2011

The Race for Cheap Aluminum: Hall Versus Héroult

Dean F. Martin

University of South Florida, dfmartin@usf.edu

Follow this and additional works at: https://digitalcommons.usf.edu/chm_facpub

Scholar Commons Citation

Martin, Dean F., "The Race for Cheap Aluminum: Hall Versus Héroult" (2011). *Chemistry Faculty Publications*. 6.

https://digitalcommons.usf.edu/chm_facpub/6

This Article is brought to you for free and open access by the Chemistry at Digital Commons @ University of South Florida. It has been accepted for inclusion in Chemistry Faculty Publications by an authorized administrator of Digital Commons @ University of South Florida. For more information, please contact digitalcommons@usf.edu.

THE RACE FOR CHEAP ALUMINUM: HALL VERSUS HÉROULT

Dean F. Martin

Institute for Environmental Studies, Department of Chemistry, University of South Florida, Tampa, FL, USA

The factors that determine priority in inventions are illustrated in the development of a commercially acceptable process for preparation of aluminum in 1886 when it was achieved by two young (age 22) men (Hall and Héroult). At least three factors were involved in the parallel achievement. The specific success of Charles Martin Hall in obtaining the US patent was a consequence of a couple of factors. One was likely the assistance of his elder sister; the other was the rule of the United States Patent and Trademark Office concerning priority, viz., first to “reduce to practice” versus the standard in France and other nations, first to submit an acceptable patent application. The Patent and Trademark Office will change rules soon to conform to the practice of other nations.

Key words: Aluminum; Charles Martin Hall; P. L. T. Héroult; Cryolite

INTRODUCTION

In most nations of the world, a patent will be granted to the inventor(s) who are the first to apply, but the situation is different with the United States Patent and Trademark Office (USPTO). The criterion that office has used has been the date of “reduction to practice.” It is proposed to make a change so that the USPTO will follow the practice of other nations (9).

It is interesting to speculate on what would have happened in the late 19th century had the revised practice been in force. One answer is the Hall Process for the electrolytic production of metallic aluminum would be named the Héroult Process, just as it is in France and other European nations. The race for cheap aluminum would have been lost, not won, by Charles Martin Hall.

BACKGROUND

Properties of Aluminum

Aluminum is the most abundant element in the earth’s crust, as noted in Table 1, and it has been

in use for over 7,000 years. But until 1886, cheap aluminum and hence wide-spread use was not possible. The potential uses were great, based on our present knowledge (1).

Aluminum has a range of uses. It has been used as siding for houses (as described in the movie *Tin Men*). The pure metal rapidly forms an impervious oxide coating that passivates it or renders it inert to further reaction (3). This property also makes it an ideal metal for decoration and decorative functions. More than 7,000 years ago potters in Persia (Iran) made the strongest pictures and bowls from clay containing aluminum as aluminum oxide (1). The ductility, comparatively low density, and excellent electrical conductivity should make it ideal for electrical transmission, and it is cheaper than metallic copper (3,8). Unfortunately, prominent failures of aluminum wire connections in residences occurred in the early 1980s; the connections were accompanied by a so-called “glow failure” (10). The aluminum wire–screw connection would develop a glow, which constituted a safety hazard in the presence of combustible material (10). This was investigated at the National Bureau of Stan-

Table 1. Selected Properties of Aluminum (8)

Property/Characteristic	Value
Atomic number	13
Abundance in earth's crust (%)	8.13
Relative atomic mass	26.981
Density (kg/m ³ (293°K)	2698
Molar volume (cm ³)	10.00
Melting point (°K)	933.52
Boiling point (°K)	2740

dards and the influence of intermetallic compounds was noted (10).

Aluminum could be favored as a structural metal, and warships were built with aluminum superstructures to take advantage of the comparative low density. Unfortunately, the British Navy recognized the potential hazard when one such structure was struck with an Exorset missile during the Falkland campaign. Aluminum by itself has limited mechanical strength, but the alloys with copper, manganese, silicon, magnesium, and zinc have been prepared and have enhanced mechanical properties (3).

Cost of Aluminum

The resistance of aluminum to the elements (3) was recognized as an asset when a metal was selected for the tip of the Washington Monument (4). The cornerstone had been laid in 1848, but it was not completed until 1885. Although aluminum was not the first choice for a capstone, it was finally selected after conversations between Col. Thomas Lincoln Casey, US Army Corps of Engineers (engineer-in-charge) and William Frishmuth, owner of a foundry, who undertook to prepare a metal pyramid that had two functions: as a capstone, and as a lightning rod. The pyramid, when finally produced, was 22.6 cm high, 13.9 cm at the base, and weighed 2.85 kg (4). The quoted price was \$75, and the final bill was \$256.10 (4). After some discussion, the final price paid was \$225 (4). By mutual agreement it was exhibited at Tiffany's in New York City for two days. It provided considerable publicity for aluminum, at the top of what was then the tallest man-made building in the world (4).

