

Introduction

Over the years, researchers of the Hall-Heroult Process for smelting aluminum have proposed various explanations of the "fog" or "metal mist" that develops in the electrolyte and for the "anode effect". Difficulty to clearly observe these phenomena in operating cells, where observation must be made by looking down into the melt, has hampered interpretation of experimental data. Vajna, Zhemchuzhina and Belyaev, and Derge and Shegog, made observations within a wall-less Hall-Heroult cell consisting of a single drop of molten electrolyte between electrodes. (1,2,3,4) The very small size of their cells, however, probably caused much different mass transport conditions than are present in a commercial cell. To achieve a somewhat closer approximation of commercial conditions, three different designs of bench-scale see-through cells were developed. Each had certain advantages and disadvantages, which will be described.

Quartz Cell

The simplest see-through cell was a large quartz test tube (70 mm ID x 406 mm long with 2 mm walls) suspended in an electric furnace (Fig. 1). The furnace had quartz windows at front and back for external illumination and viewing. Each window consisted of two 60 x 120 x 3 mm quartz plates separated by an air gap to reduce heat loss. A number 1383, 12V, miniature spot lamp was operated at an adjustable 8-16 volts to provide variable front lighting. Rear illumination was provided by a DFC motion picture projection lamp with internal reflector. The electrodes for the cell were either a pair of vertical graphite plates positioned parallel to each other (Fig. 2), or a horizontal graphite anode positioned over a horizontal graphite cathode (Fig. 3). The latter was more like the true configuration of a commercial Hall-Heroult cell. For both configurations, graphite electrical leads (sleeved with quartz in the early cell and with boron nitride in later cells) extended vertically up the test tube and served as electrode supports. These leads were brought out through electrically insulated seals in a stainless steel cover, which in turn was attached to the test tube with RTV silicone rubber. Additional sealed ports in the cover were provided for: bath addition, feeding alumina, thermocouple well, gas outlet tube, and argon purge tube. In all cases, the electrolyte was 8%  $AlF_3$ ,

## SEE-THROUGH HALL-HEROULT CELL

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See-through bench scale Hall-Heroult cells were constructed employing either quartz walls, or graphite walls with sapphire windows. Observations were made of electrolyte circulation, gas bubbles and metal mist prior to, during, and following electrolysis. Decreasing oxide content increased anode bubble size culminating in an anode effect. Hydrogen bubbles and dark violet "metal mist" streamers emanated from the cathode. The color of the streamers suggests F-centers.

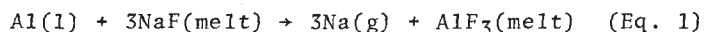
7% CaF<sub>2</sub>, 2-8% Al<sub>2</sub>O<sub>3</sub>, balance Na<sub>3</sub>AlF<sub>6</sub>. This mixture was premelted at 980°C in a platinum crucible, then the upper three-fourths poured into the cell which had been preheated to 980°C while being purged with argon to prevent air burning of the electrodes.

Surprisingly, the quartz test tube was able to hold the molten electrolyte for more than two hours without sufficient attack to cause leakage. Moreover, etching of the quartz which occurred did not affect visibility, apparently because the index of refraction of the electrolyte and quartz are quite similar. Under certain conditions which will be explained later, the quartz did stain and reduce visibility. Color motion pictures were used to confirm and augment visual observations.

When aluminum was added to the melt prior to electrolysis, hydrogen bubbles arose profusely from the molten metal as it reacted with moisture dissolved in the melt. Identification of the bubbles as hydrogen was made by mass spectographic analysis of the off-gas.

In addition to hydrogen bubbles, streamers of "metal mist" or "fog" always arose from the molten aluminum. These streamers had a dark purple color by transmitted light and a grey smoky color by reflected light. They dissipated as they rose in the melt, much as cigarette smoke does in air. Although the disappearance of the streamers was caused in part by dilution, oxidation, either by residual moisture remaining in the electrolyte or by CO<sub>2</sub> during electrolysis, also seems probable. Whenever the streamers contacted the cell walls, the quartz first turned grey; then opaque with continued contact. Electron diffraction analysis of this coating on the quartz showed it to be silicon. While Na, Al, or AlF could reduce SiO<sub>2</sub> to Si, one would expect Al to form an Al-Si alloy rather than pure Si. Hence, the "mist" probably is not a dispersion or colloid of aluminum.

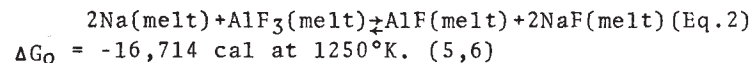
Sodium could not be produced at unit activity by the reaction:



because of the large positive free energy change:

$$\Delta G_0 = +35,733 \text{ cal at } 1250^\circ\text{K.} \quad (5,6)$$

Sodium could be formed at low activity, however, by dissolving in the melt. Bredig found solubility of Na in molten NaF. (7) Gruen et al found that alkali metals, M, dissolve in alkali halides forming M<sup>+</sup> ions and F centerlike electrons ("Solvated" electrons). (8) This could account for the purple color of the streamers. An activity of Na could not, however, be present in the melt without generating also an activity of AlF.



