Chapter 2

Synchronous discovery

Aluminum smelting has depended on alumina, a fluoride-based solution and electricity ever since the Hall-Heroult process was discovered in 1886. The process has become more efficient over more than a century of use, but the dependency on large amounts of electrical power continues. The medieval and Renaissance alchemists and chemists searching for the missing metal in alum didn't know about electrolysis, but more importantly they didn't have access to large electrical power sources. For much of the 19th century, all they had was batteries. By 1884, great advances in electrical dynamos revolutionized the aluminum production industry. Use of batteries for electrolysis was lacking – the zinc plates in the batteries were consumed in exchange for producing aluminum, as there was no way to recharge the batteries. Dynamos allowed other forms of energy to be used to produce continuous electrical power – burning coal to produce steam for an engine, or running water to drive turbines.

In 1800, the Italian physicist and chemist Alessandro Volta reported on his invention of the electrical battery to the president of the Royal Society. Another Italian physicist, Luigi Galvani, had earlier discovered a natural phenomenon created by placing dissimilar metals close together, which he called "electricity." Volta built on Galvani's discovery by creating an electrochemical cell that used copper and zinc electrodes and dilute sulfuric acid. In the process, he discovered the electrochemical series. Volta was born in 1745 and died in 1827. He married into aristocracy and was made a count by Napoleon Bonaparte. His scientific achievements included popularizing a device that produced static electricity called the electrophorus, researching and discovering methane after reading a paper by Benjamin Franklin on "flammable air," and studying what is now known as electrical capacitance. The unit of electrical potential, the volt, was named in honor of Volta's work. [1]

One of the earliest scientists to work with electricity was Sir Humphry Davy, who is credited with producing the first electric arc in 1800. Davy made his carbon electrodes from powdered wood charcoal and syrup of tar, molding them to shape using a pressure of 100 pounds per square inch, and then connecting them to Volta's recently invented electric battery. [2] Davy was the first person known to use carbon to make an electrode. [3] He experimented with alumina and was able to identify aluminum, but the metal fused to iron in the crucible he used and couldn't be separated. [4] One modern source credits the English scientist Michael Faraday for being the first to produce aluminum by electrolytic means in 1833. [5]

Judge Alfred Coxe referred to an early case of aluminum production by electrolysis during a 1903 patent infringement case involving the Pittsburgh Reduction Co., before the company became Alcoa. According to Coxe, a French scientist in 1854 exposed a small piece of disthene, a blue silicate mineral, to an electric flame. The disthene melted after three or four minutes and the resulting aluminum, freed from its oxide state, showed itself as a small silver white globule resembling pure silver. Coxe also referred to a story in the May 1882 issue of the "Transactions of the American Institute of Mining Engineers" that described a process for the reduction of aluminum. The process involved a crucible lined with carbon which was described as a cathode. The inventor, however, remained anonymous, and the report was based on hearsay. [6]

Electrodes and generators

The composition and design of carbon electrodes underwent several decades of refinement after Davy. In 1846, the Englishmen William Edward Staite and William Edwards made electrodes by mixing pulverized coke and sugar syrup, molding the mixture under relatively high pressure, and baking the electrodes at white-hot heat. In 1849, a man named Lenoult patented an electrode consisting of two parts retort carbon, two parts wood charcoal and one part liquid tar. The mixture was kneaded, molded and pressed to shape, then coated with sugar or syrup and baked at a high temperature for 30 hours. Experimentation continued to improve electrodes for strength, ability to withstand heat and electrical conductivity. [7]

In 1876, the Frenchman Ferdinand Philippe Carre was the first scientist to create baked carbon electrodes. He used coke, lampblack and sugar syrup. [8] According to an account published in 1877, Carre significantly improved the recipe by mixing 15 parts finely pulverized pure coke, five parts calcined lampblack, and seven or eight parts syrup or sugar. The mixture was pounded, kneaded and worked to a hard paste, then pressed through a draw plate at 1,500 pounds per square inch. Many of the electrodes produced up to 1880 were manufactured by hand in a laboratory and used in experiments to develop electric arc lighting. One of the first manufacturers of electrodes in the U.S. was David Thompson, of Newark, N.J. In 1877, Charles Brush and Washington Lawrence of Cleveland, Ohio, began experimenting with petroleum coke for making electrodes. Their supply of petroleum coke, or pet coke, was located just a mile away at a Standard Oil Co. refinery, a byproduct of the distillation of crude oil found at the bottom of paraffin stills. [9]

Pet coke maintained its position as a key ingredient for manufacturing anodes and cathodes in the modern aluminum smelting industry. The process for baking carbon electrodes continued to be refined over the years. In September 1956, a new method for making carbon anodes for aluminum reduction cells was announced by its inventor, Gerald J. Horvitz of the New York Testing Laboratories. The method was expected to save money in the production of carbon anodes, which burn away in the normal reduction process of alumina into aluminum. The process involved a patented carbon mixture that was placed in a metal shell about six feet high and 10 to 12 feet long. The mixture was capable of utilizing lower-grade petroleum coke formed into briquettes. Horvitz was issued a patent for his invention. [10]

