TECHNICAL NOTE

Effect of fluorspar on electrowinning of magnesium

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Received 28 May 1985

1. Introduction

Fluorides are usually added to electrowinning molten chloride systems because they lower the freezing point of the melt, decrease the viscosity of the melt and act as a fluxing agent to remove the undesired oxide coating on the metal substrate. The reason for the addition of fluorspar (CaF_2) in magnesium cells is to increase the yield of the magnesium production. Published work [1] recommends the addition of fluorspar of about 0.3 to 0.5% by weight; however, about 1% by weight of fluorspar was required to achieve a maximum current efficiency in our production cells. Unfortunately, there has been no systemmatic laboratory study to show what level of fluoride is preferred. An investigation was begun, therefore, to study the effect of fluoride on current efficiency for the electrolytic production of magnesium. Both short-term and long-term electrolysis was carried out and the data are presented and discussed in this report.

2. Experimental details

A conventional furnace and laboratory cell was used in this study. The furnace was electrically heated using a West controller and a nichrome resistance wire. Layers of fire bricks and high-temperature board minimized the heat loss due to radiation from the furnace. Control of the furnace temperature and monitoring of the melt temperature were achieved by using chromel–alumel thermocouples placed inside the furnace and in the melt, respectively. A quartz cell was employed as a melt container. The steel cathode and graphite anode were 25 cm^2 and 50 cm^2, respectively, and they were placed vertically in the cell bath with about 2.5 cm separation.

Sodium chloride-rich NaCl–$MgCl_2$ melt was used in all experiments; $CaCl_2$ and KCl were, however, present as other components in the cell bath. All chemicals used to prepare the melt were reagent grade, except $MgCl_2$; the source of $MgCl_2$ was hydrated Dow feed. The salt mixture was slowly heated under argon atmosphere to its melting point, and then the molten bath was maintained at around 700° C. The molten bath was first purified by chlorine sparging for about 1–2 h, then pre-electrolysis was carried out at 2 A for about 16 h.

Sodium fluoride was chosen as a fluoride additive because it has higher solubility in our molten bath than calcuim fluoride, and the addition of sodium fluoride does not change the melt composition appreciably since the bath is sodium chloride-rich. A known amount of sodium fluoride was added to the cell bath just before each electrolysis and the resulting bath was analysed for the fluoride concentration. Fluoride analysis was performed in triplicate. Cell bath (1 g) was placed in 20 ml of 22.5% nitric acid in a 2.5-litre Erlenmeyer flask fitted with a long condensing tube. The digestion was carried out at around 100° C for about 2 h. The sample was cooled for 45 min and then diluted to 250 ml with deionized water. Similarly, three standard fluoride samples in equivalent fluorspar concentrations of 0.6, 1.0 and 1.4 wt % were also prepared. The analyses were performed on an Orion Model 701A digital pH/mV meter using an Orian fluoride selective electrode Model 94-09 and an Ag/AgCl reference electrode. Three standards were run first in order to calibrate the instrument so that the number read on the meter for a test solution gave the wt % of fluoride directly as fluorspar.

Galvanostatic control for the electrolysis was achieved using a standard power rectifier which delivered up to 40 A d.c. current at 20 V. The applied current densities were 0.4 and 1 A cm^{-2}. At the end of each electrolysis the magnesium floating on the melt was collected, washed in water, dried and then weighed. This weight and

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the total charge consumed during the electrolysis were used for the current efficiency calculation.

For a long-time electrolysis, magnesium chloride feed was continuously supplied through an in-house screw-type feeder. The rate of feeding was regulated using a Bodine Electric Company variable speed feeder drive.

3. Results

3.1. *Short-time electrolysis*

To study the effect of fluoride on current efficiency in Dow magnesium chloride melt, the electrolysis was carried out at 1 A cm^{-2}. Duration of the electrolysis was restricted to 2 h to allow three or more runs each day at a given fluoride concentration. After each dipping the cathode was mechanically repolished while the bath was sparged with chlorine.

The cathode showed good wetting by magnesium with or without fluoride in the bath. Interestingly, once the metal was released from the cathode it appeared as small spheres when no fluoride was present, i.e. poor coalescence occurred even though the cathode was well wetted. The coalescence improved markedly with addition of fluoride to the cell bath. The current efficiency, was determined by averaging three to four electolysis runs, increased with increase in the fluoride concentration. The data are presented in Fig. 1. However, the efficiency reached a maximum value of 84% in the fluorspar concentration range of 1–1.4% and then gradually decreased with further increase in the fluoride concentration.

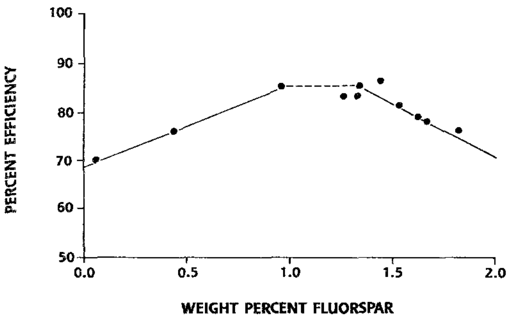

Fig. 1. The dependence of current efficiency on the fluorspar concentration. Current density = 1 A cm^{-2}, 2 h electrolysis.

