

AN EXPLORATORY STUDY OF THE POSSIBILITY OF USING CERTAIN
" INORGANIC FUSED SALTS AS ELECTROLYTES
FOR THE DEPOSITION OF ALUMINUM

by

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I. INTRODUCTION

From the earliest experience that man has had with metals to the present day, he has been plagued with the problem of corrosion. Corrosion takes on many forms, some of which are beneficial, but most of which are a source of constant trouble. Many methods of delaying and inhibiting the corrosion rate have been advanced and perfected as the years have passed, but still serious problems of utmost importance exist.

One method of controlling corrosion is by coating a metal with a second metal that is not as susceptible to corrosive action, such as nickel plating of steel. The process is essentially the passing of an electric current through an appropriate solution of the salts of one of the metals, a bar of which is used as one electrode. The protective metal deposits from an ionic solution upon the base metal which serves as the second electrode. The film thus deposited acts as a new surface and corrodes at a rate characteristic of its own physical properties.

Aluminum is one of the lightest and potentially cheapest metals known. It has excellent corrosion resistance, and therefore, it has been suggested that aluminum be used as a coating for metals that are more susceptible to corrosive action.

It is the purpose of this investigation to study the possibilities of using the inorganic molten salt systems aluminum chloride - alkali chloride, aluminum fluoride - alkali fluoride, aluminum sulfide - alkali sulfide, aluminum cyanide, aluminum fluoborate, aluminum formate and aluminum thiocyanate as electrolytes for the electrodeposition of aluminum.

II. LITERATURE REVIEW

In order to obtain a thorough understanding of the reasons for and the principles involved in the study of the electrodeposition of aluminum, a survey of the literature was made.

History of Aluminum

To trace the story of aluminum it is not necessary to go back very far, since aluminum is a recent development.

Discovery of Aluminum. Aluminum was first recognized as a metal in the middle of the eighteenth century⁽²¹⁾. It was 1809, however, before an attempt to separate it from its oxide was made by Sir Humphrey Davy⁽¹⁸⁾. This attempt was made by passing an electric current from a voltaic pile through a fused bath of iron and aluminum oxide. The product was an alloy of aluminum which could not be separated. Davy abandoned his search at this point, but he had contributed to the meager knowledge of the metal the important discovery that the aluminum oxide could be reduced.

Oersted⁽⁵⁴⁾ produced the first metallic aluminum in 1824 by gently heating potassium amalgam with aluminum

chloride and then distilling off the mercury, leaving a small lump of aluminum metal.

Wohler⁽⁸³⁾ repeated Oersted's experiment in 1827, but was unable to reproduce the results. By using metallic potassium instead of the amalgam, he produced aluminum as a metallic powder. In further experiments in 1844, Wohler produced enough aluminum metal to begin the study of its properties⁽⁸⁴⁾.

In 1854, Deville⁽¹⁹⁾ improved on Wohler's method by substituting sodium for potassium. In the presence of sodium chloride, a double salt - $\text{NaCl} \cdot \text{AlCl}_3$ - was formed with the excess aluminum chloride. This salt acted as a flux, thus allowing the small particles of metal to coalesce. Deville set up the first plant for manufacturing aluminum in Nanterre, France, and produced about 60 pounds of the metal at about 27 dollars per pound. In 1866, Castner⁽¹²⁾ developed a cheaper method of producing sodium which eventually led to the production of 500 pounds of aluminum per day at about four dollars per pound. In three years of operation, approximately 250,000 pounds of aluminum were produced by the Deville-Castner method.

Gurbau⁽³⁴⁾ patented a process in 1888 in which aluminum fluoride was employed as the source of aluminum and using sodium as the reducing agent. Pure granular

aluminum fluoride was heated to 600 °C and dropped into molten sodium. The sodium fluoride produced in the reaction formed a slag under which the aluminum collected. He claimed that the aluminum that was produced was very pure and the sodium was used more efficiently.

The present process for commercial production of aluminum was developed simultaneously and independently by Charles M. Hall in the United States and Paul Heroult in France^(35,38). The essential of the process was the use of cryolite as the electrolyte in which pure aluminum oxide was dissolved. Electricity of low voltage, high current was passed through the fused bath. The container was of cast iron with a heavy carbon lining, which served as the cathode. The anode was a carbon rod that was suspended in the molten solution. The aluminum oxide was decomposed by the current, while the cryolite was unaffected. The aluminum metal, at 1000 °C, was heavier than the cryolite and therefore, settled to the bottom of the electrolytic cell. Oxygen was liberated at the anode which reacted with the carbon to form carbon monoxide and dioxide.

Heroult did not immediately commercialize on his discovery, but Hall saw the potentialities and in 1888 started to produce aluminum in Pittsburgh, Pennsylvania.

Aluminum was soon selling at about one dollar per pound which forced the closing of the sodium reduction plants by 1891.