The operating principle behind electromagnetic generators was discovered by English scientist Michael Faraday in 1831 to 1832. Faraday's law states that an electromotive force is generated in an electrical conductor which encircles a varying magnetic flux – in simple terms, to generate electrical power one needed a magnet, a coil of wire and a means to move the coil of wire near the magnet. To demonstrate his principle, Faraday built the first electromagnetic generator, called the Faraday disk, which produced a small amount of direct current power. [11] The Woolrich Electrical Generator was the earliest electrical generator used in an industrial process. Built in February 1844 at the Magneto Works of Thomas Prime and Son, in Birmingham, England, according to a design by John Stephen Woolrich, it was used by the firm of Elkingtons for commercial electroplating. [12] In Germany, scientist Werner von Siemens led the way in electrical research and applications. He developed a telegraph machine with a needle pointing to letters instead of relying on Morse Code, he built the world's first electrical elevator in 1880, and he helped produce the electronic tubes used by Conrad Roentgen to investigate X-rays. Von Siemens' claim to have invented the first dynamo has been widely disputed. [13] Moses G. Farmer, a U.S. scientist, is credited with "co-conceiving" of the self-excited dynamo in 1859 and building the first operating one in 1860 along with Siemens, Søren Hjorth, Anyos Jedlik, Charles Wheatstone and Zenobe Gramme. [14]

The first electric dynamos capable of providing sufficient electricity for electric furnaces appeared in 1867. [15] Belgian inventor Zenobe Gramme demonstrated his electrical generator, the Gramme machine or Gramme magneto, to the Academy of Sciences in Paris in 1871. He was inspired to build the machine after learning of an earlier electrical generator invented by Antonio Pacinotti in 1860. The Gramme machine produced direct current and was the first electrical generator capable of producing electrical power on a commercial scale for industry. In 1873 one of his assistants, Hippolyte Fontaine, accidentally miss-wired two Gramme machines during an industrial exposition in Vienna and discovered that the second Gramme machine acted as an electrical motor energized by the other Gramme machine. [16] By 1880, the technical development of electrical dynamos had reached the point where they were capable of producing sufficient power to reduce ores by electrical means. [17]

U.S. entrepreneur and engineer George Westinghouse led the way in developing a modern electrical power distribution system in the U.S. By 1879, Thomas Edison had invented an improved incandescent light bulb, and by 1882 he had fired up the world's first electrical power grid – serving 110 volts direct current to 59 customers in Lower Manhattan, N.Y. But Edison's system was limited to transmitting power about half a mile from the generating station because of the low voltage and resulting line losses. By 1885, Westinghouse was aware of power systems in Europe using alternating current, and he teamed up with physicist William Stanley to investigate a better way to transmit power in the U.S. With alternating current systems, voltages can be stepped up for long-distance transmission with less line losses and then stepped back down for use by residential, commercial and industrial customers. Westinghouse imported a number of Gaulard-Gibbs transformers and a Siemens alternating current generator for his investigations. Westinghouse's first alternating current grid was installed in Great Barrington, Mass., in 1886. Westinghouse licensed Nikola Tesla's improved polyphase generator and induction motor designs in 1888, which added to the superiority of the alternating current system. Westinghouse won the bid to light the 1893 World's Columbian Exposition in Chicago with alternating current, beating a General Electric bid by $1 million. That fame led to Westinghouse winning the contract to install alternating current generators at the Adams Power Plant at Niagara Falls in 1895. [18]

The Englishman Charles Watt described the underlying principles for the electrolytic refining of metals for the first time in 1851. His ideas were put into practice by James Elkington, who began refining copper on an industrial scale in 1869 in south Wales by electrolyzing a solution of copper sulfate. [19] Other industrial scientists were interested in breaking down metallic ores or fusing metal alloys by means of electrical arc in a furnace. In 1878, Ernst Werner von Siemens of Germany designed and built vertical and horizontal electric furnaces for the melting of metals. [20] In 1879, the Siemens Company received a patent from England which described the use of an electric arc for the fusion of metals. The patent did not involve electrolysis, and the process described in the patent could not have been used for electrolysis. [21] In 1880, the French scientist M. Camille Faure received a French patent for a device used to produce sodium. The device utilized electrical arcs and external heat to produce high temperatures and used chemical reactions to produce sodium. [22]

An important moment in the early history of the aluminum industry occurred on Feb. 23, 1883 when Charles Schenck Bradley filed a patent application broadly claiming the idea of fusing ores by use of an electric arc that would both reduce the ores to their metallic form and maintain the metal in a fused state by internal electrical-resistance heating. In his patent application, Bradley used the reduction of cryolite as an ore of aluminum as an example. The U.S. Patent Office rejected his application on the basis of prior art, citing in particular the work of Davy 80 years earlier. Davy had written, “I only attained my object by employing electricity as the common agent for fusion and decomposition.” Bradley amended his application and re-filed it several times over the next six years, inevitably dragging the Pittsburgh Reduction Co. into a litigious patent war that lasted several decades. [23]