The cost of aluminum has varied considerably

over the years, as may be seen in Table 2 (14). Frishmuth may have paid \$1 an ounce, \$16 per pound (4). And, of course, that is expensive by present standards, but Binczewski (4) placed the cost in good context. In 1884, a laborer working on the Washington Monument was paid \$1 a day when the workday was commonly 10 h, sometimes longer. The highest skilled craftsman earned \$2 per day (4).

Clearly, with all the publicity about aluminum, there was enthusiasm for cheap aluminum, and two young men, Hall and Héroult, won the race in 1886 (6,7,12,13). They did not win the race in vacuo, as it were, as may be indicated in the next section.

Electrolytic Approach to Preparation of Aluminum

The preparation of aluminum from aluminum salts clearly required a reducing agent. And during the early part of the 19th century, a chemical agent was used, including sodium, potassium, and potassium amalgam (13). The reducing agents were hazardous, and the form of aluminum used was expensive to prepare.

The closeness of the race (both protagonists were successful in 1886) may be due to three factors. First, finding a successful method for a large-scale, inexpensive method for the preparation of aluminum was widely recognized "as a prime target for invention" (13).

A second factor was that during the latter quarter of the 19th century electrolytic reduction as a commercial process was "much in the air," as a few examples should indicate (13).

Table 2. Price of Aluminum 1855–1990 (1,4,14)

Year	Price (\$/lb)
1855	100,000
1884	16
1888	4.86
1890	2
1893	0.78
1895	0.50
~1938	0.20
1970	0.30
1980	0.80
1990	0.74

- 1883: V. A. Tyurin, a Russian chemist, proposed preparing aluminum by electrolysis of molten cryolite (Na_3AlF_6) and sodium chloride.
- 1884: Jozef F. Boguski received a British patent concerned with synthesis of aluminum bronzes by electrolysis of aluminum compounds.
- Cowles and Company (Lockport, NY) acquired the Boguski patent and used the process to produce alloys of aluminum.

A third factor was the recent availability of large dynamos for generating electricity (6).

THE PROTAGONISTS

Charles Martin Hall, an American, and Paul Louis Toussaint Héroult, a Frenchman, had parallel lives. Both were born in 1863, they made their most significant discovery in 1886, and they died in 1914 (13).

Charles Martin Hall

Useful biographies of Hall are available (6,7,13). What follows here are the salient features of his life.

Hall was a student at Oberlin College, and was inspired by Professor Frank Fanning Jewett, who described his experiences in Germany working for Friedrich Wöhler. The latter had prepared impure aluminum by reduction of anhydrous aluminum chloride using potassium as a reducing agent. Hall had made a crude laboratory in the woodshed next to the family home. Using homemade batteries, an iron frying pan, and cryolite, Na_3AlF_6 (a mineral found in Greenland), he managed to prepare a handful of aluminum buttons on February 23, 1886. He rushed into Professor Jewett's office and showed them to him (6,7).

There were two reactions to Charles Martin Hall's achievement: his supporters and financiers. Potential financial backers were not necessarily impressed by some small buttons. But in due course, Hall obtained financial backers that formed The Pittsburgh Reduction Company. Hall scaled up the reduction process, and in time it became a noted success. The Pittsburgh Reduction Company led to the Aluminum Corporation of America (Alcoa) (1,5). The original buttons were carefully preserved

in a chest by Alcoa in Pittsburgh, where they were referred to as the aluminum "Crown Jewels" (5,6). The effect of the process may be seen in Table 2 (i.e., the difference in price of aluminum before and after 1886) (14).

Hall had competition and problems. One source was from Cowles and Company. He had worked in the Cowles plant as he tried to interest them in supporting his project, without success. But after the successful establishment of the "Hall Process," he was sued by the Cowles family who claimed patent infringement. The complicated suit that followed was won by Hall (6,7).

Paul Louis Toussaint Héroult (13)

Competition came from another source in south France. At 15, Héroult had read a famous treatise on aluminum written by Sainte-Claire Deville, whose sodium reduction process was responsible for one significant drop in price (13).