3.2. *Long-time electrolysis*

To confirm the findings of the 2 h experiments, continuous electrolysis was carried out for longer periods to simulate the production cells. During the day experiments the applied cathodic current density was 1 A cm^{-2} and the metal removal interval (dipping) was about 8 h. For the overnight experiments, in which the dipping interval was about 16 h, a lower cathodic current density of 0.4 A cm^{-2} was applied so that the total amount of metal collected was approximately the same for the day and the overnight electrolysis. The steel cathode was cleaned only before the first run in this series of experiments. The cell was fed continuously during the electrolysis using hydrated Dow feed. The current efficiencies for magnesium electrodeposition at various fluorspar concentrations are given in Table 1. As anticipated, these data are in excellent agreement with the results obtained for short-time electrolysis.

4. Discussion and conclusions

Under favourable electrolysis conditions, it has been shown that a maximum current efficiency of up to 84% is possible in Dow magnesium cell bath when the fluorspar concentration is maintained around 1–1.4%. These results are in better agreement with those observed in our production cells compared with other published work for a similar or other magnesium chloride baths [1].

Although the wetting of magnesium on the mechanically polished steel cathode was excellent during electrolysis in baths with or without fluoride (as shown in this work), this does not

Table 1. Effect of fluorspar concentration on current efficiency

Fluorspar concentration (wt %)	*Current efficiency (%)*
0.4	74
0.8	80
1.2	84
1.4	80
1.6	73

preclude the fluxing action of the fluoride in removing the surface oxides if present on the electrode, thereby enhancing the magnesium wetting [1].

The beneficial use of fluorspar as an additive is known to be due to the fluxing action of the fluoride on the surface oxide of the growing magnesium balls, since the small spheres coalesce to bigger balls in cell baths that contains fluoride ions [1]. With bigger balls the effective surface area of the magnesium in the cell bath for chlorine attack is reduced and hence the current efficiency for magnesium production is maximized.

In addition the fluoride ions can modify the electrochemical reactions at the electrodes. According to Jurewicz [2], the addition of a small quantity of fluoride ion to an aqueous sodium chloride solution causes a distinct decrease in the current efficiency of chlorine evolution with an increase in the production of carbon monoxide at the graphite anode. Such changes in the rate of the anodic reactions are possible in magnesium cells since the cell bath contains about 1% fluorspar. A reduction in the amount of chlorine in the cell bath should decrease the rate of rechlorination of magnesium and hence increase the current efficiency of the magnesium electrodeposition. Moreover, simultaneous liberation of carbon monoxide and chlorine on a graphite electrode may produce phosgene, a powerful chlorinating agent. This would consequently reduce the amount of oxides, in particular MgO and CaO, in the melt.

In recent work [3], there is evidence for a change in the mechanism of the cathodic reaction in the presence of fluoride ions in a chloride melt. When sodium fluoride was added to a $NaCl-KCl-ZrCl_4$ melt, the reduction of Zr^{4+} ions to zirconium metal proceeded by a single four-electron step instead of the two-electron steps normally observed in the fluoride-free chloride bath. No experimental proof is as yet available to confirm or deny the different mechanisms for the electrodeposition of magnesium from our cell bath with or without fluoride ions; however, more fundamental work is currently in progress in this laboratory which will provide further evidence.

The loss of current efficiency for the electrolytic production of magnesium when the fluorspar concentration was less than 1% and greater than 1.4% needs explanation. In the presence of small amounts of fluoride ions, i.e. less than 1% fluorspar, the growth of the oxide layer on the magnesium balls accelerates to give tiny spheres. These spheres are hard to dip and, moreover, settle at the cell bottom as a sludge due to their high density. Above the critical fluoride concentration, i.e. greater than 1.4% fluorspar, the fluoride ions not only attack the surface oxide on the magnesium but also oxidize the magnesium itself. A similar explanation was recently given [4] for the observed decay in the photocurrent of n-type silicon, an element with high affinity for oxygen, in an aqueous solution containing fluoride together with a reducing agent. Therefore the critical fluorspar concentration (1–1.4%) which is sufficient to remove only the surface oxide, is essential to achieve the maximum current efficiency in Dow magnesium cells.

5. Summary

The effect of fluorspar on current efficiency was studied in a laboratory scale cell using a Dow magnesium cell bath. Both short-time (2 h) and long-time (8–16 h) electrolyses gave a maximum current efficiency of 84% for the electrolytic production of magnesium using a fluorspar concentration of 1–1.4 wt %. The beneficial effect of the fluorspar has been attributed to the fluxing action of fluoride on the surface oxide of the electrolytically produced magnesium balls.

Acknowledgements

The technical assistance of Mr Juan J. Lopez and the advice of Dr Ken G. Claus are gratefully acknowledged.

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