Bradley was not alone in his pursuit of aluminum by electrical means – scientists around the world were still working on the problem of the “missing metal,” and by the end of the 19th century they had turned to electricity for a solution. In 1883, Russian chemist V.A. Tyurin reported finding a new and less expensive way to produce aluminum. Tyurin passed an electric current through a molten mixture of cryolite and sodium chloride. The sodium replaced the aluminum in the cryolite and the mixture produced aluminum. [24] In 1884, a patent was issued in England to Joseph Boguski, an inventor living in Warsaw, Poland, for the production of aluminum bronze alloy by an electrolytic process. On Jan. 11, 1887, an agent representing the Cowles brothers in the U.S. purchased all of Boguski’s inventions, including the British patent, for about $16,680. According to Alfred Cowles’ court testimony in one of the Pittsburgh Reduction Co. patent cases, the Boguski invention was used at the London Industrial Exhibition in 1884 to produce aluminum bronze through electrolysis by fusing a mixture of alumina and cryolite. [25]

In 1882, Ludwig Grabau, of Hanover, Germany, purchased an electric arc furnace from Sir W. Siemens, who had used the furnace for melting steel. Grabau intended to reduce alumina, and after some experimenting found that he could produce aluminum alloys. The alloys, however, contained too much impurities, and Grabau gave up the effort. A process to fuse alumina into aluminum alloys discovered by Paul Heroult was put into operation at the Societe Metallurgique Suisse at Neuhausen, near Schaffhausen, on July 30, 1888. The process was successful enough to attract the attention of the Allgemeine Electricitats Gezellschaft of Berlin, which sought to purchase the Heroult patents for Germany. As a result, a new company took over the works at Neuhausen in December 1888. Meanwhile in France, the Societe Electro-Metallurgique Francaise had set up a similar operation at Froges, near Grenoble, using Heroult’s processes for alloyed aluminum with modifications by Kiliani. No pure aluminum was produced by the Swiss or French companies using this Heroult process. An attempt was made to use Heroult’s aluminum alloying process in Bridgeport, Conn. in 1889. [26]

The Cowles brothers

The benefits of joining scientific research and industrial know-how were clearly shown by the achievements of Eugene and Alfred Cowles. Sons of the Cleveland, Ohio newspaper publisher Edwin Cowles, the brothers purchased a copper and zinc mine in

New Mexico in 1883. That year, Eugene developed an electric arc furnace to extract zinc from the ore. [27] The furnace consisted of a graphite crucible and a one-inch diameter carbon rod. Alfred Cowles later testified in court that his interest in the concept of an electric furnace began while he was a student at Cornell University from 1877 through 1882. [28] On March 18, 1885, the brothers joined their father to organize the Cowles Electric Smelting and Aluminum Co. The company acquired a site at Lockport, N.Y., where they received inexpensive water power from a tailrace 15 miles away at Niagara Falls. In September 1885, the company installed a dynamo built by the Brush Electric Co. Christened the "Colossus," the dynamo weighed 10 tons and delivered nearly 400 horsepower of electrical power. The company put eight furnaces into operation and produced up to 1.5 tons of aluminum bronze alloy per day at a cost of $3.30 per pound. [29]

On Dec. 24, 1884, the brothers applied for the first of many patents in which they described the reduction of various metals and alloys, including aluminum, by their electric furnace. Their first patent, issued in June 1885, referred to the smelting of aluminum ores and stated that the process involved both the heating of the ores by electricity and the decomposition of ores by an electrochemical reaction "not unlike the effect produced by an electric current in a solution." The brothers applied for 10 more patents between 1884 and 1888. The importance of electric smelting was recognized immediately by scientific professionals, as demonstrated by a paper read by Professor Charles F. Mabery at a meeting of the American Association for the Advancement of Science at Ann Arbor, Mich. on Aug. 28, 1885. [30] The process was also patented in England and Germany. According to Mabery, a professor at Case School of Applied Science in Cleveland, who worked for the Cowles brothers as a consulting chemist, the Cowles' process was capable of "reducing an aluminium compound in company with a metal in presence of carbon in a furnace heated by electricity; the alloy of aluminium and the metal formed being further treated to separate out the aluminium." [31]

The principle process employed by the Cowles brothers was to use a strong electrical current to fuse a mixture of alumina, carbon and a metal to be alloyed. The time required for complete reduction of a metal oxide was about an hour. The Cowles brothers found they could reduce oxides of aluminum, silicon, boron, manganese, sodium and potassium with ease. In addition to producing aluminum bronze using copper, the Cowles brothers also produced aluminum silver. According to a paper by Dr. Hunt for the National Academy of Science in Washington D.C., the Cowles brothers could produce pure aluminum by first producing an alloy of aluminum and tin, and then melting the alloy with lead. The molten lead would combine with the tin, and the two would sink beneath the molten aluminum. According to Mabery, Hunt and Kosman, the reduction process relied solely on heat and not on electrolysis. In opinion of metallurgy professor Joseph Richards, writing in 1896, “I think the arrangement of the furnace shows no attempt to fulfill any of the usual conditions for electrolysis, but is one of the best arrangements for converting the energy of the current entirely into heat.” The chief expense for the operation was large quantities of electrical power. [32]