Although we do not know  $\Delta G_f$  of AlF<sub>3</sub>(l), or the activities of AlF<sub>3</sub> and NaF well enough to calculate accurately the activity of either Na or AlF in the melt, we do know that the vapor pressure of Na exceeds many times the vapor pressure of AlF over the melt. (9) Hence, we can reasonably assume that streamers: 1) represent some reduced species in process of being dispersed in the electrolyte; 2) have a low activity of Na and an even lower activity of AlF; 3) provide electron traps that give the streamers their color.

Co-author Haupin previously reported that the so-called "metal mist" was hydrogen bubbles. (10) This explanation was based upon the simultaneous cessation of hydrogen evolution and disappearance of foginess in a cryolite base melt held over molten aluminum. He now retracts that conclusion. When those earlier tests were repeated, he found that a quiescent pool of aluminum formed an oxide film over its surface, causing a simultaneous disappearance of hydrogen evolution and metal fog. However, if the metal was stirred, the metal fog persisted after hydrogen evolution stopped. The present experiments show clearly that hydrogen is evolved but in a distinctly different process from that responsible for formation of the metal mist.

#### Phenomena During Electrolysis

When electrolysis was started in the cell, gas bubbles were immediately observed forming on the anode. A smaller quantity of gas bubbles were also observed forming on the cathode. The latter probably resulted both from the electrolysis of water to produce hydrogen and from gas driven out of the pores as electrolyte entered the cathode under electrolysis. After a short period of electrolysis, metal began to desposit on the cathode

and streamers appeared in the melt, identical in appearance to the streamers that arose from a pool of molten aluminum without electrolysis. With continued electrolysis at commercial current density, the entire bath became foggy and soon all visibility was obscured. It was surprising in the early runs in quartz to find that the deposit on the cathode was solid rather than molten. Analysis of the deposit showed that it was mostly silicon, which came from quartz that had dissolved in the electrolyte.

It was observed that the size of the bubbles formed on the anode was inversely related to the oxide concentration in the electrolyte, regardless of whether the oxide was silica or alumina. When the concentration of oxide, expressed as oxygen, exceeded 4% by weight in the electrolyte, tiny froth-like bubbles were evolved from the anode. This condition caused vigorous agitation of the bath. At oxygen contents below 1.5%, bubbles clung to the anode and traveled up its surface to escape, rather than breaking free into the bath. This condition caused very little agitation of the electrolyte. Increasing the current density also increased bubble size. Progression from small bubbles to anode effect was continuous and gradual. Bubbles progressively grew larger and larger, until finally one bubble completely enveloped the entire anode. The inductive surge as the current broke through the insulating gas film caused violent local agitation of the bath. This agitation sometimes broke the anode effect, only to have it re-establish itself a fraction of a second later. Sometimes there would be three or four rapid oscillations on and off anode effect before a stable anode effect was established. A stable anode effect was characterized by a complete envelope of gas around a non-wetted anode. This gas envelope was bridged by thousands of tiny, moving electrical arcs. Since no electrolyte contacted the anode during anode effect, and we know from gas analysis that carbon monoxide was being formed continuously, either carbon must be transported across the gas film in one direction, or oxygen in the other.

#### Graphite-Lined Quartz Cells

In order to prevent heavy contamination of the bath with silica dissolved from the cell walls, with the resultant silicon alloy deposit on the cathode,

the quartz test tube was lined internally with graphite except for 25 mm x 100 mm openings at the front and at the back to provide a window for viewing within the cell. Even this decreased accessibility of the electrolyte to silica, however, was not sufficient to keep the bath from becoming severely contaminated. Therefore, it was decided to replace the graphite-lined quartz cell with a graphite container having clear sapphire windows.

#### Graphite Cell With Sapphire Windows

Sapphire windows 25.4 mm diameter x 3.2 mm thick were obtained from Union Carbide. The windows were held in place by an Inconel retaining ring threaded into the graphite crucible (Fig. 4). Although the window maintained a tight seal at room temperature, it was feared that different coefficients of expansion might cause loosening of the seal at elevated temperatures. Therefore, the entire graphite cell was encapsulated in quartz and the space between the two filled with molten sodium chloride. The hydrostatic head of sodium chloride outside the cell balanced the hydrostatic head of electrolyte within the cell, thus eliminating any pressure differential which might cause leakage. Any leakage would have to be by diffusion. No evidence of such leakage was observed. No electrical contact was made to the graphite wall of the cell. Electrodes of the type shown in Fig. 2 were used. This cell operated very well and produced fairly pure aluminum. Streamers that looked identical to those in the quartz cell emanated from the cathode. The size of bubbles on the anodes was a function of alumina in the same manner that it was a function of alumina plus silica in the quartz cell. All observations in the quartz cell seemed to be confirmed in the sapphire window cell. The principal difficulty with this cell was the limited field of view, caused by the small size of the sapphire window. This was a more serious limitation to photography than to visual observation since one can effectively increase his field of vision by moving his head.

