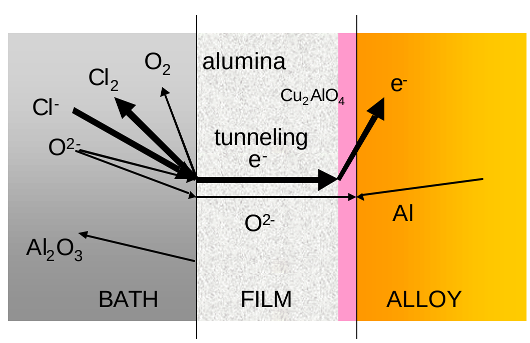
Nonconsumable Metal Anodes for Primary Magnesium Production

Problem/Opportunity

Over half of the world's magnesium metal is produced by molten salt electrolysis, with magnesium metal produced at the cathodes and chlorine gas generated at carbon anodes. The anodes react with residual oxygen in the electrolysis cell to form carbon dioxide gas. The reaction slowly consumes the anode and results in an ever-increasing anode-to-cathode distance, leading to increased voltage and increased energy use in the cell. In addition, chlorine gas reacts with residual hydrocarbons in the carbon anode, resulting in the formation of chlorinated hydrocarbons (CHCs). CHCs are toxic and pose a threat to the environment. The magnesium industry has an opportunity to realize energy savings and eliminate CHCs by developing nonconsumable metal anodes for use in primary magnesium production cells. Metal anodes are incapable of forming CHCs in magnesium electrolysis cells because there is no carbon source. However, metal anodes can readily react with chlorine to form metal chlorides that destroy the anode and contaminate the magnesium metal product. The challenge is to find a suitable metal alloy that does not react or become consumed when used as an anode in electrolysis cells.

Approach

Argonne is investigating certain metal alloys that form protective oxide films on their surface. The oxide films would be thick enough to protect the underlying metal from chlorination, yet thin enough to allow current to pass without a substantial voltage drop. The alloys under consideration are those that contain aluminum as the oxide film-forming metal. The alumina films are slightly soluble in the molten chloride salt used in the electrolysis cell. However, residual oxygen in the cell is available to diffuse through the oxide film to the metal/film interface in the anode and reform the film by reacting with segregating aluminum metal. This mechanism will also self-heal the film should it become scratched or damaged. Argonne is performing basic research to determine oxidation rates, segregation rates, and films dissolution rates on various alloy systems. In addition, Argonne is also determining film dissolution rates to identify the mechanisms of film formation and maintenance. Chlorination studies are used as a screening tool to help identify candidate alloys. Candidate alloys are tested in bench-scale magnesium electrolysis cells to determine anode durability, wear rate, and product magnesium metal purity. Cell gases are analyzed in line with UV-Vis and Fourier Transform Infrared (FTIR) spectrometers. In addition to the metal anode work, the project also addresses cell-operating

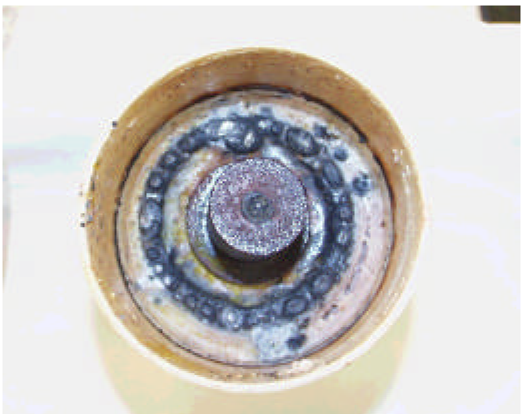


The anode/bath interface

parameters that affect the formation of CHCs.

Results

Several alloy compositions were investigated, most of which were based on the copper-aluminum system. Analyses of their surface films indicate that this class of



Top view of cell after electrolysis test to investigate CHC formation. The cylindrical carbon anode and tubular concentric steel cathode were raised to the surface of the salt before solidification. Anode and cathode current leads were removed. Note the spheres of magnesium metal product that collect at the top surface of the cathode.

alloys form a thin self-limiting alumina film. This phenomenon may be due to this thin copper aluminate layer ($Cu2AlO4$) that forms between the alumina. Electrolysis testing of these alloys in bench-scale cells (70 A) showed that their corrosion rate during electrolysis is significantly less that that of pure metals. However, thermal cycling of the alloy prior to use appears to damage the protective film. New alloys that overcome this problem are being developed. In addition to tests with alloys, several purity grades of carbon were evaluated in electrolysis tests. Preliminary results indicate that carbon purity has a substantial effect on the amount of CHC formation during electrolysis.

Future Plans

Alloy development work will continue to optimize the alloy chemistry of those alloys that showed promise in bench-scale electrolysis cells. Larger-scale testing in 200-A cells are planned. These tests would last 100 hours and would require development of cell feeding and Mg product removal techniques. A gas sampling procedure to collect CHC samples for analysis is being developed. Upon completion of the 200-A cells, Argonne will determine whether to test the metal anodes in pilot-scale electrolysis cells in 2002.