The Cowles Electric Smelting and Aluminum Co. formed and set up a plant at Lockport N.Y., where they acquired 1,200 horsepower of water power and set up the largest dynamo in the world, specially built by the Brush Electric Co. The steam-driven dynamo produced 3,400 amps at 68 volts when driven at 423 revolutions per minute, or 3,200 amps at 83 volts when driven at 405 revolutions per minute. Over time, the Cowles brothers developed ways to control the large electrical current with special switching and metering equipment. By 1888, the Cowles brothers had two of these large dynamos powering eight furnaces. With two-hour runs per furnace, and one furnace tapped per hour, about 80 pounds of aluminum bronze with 18% aluminum could be produced per hour. They believed that the reduction process could operate using alternating current as well as direct current, but by 1896 they had not tried alternating current. Following the success of this plant, the Cowles Syndicate Co. organized to work on patents in England and set up a plant at Stoke-on-Trent that soon produced 300 pounds of aluminum per day using a dynamo that produced 5,000 to 6,000 amps at 50 to 60 volts. The English plant had two furnace rooms with six furnaces each, one room for aluminum-silicon bronze and the other for ferro-aluminum. The Cowles brothers also organized the Aluminum Brass and Bronze Co. in Bridgeport, Conn. in July 1887 to produce aluminum alloys in sheet, rods and wire. [33]

Writing 20 years later, Adolphe Minet described the furnaces as an electrochemical process that produced 20 percent pure aluminum. [34] At a meeting of the Franklin Institute in Philadelphia, Pa., on Jan. 20, 1886, Eugene Cowles made the claim that his company was able to produce aluminum in at least three different ways in their electric furnaces. A fire, however, destroyed the company’s Lockport offices on June 13, 1888. Gone forever were most of the records and notes from years of experiments by the Cowles in the use of their electrical furnaces to reduce ores. [35]

Bauxite, alumina and cryolite

While electrical power sources became more powerful and reliable in the last half of the 19th century, the raw materials needed to produce aluminum were also being developed. Bauxite, the industry’s main source of alumina, was first discovered in the village of Les Baux in southern France by Pierre Berthier in 1821. The generic term bauxite refers to an ore or a mixture of minerals rich in hydrated oxides formed of aluminous rocks, such as nepheline, feldspars, serpentine, clays and others. During geological weathering, the silicates were decomposed and leached out as silica, lime, soda, potash and other compounds. What was left was an ore enriched in alumina, iron oxide and titanium oxide with a little silica. [36] The ore found near Les Baux contained 52% alumina. [37]

Berthier was born in Nemours, France in 1782. The French geologist and mining engineer was the chief of the laboratory at the Ecole des Mines in 1816. He discovered bauxite while working in the village of Les Baux-de-Provence in 1821. He was elected to the French Academie des Sciences in 1825 and became a chevalier of the Legion of Honor in 1828. The mineral berthierite was named for him, and he is noted for his research into blast furnaces and the use of phosphate by plant life. Berthier's name is one of 72 names of scientists, engineers and mathematicians inscribed on the Eiffel Tower. He died in 1861. [38]

Even after screening and washing, bauxite contains too many impurities to efficiently produce aluminum metal. Aluminum exists in bauxite in mineral form as gibbsite, boehmite or diaspora. [39] In 1855, Louis LeChatelier, the French Inspector General of Mines, developed a process to make alumina from bauxite. Part of the process included precipitating hydrated aluminum hydroxide from sodium aluminate solution by using carbon dioxide. This became the principle commercial process for making alumina until the Bayer process became widely available. [40] The Deville process for producing alumina from bauxite was developed by Henri Sainte-Claire Deville in 1859. It was sometimes called the Deville-Pechiney process and was based on the extraction of alumina with sodium carbonate. The process was used in France at Salindres until 1923 and in Germany and Great Britain until the outbreak of the Second World War. The Deville process eventually was replaced by the Bayer process. The first stage of the Deville process was the calcination of bauxite at 1,200 degrees Centigrade, using sodium carbonate and coke, which converted alumina into sodium aluminate. Iron oxide remained unchanged, and silica formed a polysilicate. Sodium hydroxide solution was next added, which dissolved the sodium aluminate and left impurities as a solid residue. The amount of sodium hydroxide solution needed for this second stage depended upon the amount of silica present in the bauxite. The solution was filtered, and carbon dioxide was bubbled through the solution, causing aluminum hydroxide to precipitate, leaving a solution of sodium carbonate, which could be recovered and reused in the first stage. The aluminum hydroxide was then calcined to produce alumina. [41]

The truly economical method to extract alumina from bauxite was discovered in 1887 by Karl Josef Bayer, an Austrian chemist who was working in St. Petersburg, Russia. [42] Bayer's goal was to supply alumina to the textile industry, where it was used as a mordant for dyeing cotton. Bayer had discovered that aluminum hydroxide precipitated from an alkaline solution was crystalline and could be easily filtered and washed, whereas aluminum hydroxide precipitated from an acid medium by neutralization was gelatinous and difficult to wash. [43]