#### Conclusions

Observations within see-through cells led to the following conclusions:

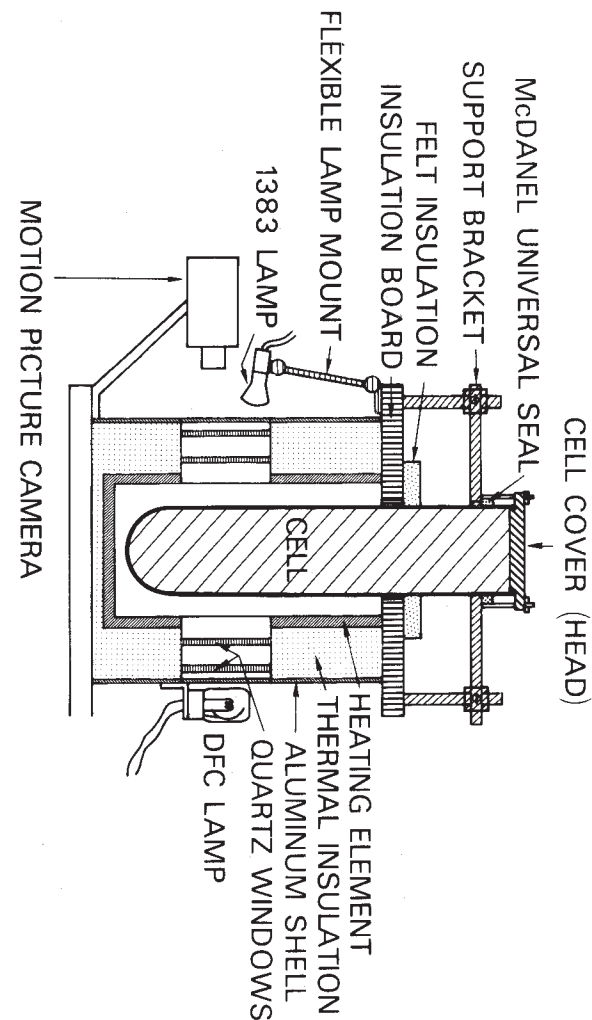
1. Streamers have the same appearance when depositing silicon as when depositing aluminum.
2. Streamers appear to be highly concentrated "fog" in the process of dispersing in the melt.
3. Streamers contain as yet unidentified reduced species that produce a low activity of Na and a lower activity of AlF in the melt.
4. Streamers probably contain "solvated" electrons (F-centers) which produce their characteristic color.
5. Bubble size on the anode increases with increasing current density and decreasing oxide content in the electrolyte.
6. Anode effect occurs when a single bubble grows large enough to envelop the entire anode.

