hours it was kept at nearly same height as the top. As seen from the figure, the net current efficiency stays in the range from 40 to 50% for high level of melts, but by keeping the melt level low it reaches nearly 70%.

Taking into account the above results, electrolysis experiments at low melt levels were carried out at 750°C. The results are presented in Fig. 9. The arrows in the figure indicate that a liquid MgCl₂ of 200 g was added at that points. From this figure it is shown that a net current efficiency over 70% is attained by keeping the melt levels nearly same as the top of the guiding tube, though it decreases a little just after the addition of liquid MgCl₂ which causes the acceleration of the melt circulation. In order to improve the net current efficiency further, it is preferable not to add MgCl₂ to the melts frequently.

CONCLUSIONS

A stacked-type bipolar electrode cell was developed for energy-saving electrowinning of liquid magnesium from magnesium chloride. The cell was composed of three bipolar electrodes, an end cathode, and an end anode; those electrodes were stacked at equal intervals of 15 mm from the end anode at the bottom to the end cathode in the top. The active surfaces of the bipolar electrodes have an inclination of 30° to the horizontal.

A cell efficiency was calculated from analysis of the linear relation between applied current and bath voltage under the multi-working state of the cell, and a gross current efficiency was determined by the amount
of evolved chlorine gas. A net current efficiency at the electrode surfaces was calculated from both current efficiencies. The performance of the constructed cells was evaluated from the time variation of the net current efficiency.

The constructed cells are classified into two groups by the type of stacking of the bipolar electrodes; the first is the stacked funnel-type electrode design and the second is a stacked conical-type cell. Judging from the net current efficiency obtained from both these cells, the conical-type cells are superior to the funnel-type cells. In order to improve the current efficiency further, it is essential to separate effectively magnesium particles from chlorine gas bubbles and prepare a gentle circulation of melts.

REFERENCES

1. Ishikawa, T. and Konda, S., Proc. of 1st International Symposium on Molten Salts Chemistry and Technology (Kyoto), p.5 (1983).
2. Ishikawa, T., Konda, S., and Narita, T., Proc. of 6th International Symposium on Molten Salts, p.734 (1987). The Electrochem. Soc.
Table 1 Dimension of Graphite Electrode Stacked

| Electrode     | Outer-diameter (mm) | Center Hole-diameter (mm) |
|---------------|---------------------|--------------------------|
| E. Cathode    | 83.4                | 23 (30)                  |
| Bipolar 3     | 86.5                | 20 (26)                  |
| Bipolar 2     | 89.4                | 16 (21)                  |
| Bipolar 1     | 92.2                | 11 (15)                  |
| E. Anode      | 89.4                | 16 (21)                  |

Fig.1 Schematic Diagram of Experimental Apparatus.
Fig. 2 Calculation of Cell Efficiency from Linear Relation between Applied Current and Bath Voltage.

\[ \beta' = \frac{R_e}{R_a} + \frac{(n[V_d - d')}{(d' - V_d)} \]

\[ I_{2M}^\beta = \frac{(n[V_d - d')}{c'} \]

\[ \eta_{el} = \frac{(n + \beta')(n - (1 + \beta')}{\{(n - 1)/(n + \beta')\} I_{2M}^\beta / I_T} \]

\[ \eta_{el}^{max} = A / I_T \]

\[ (l_T - V_d) \rightarrow c', d' \rightarrow \beta', I_{2M}^\beta \rightarrow \eta_{el} - I_T \]

Fig. 3 An Example of Linear Relation between Applied Current and Bath Voltage.

700°C, n = 4
NaCl–BaCl₂(7:1), 25 mol% MgCl₂

\[ 81.8\% \]

0 10 20 30 40 50 60

0 2 4 6 8 10 12 14

BATH VOLTAGE \( V_d \) (V)

APPLIED CURRENT \( I_T \) (A)
Fig. 4 Circulating Path of Chloride Melt in the Funnel-type Bipolar Cell.

Fig. 5 Time Variation of the Net Current Efficiency Calculated and Magnesium Chloride Content in the Melt. Smaller Center-hole and Solid Continuous Feeding.

608
Fig. 6 Time Variation of the Net Current Efficiency Calculated and Magnesium Chloride Content in the Melt. Larger Center-hole and Molten Intermittent Charging.

Fig. 7 Circulating Path of Chloride Melt in the Conical-type Bipolar Cell.
Fig. 8 Time Variation of the Net Current Efficiency Calculated and Magnesium Chloride Content in the Melt. Melt Level Changing and Solid Continuous Feeding.

Fig. 9 Time Variation of the Net Current Efficiency Calculated and Magnesium Chloride content in the Melt. Melt Level Controlling and Molten Intermittent Charging.