Bayer was born in Bielitz, Silesia, on March 4, 1847, not far from Cracow, Poland. Following his father's wishes, he studied to be an architect but later switched to science. He went to Wiesbaden, Germany, to work in the laboratory of the well known chemist Remigius Fresenius, then spent time in a steel factory in Belgium. After that, he enrolled at the University of Heidelberg, where he worked for three years under Robert Bunsen, who was visited often by other famous chemists. Bayer completed his doctorate at Heidelberg at age 24 with a thesis on "A Contribution to the Chemistry of Indium," an element discovered in 1863. Bayer returned to his home country of Austria, where he was appointed lecturer at the University of Technology at Brunn. [44]

Bayer, who could speak six languages, moved to St. Petersburg in 1885, where he grew his beard in the Russian style and went to work at the Tentelev Chemical Plant. At that time, the plant was using the Le Chatelier process to produce aluminum hydroxide, a mordant for dyeing cotton, wool and silk. In 1887, Bayer discovered that aluminum hydroxide could be precipitated from sodium aluminate solution if a seed of freshly precipitated aluminum hydroxide was agitated vigorously in the cold solution. The pure product could be collected by filtration and washed. The process was adopted by the chemical plant and patented by Bayer in England, the U.S. and Germany in 1888. Four years later, he discovered a way to remove alumina from bauxite by heating a solution of bauxite in sodium hydroxide under pressure in an autoclave to form sodium aluminate solution. Bayer patented this method in England, the U.S. and Germany in 1892. [45] Bauxite with more than 10 percent silica cannot be economically processed by the Bayer method, and the process has remained largely unchanged for more than a century. [46]

While in St. Petersburg, Bayer married the niece of Count Sergei von Witte, a Russian statesman of German origin who briefly served as Russia's prime minister during the reign of Tsar Nicholas II. After seven years in St. Petersburg, Bayer worked at a chemical plant in Yelabuga, on the Kama River in the Tatar region near the Ural Mountains, where he built a second plant to manufacture alumina. During the two years that he was at Yelabuga, Bayer received numerous contract offers from foreign countries to build alumina factories. Bayer returned to Austria, apparently with the intention of starting an aluminum industry there. He settled in Rietzdorf, in southern Styria, and devoted his time to scientific research, including finding a way to synthesize cryolite and developing the first bauxite deposit in Austria with a plant to produce alumina. Unable to raise the needed capital, his plans fell through and he died suddenly in 1904. All of the companies around the world using his patents – except two – stopped paying royalties after his death, leaving his family and laboratory in a financial crisis. Bayer's home in Rietzdorf later became a meeting center for famous industrialists, including Paul Heroult and Charles Martin Hall. Bayer's collection of minerals was displayed at the Chicago Exposition in 1890, and medals were named in his honor and awarded to chemists and metallurgists. [47]

Meanwhile, in the frigid North Atlantic, the development of the world's greatest cryolite deposits was underway. In 1865, mining for cryolite began at Ivigtut on the southwest coast of Greenland, the only site in the world with commercial quantities of the mineral. The Danish government offered two 75-year concessions – one to the Pennsylvania Salt Co. of Philadelphia, with exclusive selling rights in North America, and another to the Oresund Co. of Copenhagen, with exclusive selling rights for the rest of the world. This created a monopoly that impacted the emerging global aluminum industry and drove interest in developing a cost-effective method to manufacture synthetic cryolite. [48]

All the necessary ingredients for the Hall-Heroult process existed by the 1880s – a good supply of alumina and cryolite, the know-how to manufacture electrodes, and the availability of powerful electrical dynamos. All that was needed was to put those ingredients together in the correct way to produce inexpensive aluminum metal. Numerous scientists were working with these same ingredients and were closing in on a practical way to reduce alumina to aluminum metal, but nobody expected the discovery to take place nearly simultaneously by two amateur scientists working alone thousands of miles away from each other – Charles Martin Hall and Paul Louis Toussaint Heroult. Over time, their story of discovery has been embellished, as myth was interwoven with fact in an effort to promote a science-based Horatio Alger story of rags to riches, to promote the interests of the aluminum industry or to boost national pride. To add to the odd synchronicity, both men were born in 1862 and died in 1914. [49] The two inventors had never met before 1886, but they later became good friends. The electrolysis process they patented became known as the Hall-Heroult process and continues to be the dominant aluminum smelting process to this day. [50]