In 1885, Héroult attempted to electrolyze various aluminum compounds. Using a steam engine and the dynamo of the small tannery he had inherited, he tried to electrolyze cryolite using an iron electrode and a carbon electrode, and he found that the iron electrode melted. He realized that an alloy had been produced. So to lower the temperature, he added sodium aluminum chloride, repeated the electrolysis, then noted that the carbon electrode had been attacked. He realized that the aluminum compound was impure, that it contained aluminum oxide because of moisture. He subsequently obtained a patent in France (April 23, 1886).

THE ROLE OF JULIA BRAINARD HALL (12)

At a patent interference case brought by Dr. Héroult, Hall was forced to establish that he had reduced his invention to practice before April 23, 1886, the date that Héroult's French patent was awarded. Hall was a witness, as were two Oberlin professors, including Dr. Jewett. But it seems likely that the key witness was Julia Brainard Hall (2,12).

Julia Hall's Background

Trescott (12) claimed that Ms. Hall had several qualities that made her a significant witness at the

patent infringement trial. These include the following:

- Proximity: As the eldest sister, she cared for her mother in the days of her final illness, then upon her mother's death assumed responsibility in running of the household. Her headquarters were in the kitchen next to the woodshed laboratory.
- Education: Julia Hall, an alumna of Oberlin, was also a student of Professor Jewett, and in fact had slightly more credits in science than her brother, although she received a diploma (not a degree) for successful completion of the "Literary Course" (12).
- Involvement/eye witness: Trescott (12) noted that Julia Hall was often in the woodshed laboratory, assisting Charles and "consulting with him on technical and scientific matters."

Julia Hall's Technical Assistance

- Secretarial assistance: From childhood Julia and Charles Hall wrote to each other, even though they were in the same household. That practice continued into adulthood and was probably invaluable. Julia Hall maintained order in the letters that her brother wrote concerning his experiments as well as maintained copies of letters he wrote seeking information (12).
- Laboratory documentation: Ms. Hall recorded the results of a given day's work with appropriate technical detail, together with date and evidence that would support the correctness of the date (12).
- The history document: In 1887, Julia Hall prepared a six-page document "History of C. M. Hall's Aluminum Invention." This document served as an important contribution in the Hall-Hérault patent interference case (12).

It needs to be noted that Emily Acton Phillips, a great-granddaughter of Emily Brooks Hall, a sister of Charles and Julia Hall, expressed concern that Trescott had advanced a hypothesis that Julia Hall was a coinventor, and Ms. Acton believed that this was a misinterpretation of the efforts of Julia Hall "to provide encouragement and family support" (11).

THE CASE

The key point in the patent interference trial centered on the date at which the invention was "reduced to practice."

- Hall filed his patent application: July 9, 1886
- Hérault's patent (France): April 23, 1886
- Aluminum produced by Hall: February 23, 1886
- Hall disclosed his ideas about invention: February 10, 1886

The trial is disclosed in official documents, but the important feature is that Mr. Hall won the infringement case, and he was also the winner of the race for cheap aluminum (Table 2).

THE PATENTS

The litigation delayed awarding patents to Charles Martin Hall, but in April 2, 1889, some five patents were awarded (5,7). In his lifetime, Charles Martin Hall would be granted over 20 patents, most associated with aluminum. A visit to the U.S. Patent and Trademark web page (<http://www.uspto.gov>) shows three closely related ones:

No. 400,664 "Process for reducing aluminum from its salts": Indicates the importance of $[AlF_6]$ 3-salts.

No. 400,665 "Manufacture of aluminum": Describes design of carbon-lined iron crucible with carbon anodes, general process, composition of mixture, products.

No. 400,666 "Process for electrolyzing crude salts of aluminum": Describes an improvement in the method for preparing aluminum by fusing and electrolyzing a combination of aluminum fluoride, calcium fluoride, sodium fluoride, and calcium chloride. One may suspect the purpose of first three was to prepare synthetic cryolite and the last to depress the melting point and save electricity.

Hall was no doubt proud of the patents that were in fact printed objects of beauty (7). It was later that he came to appreciate that a patent gives the inventor the right to defend an invention; much litigation followed (6,7).

WHAT HAPPENED LATER?

Alcoa became a major firm and, in 1994, it had become a major global presence through “internal growth, worldwide partnerships, and major acquisitions in Europe and the U.S., doubling its revenues and tripling its earnings” (1). Alcoa has remained the world’s leading aluminum company (1). The growth is described in more detail by Carr (5), who noted the remarkable growth of the operation from the early days of the Pittsburgh Reduction Company. The impact on early employees was remarkable; some became notably rich. In the early days, a new graduate of Amherst (Arthur Vining Davis) was hired to work at night and ease Charles Martin Hall’s time burdens. Davis remained with the company, later becoming Chairman of the Board, and, in time, he was executor of C. M. Hall’s will (5).