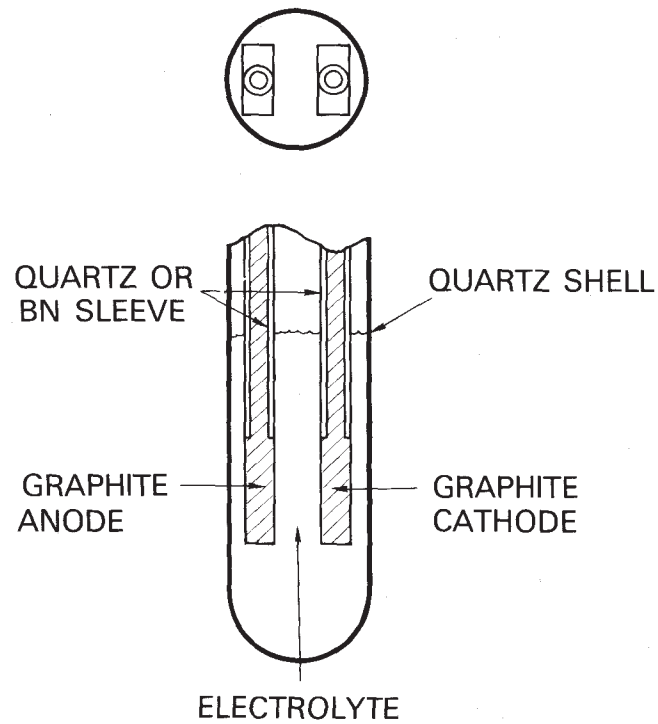
References

1. Vajna, A., Metallurgia Ital., Vol. 44, 1952, pp.585.
2. Vajna, A., Electrochim Metallorum, Vol. 3, 1968, pp. 376.
3. Zhemchuzhina, E.A. and Belyaev, A.I., Tsvetnaya Metallurgiya, No. 5, 1961, pp. 123.
4. Derge, G. and Shegog, J.R., Light Metals, Vol. 1, 1973, pp. 135; pub. TMS-AIME.
5. JANAF Thermochemical Tables, 2nd Ed., NSRDS--NBS 37.
6. Grotheim, K.; Holm, J.L.; and Welch, B.J., Acta Chem.Scand., Vol. 25, 1971, pp. 2370.
7. Bredig, M.A. and Bronstein, H.R., J.Phys.Chem, Vol. 64, 1960, pp. 64.
8. Gruen, D.M.; Krumpelt, M.; and Johnson, I., Molten Salts, Mamantov, G., Editor; pub. Marcel Dekker, New York, 1969, pp. 169.
9. Frank, W.B., Discussion of Paper, Gjerstad, S. and Welch, B.J., J. Electrochem, Vol. 112, No. 6, 1965, pp. 649.
10. Haupin, W.E., J. Electrochem Soc., Vol. 107, No. 3, 1960, pp. 174.

EXTERNAL HEATING FURNACE

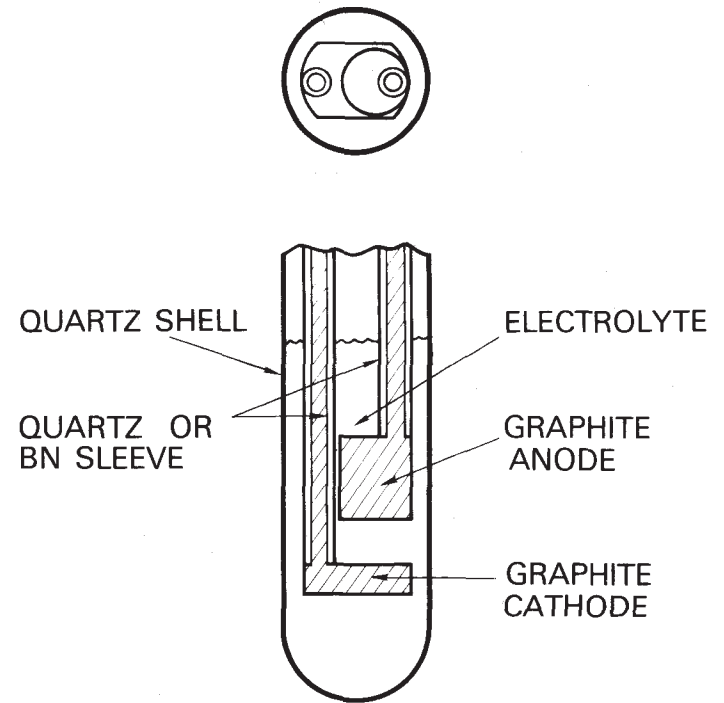
Figure 1





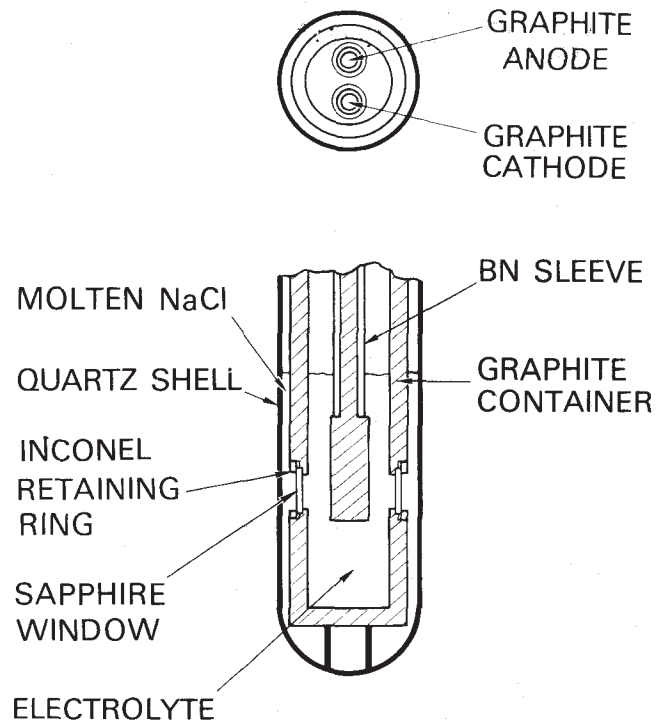
VERTICAL ELECTRODES

Figure 2



HORIZONTAL ELECTRODES

Figure 3



CELL WITH SAPPHIRE WINDOW

Figure 4