It is not feasible to convert alumina into aluminum by use of a blast furnace, in the same way iron oxide is made into iron, because alumina is too stable. Instead, alumina is reduced to aluminum by an electrolytical process in large heated carbon-lined steel pots where the alumina is dissolved in a bath of molten sodium aluminum fluoride or cryolite. In a modern aluminum reduction cell, electrical current running through the solution creates heat which maintains a bath of molten cryolite. Alumina is added to the pot and dissolves in the cryolite bath. The voltage difference across the pot draws positively-charged aluminum atoms, with a valence of plus three, to the negatively-charged cathode. The cathode is essentially the carbon-lined bottom of the pot. As molten aluminum collects at the bottom of the pot at around 648 degrees Celsius, it is periodically tapped by suction into transport crucibles so more alumina can be added to the bath. The negatively-charged oxygen atoms are released from the alumina and drawn to the positively-charged anodes. The anodes are made mostly of carbon, which combines with the oxygen by burning off a little at a time to form carbon monoxide. Anodes are consumed in modern smelters at the rate of approximately 1,300 pounds of carbon per ton of aluminum produced. [51]

An early form of electrolysis to produce aluminum metal was patented by Gratzel in Germany in 1883 and used industrially at Hemelingen, near Berlin. The process called for the electrolysis of a bath of fused aluminum salt, such as chloride or fluoride. But the process did not succeed, and the company turned to the process developed by Saarburger. By October 1888, the company was producing 12,000 kilos of aluminum per year, in addition to a large amount of aluminum bronze and ferro-aluminum. But the company shut down its aluminum production two years later and turned to magnesium production. A similar electrolytic process was patented by Edmund Kleiner, of Zurich, in 1886, in which molten cryolite was decomposed by two carbon poles – the current provided the heat to fuse the cryolite and then to electrolyze it. In France in 1887 and 1888, Adolphe Minet experimented on the electrolysis of a molten bath containing aluminum fluoride and sodium chloride that was fed alumina and aluminum fluoride. Run on an experimental level, Minet's process produced 35 pounds of aluminum per day at the Bernard Brothers works at Creil. A larger plant was established in 1890 at Saint Michel, Savoy, using water power to drive the dynamo and producing up to 1,000 pounds of aluminum per day. The plant was acquired by a French company to use the Hall process in 1895. On Aug. 6, 1887, M.G. Farmer patented a novel way to produce aluminum metal using electrical power. According to his English patent, an aluminous material was mixed with molasses or pitch to make a paste that was formed into rods that were used as electrodes in a furnace. As the rods carried an electrical current and an arc was produced, molten aluminum dripped from the rods into a crucible placed immediately underneath. [52]

The U.S. inventor

Charles Martin Hall, the son of Rev. Heman Hall and Sophronia Brooks, moved with his family to Oberlin, Ohio, in 1873, where he attended high school. Hall enrolled in Oberlin College in 1880 and graduated with a bachelor of arts degree in 1885. He was later awarded an honorary A.M. degree in 1893 and an honorary L.L.D. degree in 1910 from Oberlin College, and he was on the college's board of trustees from 1905 to 1914. [53] Hall's childhood years are not well known, but by the age of 12 he was performing chemical experiments at home. The commonly told story is that Hall was inspired by his chemistry professor at Oberlin, Frank Jewett, who had suggested that "if anyone should invent a process by which aluminum could be produced on a commercial scale, not only would he be a great benefactor to the world but would also be able to lay up for himself a great fortune." According to other accounts, Hall's interest in the production of aluminum began when he was 16. [54]

While at Oberlin, Hall read about patent applications, worked on a new battery design and experimented with copper alloying. [55] After graduating from Oberlin, he continued to work with Jewett in a woodshed laboratory behind his parents' home, with encouragement from his sister Julia. [56] Using equipment he borrowed from Jewett, Hall followed conventional empirical methods of the time in his experiments. Chemical research was still in its infancy, and few scientific journals existed promoting the latest research findings, but Hall relied on the experiments of his predecessors and his skill in fashioning homemade laboratory equipment. [57]

Hall began by using methods used to manufacture iron before turning to electrolysis. He tried electrolysis with aluminum fluoride in 1884-1885 without result. He knew that the use of electrolysis had been tried by both Davy and Deville and then abandoned. He also tried a Bunsen-type cell. After June 1885, he applied electrolysis to fused salts of fluorides. [58] Reading about Deville had inspired Hall to pursue the production of aluminum metal. "Later I read about Deville's work in France, and found the statement that every clay bank was a mine of aluminum and that the metal was as costly as silver," Hall recalled years later. "I soon after began to think of processes for making aluminum cheaply." [59] Hall looked for a way to dissolve alumina at a low enough temperature to pass an electrical current through the fused mixture. Alumina's melting temperature was 2,050 degrees Celsius, much too high for ordinary industrial applications. Hall needed a salt with a reasonably low melting temperature into which alumina could be dissolved, and he found it in cryolite, the double fluoride of sodium and aluminum. Cryolite had several distinct advantages – a reasonably low melting point, a reasonably low operating voltage of about six volts and a low enough specific gravity to allow pure aluminum to sink through the electrolyte to the bottom of the crucible where it could be collected. [60]