When Hall was a vice president at Alcoa, this company had a monopoly on the preparation of aluminum, a condition that continued some 40 years after his death. During World War II, Alcoa made significant contributions in the expansion of the production of aluminum, building and running government-mandated aluminum factories. Afterwards, antitrust actions caught up, and Alcoa was forced to reduce the capacity share from about 90% to 51%, with about 29% for Reynolds, and 20% for Kaiser (5).

Charles Martin Hall received the Perkin Medal of the American Chemical Society, the highest award of the Society, in 1911. Dr. Héroult came from France to be present, and he made a contribution to the tributes (5). In the acceptance speech, Hall did not specifically credit Julia when he told of “family involvements in the invention and innovations leading to the Pittsburgh Reduction Company” (12).

Charles Martin Hall became extremely wealthy. By the time he died, his Alcoa stock alone produced an annual income of \$170,000. His sister Julia, at the time she died in 1925, was averaging about \$8,000 annually (1909–1925) from Alcoa stock, a considerable income for the time. Her sister Edie also benefitted from common stock dividends (1909–1919) as did her sister Louie (1909–1925) (12).

Hall, an alumnus of Oberlin College, was generous to the college. He served as a Trustee (1905–

1914). He endowed to Oberlin College most of his material possessions, roughly one third of his Alcoa stock, and other investments (10). His contributions were undoubtedly appreciated, and he is memorialized in a statue of him in the chemistry area (12). The statue is made of aluminum.

ACKNOWLEDGMENTS: I am grateful to Mrs. Barbara B. Martin for helpful criticism, to Ms. Marianne McDonough (University of South Florida Library Acquisitions) for providing a copy of a useful article, and to two anonymous reviewers for helpful comments. The author declares no conflict of interest.

ABOUT THE AUTHOR

Dean F. Martin, Ph.D., is Distinguished University Professor Emeritus in the Department of Chemistry at the University of South Florida. He was educated at Grinnell College (B.A., 1955), The Pennsylvania State University (Ph.D., 1958), and University College, London (NSF Postdoctoral fellow, 1958–59). He was a faculty member of the University of Illinois-Champaign-Urbana before joining USF in 1964, retiring in 2006. He is the author or coauthor over 300 publications, and several books, including *Laboratory Chemistry*, *Marine Chemistry*, and *Marine Pharmacognosy*. He is a charter member of The Academy of Inventors. He was the 2010 recipient of the USF Alumni Association “Class of ’56 Award.”

REFERENCES

1. Anonymous. It all starts with dirt. The making of aluminum at ALCOA. Pittsburgh: Alcoa, Inc.; 2002.
2. Anonymous. Charles M. Hall vs. P. T Héroult. In: Interference in the United States Patent Office, October 24, 1887, pp. 5–8 (J. B. Hall testimony).
3. Banks, A. J. What’s the cost. *J. Chem. Educ.* 64(1):18; 1992.
4. Binczewski, G. J. The point of a monument: A history of the aluminum cap of the Washington Monument. *JOM* 47(11):20–25; 1995.
5. Carr, C. C. Alcoa. An American enterprise. New York: Rinehart & Company, Inc.; 1952.
6. Craig, N. C. Charles Martin Hall—the young man, his

- mentor, and his metal. *J. Chem. Educ.* 63:557–559; 1986.
7. Edwards, J. D. *The immortal woodshed*. New York: Dodd, Mead & Co.; 1996.
 8. Emsley, J. *The elements*, 2nd ed. Oxford: Clarendon Press; 1991.
 9. Guten, H. M. Protecting your competitive advantage. Paper presented at a symposium on The Basis of Intellectual Property Protection, sponsored by the University of South Florida (USF) Chapter of the National Academy of Inventors™ in collaboration with the USF Office of Research & Innovation, Division of Patents & Licensing, held at USF, Tampa, April 22, 2011.
 10. Newbury, D. E. What is causing failure of aluminum wire connections in residential circuits. *Anal. Chem.* 54:1059A–1064A; 1982.
 11. Phillips, E. A. Letter. *Invent. Technol.* Winter:4; 1999.
 12. Trescott, M. Julia B. Hall and aluminum. *J. Chem. Educ.* 54(1):24–25; 1997.
 13. Weeks, M. E.; Leicester, H. M. Elements isolated with the aid of potassium and sodium—aluminum. In: Weeks, M. E.; Leicester, H. M., eds. *The discovery of the elements*, 7th ed. Easton, PA: Journal of Chemical Education; 1968:557–579.
 14. Zumdahl, S. A.; Zumdahl, S. A. *Chemistry* (5th ed.). Boston: Houghton Mifflin; 2000.