On Feb. 9, 1886, Hall discovered that cryolite had a sufficiently low melting point and was a good solvent for alumina. In hindsight, it is known that cryolite is more stable than alumina, so the dissolved alumina can be reduced electrochemically without reacting with the cryolite solvent. On Feb. 23, 1886, Hall finally put all the pieces together while working in a woodshed behind his parents' home on a cold winter day. [61] Using a galvanic battery, he passed an electric current through a cryolite bath with dissolved alumina contained in a carbon-lined crucible heated by a gasoline burner. Hall produced the alumina he used in the experiment, and he fashioned the crucible on his own. After allowing the current to work, he waited for the mixture to cool and then shattered the congealed mass. [62] In his sister's presence, Hall poured the "small globules" of nearly pure metal from the crucible. [63] The resulting congealed mass, when cooled and struck with a hammer, yielded small pellets of pure aluminum, he wrote. [64]

The globules of aluminum metal that Hall produced that day were later called Alcoa's "crown jewels." [65] Hall's discovery and his eventual success benefited from a growing body of scientific knowledge about chemistry and metallurgy, as well as the steady progress of industry. Knowledge about aluminum and metal reduction came from scientists such as Davy, Oersted, Wohler, Deville and Bunsen. Electrical power for industry came with the development of large dynamos in the 1870s. Historically, the interaction of scientists and industry included such people as Samuel F.B. Morse, Silas McCormick, Elias Howe, Alexander Graham Bell and Thomas Edison. [66]

Hall immediately recognized the value of his discovery and applied for a U.S. patent for "The Process of Reducing Aluminum by Electrolysis" on July 9, 1886. [67] The patent was granted three years later on April 2, 1889. [68] The patent expired in 1906. [69] On Aug. 29, 1886, Hall explained the benefits of internal heating by electrical resistance in a letter to his sister. "In some respects this invention is going to be better than I anticipated; thus the resistance of the liquid is exceedingly low," he said. "Also it is evident from the experiments that the waste heat of electricity, which must be used anyway, will be nearly or quite enough to keep the solvent melted." But when it came time to file his patent claim with the U.S. government, Hall described a form of his apparatus that he knew worked well but which used an externally heated crucible on a small scale. [70] Employing internal electrical-resistance heating to keep the fluoride-based bath in a molten form, as opposed to using an external heating source such as coal or gas, is fundamental to the modern aluminum smelting process. Hall's mistake in not mentioning this concept in his patent application led to decades of litigation.

The French inventor

Meanwhile across the Atlantic, the Frenchman Paul Heroult had successfully used cryolite and electricity to produce aluminum metal. With limited means, Heroult worked out of a small tannery in Gentilly near Paris. [71] Hall and Heroult shared their interest in aluminum, but they led very different lifestyles. Heroult was well-traveled, bilingual, married and worldly. He played at billiards and socialized at Parisian cafes, and his record-keeping was more casual than Hall's. Heroult recognized early that the advent of electrical dynamos meant electrolysis could provide an inexpensive commercial method for aluminum reduction. With access to a dynamo, Heroult and a group of students from the Ecole de Mines successfully reduced alumina on April 23, 1886. [72]

Heroult had been carrying out tests with chlorides, but those halogenated compounds of aluminum did not conduct electricity well. He then successfully dissolved alumina in molten cryolite, which did conduct electricity, enabling him to reduce alumina into aluminum metal by electrolysis. He noted that during electrolysis, the oxygen from alumina went to the anode, where it burned off, while the aluminum fixed itself to the sides of the crucible, which acted as the cathode. “The bath, which remains constant and can be used indefinitely, is supplied with alumina,” he wrote in his patent application. “The positive electrode, that is the anode, has to be replaced after combustion, but this combustion prevents polarization and ensures consistency in the energy and action of the electric current.” [73]

An important difference existed between the Hall and Heroult methods. Hall’s method was better suited for producing pure aluminum, while Heroult’s was better suited for making alloys. Heroult received a French patent for his discovery on April 23, 1886, but unlike Hall, Heroult failed to grasp the importance of his discovery because most metals experts were focused on making aluminum alloys. [74] On April 15, 1887, Heroult took out another French patent for a totally different process that produced aluminum alloys rather than aluminum metal by using a copper anode, and he began to promote this new process for commercial purposes. For this reason, many historians believe Heroult did not recognize the significance of his first discovery and patent. [75]

Heroult later recalled that in 1886, while seeking financial assistance to develop his new discovery, he tried to interest A.R. Pechiney, the French businessman who managed the Merle Chemical Aluminium Co., into sponsoring his new process. According to legend, Heroult overwhelmed Pechiney at billiards and Pechiney subsequently dismissed the idea of aluminum as a consumer metal. As Heroult recalled the incident, Pechiney said aluminum “was for opera glasses.” [76] Pechiney summed up the future of aluminum by saying, “Aluminum is a metal with limited markets, and should you sell it for 10 francs or 100 francs per kilo, you would not sell one more kilo. Should you make aluminum bronze, that would be a different matter, for substantial quantities of the latter are used.” [77]

Heroult failed to secure financing from the Rothschild Bank, but members of the German steel industry took an interest in his discovery. [78] The Societe Metallurgique Suisse was formed to acquire Heroult’s patents, and works were erected at Neuhausen, Switzerland, to use the alloy process. As development of the new alloying process succeeded, a new company was formed, Aluminium Industrie Aktiengesellschaft, which enlarged the operations at Neuhausen. But once the success of Hall’s methods in the

U.S. became known, the German company turned away from the alloy process and began producing aluminum metal, with very little change in the equipment. [79]

Heroult applied for a U.S. patent on May 22, 1886. Hall's U.S. patent application was not made until July 9, 1886, and a patent interference was declared. [80] Heroult failed to provide a "preliminary statement," which limited his date of discovery to May 22, 1886, in accordance with U.S. patent law. Hall provided the needed statement and was able to use his sister's records to prove that he had actually discovered his process on Feb. 23, 1886. [81] The U.S. patent office ruled in Hall's favor in the interference proceeding for several reasons – first, there was no evidence that Heroult had discovered the process before Hall and secondly, U.S. patent law provided that inventors in the U.S. could claim a patent for something that had already been patented in a foreign country so long as the invention had not been in use inside the U.S. for more than two years. Hall was granted U.S. patent No. 400,766 on April 2, 1889. This ruling was later affirmed in a patent infringement case decided in 1893. [82]

Following Pechiney's advice, Heroult eventually abandoned the production of pure aluminum and followed other scientific pursuits. [83] In May 1889, Heroult came to the U.S. from France with the idea of producing aluminum bronze alloys. He set up experimental work in Bridgeport, Conn., but a short circuit damaged his only available dynamo and he left without resuming operations. Heroult was fluent in English, and he traveled often to the U.S. Later he became involved in the French-backed Southern Aluminium Co., which started building an aluminum smelter at Badin, N.C., under the direction of one of the leaders in the French aluminum industry, Adrien Badin. Heroult died before the Badin project was completed. [84]

In 1897, Heroult and a man named Hardmuth, of France, worked on developing an electric furnace for melting metals. Heroult came to the U.S. shortly after developing his electric furnace and began manufacturing electrodes in Canada in 1908. He opened an electrode manufacturing plant in the U.S. in 1911. The two companies later joined to create the National Carbon Co., which made significant improvements in electrodes for arc lighting and later electric furnaces. [85] In 1911, Heroult finally met Hall when he traveled to New York to congratulate Hall on being awarded the Perkin Medal for contributions to chemistry. Three years later, in 1914, they both died – Heroult of typhoid and Hall of leukemia. [86]

The Hall-Heroult discovery was the breakthrough needed to establish a global aluminum industry, as prices fell and markets were developed in the next few decades. Prices fell first. In 1850, aluminum sold for $17 per pound, according to the U.S. Geological Survey's 1999 Minerals Yearbook. The price steadily dropped to $9 in 1872, to $8 in 1887 – one year after the Hall-Heroult process was patented, to 59 cents in 1895 and to

18 cents in 1914 – on the eve of World War I. The price increased to 60 cents in 1916 before falling to 19 cents by 1937 – in the midst of the Great Depression. Prices stabilized at 15 cents per pound during World War II before steadily increasing to 43 cents in 1974 and 76 cents in 1980. The price of aluminum broke the dollar mark at $1.10 in 1988 before declining again to 65 cents in 1998. [87] This price volatility marks aluminum as a commodity that is vulnerable to political and economic events as well as changing technology, new aluminum projects overseas and unusual market influences.

Richards reported on the demise of the aluminum alloy industry promoted by the Cowles brothers and Paul Heroult in his 1896 book on aluminum. “Since 1892, no aluminium has been made in England by this process, as the low price of pure aluminium killed the market for ready-made aluminium alloys,” he wrote. “I cannot say to what extent the Lockport works is running at the present time, but it is probable that the death of one of the Cowles brothers in 1893 and the sharp competition from pure aluminium have seriously hampered the business of the American company. At least, their products are not frequently seen on the market.” [88]

Richards also provided a scientific explanation for the reduction of aluminum compounds by the use of electricity. According to the principles of electro-metallurgy as understood at the time, the atomic weight of aluminum was 27 so its “combining power to one part of hydrogen” was nine. Therefore according to the fundamental law of electrical decomposition, an electrical current of sufficient quantity to liberate one part of hydrogen from a compound in a specific time would be capable of liberating nine parts of aluminum. Researchers had already determined that one coulomb of electricity, that is one ampere of current for one second of duration, would liberate 0.00001035 grams of hydrogen, so one coulomb would liberate 0.00009315 grams of aluminum. “This is the electro-chemical equivalent of aluminium,” Richards wrote, noting that from thermo-chemical data it was known that the actual figures could vary from compound to compound. To apply this theory to the Anaconda Aluminum Co. smelter in Columbia Falls, Mont., where 100,000 amps of current ran through 600 reduction cells, begin with the electro-chemical equivalent of aluminum, which is one amp liberating 0.00009315 grams of aluminum from alumina per second, or 100,000 amps liberating 9.315 grams per second, which is 804,816 grams per day per cell, which is 1,774 pounds per day per cell, which is 1,064,400 pounds for 600 cells. The figure of 1 million pounds of aluminum metal produced per day at the smelter was often stated, confirming the calculation. [89]

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