Present Production Methods. The essentials of the Hall-Heroult process are used today for large scale production of aluminum. An electrolytic cell is made up of a strong steel box, one to two inches thick, either circular or rectangular in shape having a carbon lining six to ten inches thick. The size of the cell varies with the number of amperes of current for which it is intended. The amperage may vary from about 8000 to 30,000 amperes⁽³⁵⁾. Approximately fifty cells are connected in series at from 5.5 to 6.5 volts each. Enough cryolite is used in each cell to dissolve about fifty pounds of purified aluminum oxide. The bath is kept molten at about 950 °C by the heat dissipated in the electrolysis. Each cell is capable of producing about 150 pounds of aluminum per day. Approximately 0.5 ton of carbon electrode is required and about 0.1 ton of cryolite must be replaced for every ton of aluminum produced⁽¹⁵⁾.

Electrolytic Refining of Aluminum. Aluminum produced by the Hall process is seldom less than 97 per cent pure. Hoopes⁽³⁹⁾ developed a process for refining aluminum electrolytically to produce a metal that is 99.99 per cent pure. Hoopes patented this process in 1921.

The aluminum to be refined is alloyed with copper and silicon and rests in the bottom of a cell under a layer of a fused mixture of cryolite and aluminum and barium fluorides nearly saturated with alumina. The temperature is between 900 and 1100 °C. A thick crust that is rich in alumina solidifies on the walls of the cell insulating it electrically and thermally. The aluminum cathode floats on this bath, and contact is made by graphite electrodes. The aluminum is covered with a frozen crust of the bath, except where the electrodes dip into it. The cells operate at from five to seven volts and about 20,000 amperes⁽⁶⁸⁾.

Coating with Aluminum

While the electrodeposition of aluminum has not proven economical as yet, other methods of covering surfaces with this metal have been devised which are satisfactory for some applications⁽²¹⁾.

Calorizing. Calorizing is a trade name for alloying aluminum with steel by diffusion. The depth of penetration of the aluminum-iron alloy ranges from 0.005 to 0.040 inch⁽⁶²⁾. This alloy surface usually contains about 25 per cent aluminum. It may be obtained by three methods; retorting, packing and dipping.

Revolving Retort Calorizing. Prior to 1935 the metal to be calorized was packed into a mixture of finely divided aluminum, alumina, and a filler such as ammonium chloride to facilitate the coating. The container was sealed gas tight in a heated, revolving retort for from four to six hours at 1550 to 1700 °F. The surface obtained was an aluminum-iron alloy about 0.001 to 0.006 inch thick and containing about 60 per cent aluminum. The surface was brittle and weak, which led to the modern improvements in this process. The only essential difference in the new and the old method is that the calorized surface is heat treated for from twelve to twenty-four hours at temperatures from 1500 to 1800 °F. This heat treatment increases the depth of penetration and improves the properties of the surface. The new surface is generally heat and corrosive resistant, as well as being ductile and tough^(21,62).

Pack Calorizing. The only difference in this method and the rotating retort is that the time of heating is longer and the calorizing container remains stationary during the treatment. This method is used for articles that would be damaged by tumbling⁽⁶²⁾.

Dip Calorizing. The article to be treated is thoroughly cleaned with a flux, such as zinc-ammonium chloride, to remove the oxide film, and then is dipped into a bath of molten aluminum⁽¹¹⁾. Subsequently the article is heat treated to facilitate diffusion.

Spraying. In the spraying method, aluminum in the form of a thin strip or wire is fed into an electrically or gas heated chamber, where the aluminum is melted. The molten aluminum is then sprayed through a nozzle by gas pressure onto the base metal⁽²¹⁾. The surface obtained is very porous and consequently is not very resistant to corrosion, but it does offer some protection against oxidation.

Hot Rolling. Aluminum may be bonded to iron by heating thin sheets of aluminum and sheet iron to about 350 °C and passing them between rolls that press the two sheets together⁽⁶²⁾. The combined metals are subjected to a second rolling to give thickness and to strengthen the bond. The result is a uniform coating of the iron with the aluminum, each metal retaining its own properties. The method combines the strength of iron with the corrosive resistance of aluminum.

Painting. So called aluminum paint⁽⁶²⁾ is a mixture of several ingredients; the aluminum is the active agent in preventing corrosion of the metal to which the paint is

applied. Powder made from pure aluminum sheets by stamping into small chips and then hammering into thin foil-like pieces is mixed with a vehicle, such as varnish, lacquer, bronzing liquid or bodied oils, to make the paint. This paint is especially good as a moisture resistant agent, and is widely used because it may be easily applied like standard paints.

Thermal Evaporation. One of the new methods for metal coating which has been applied to aluminum is thermal evaporation(44). This method results in a thin film which is defined as a structure essentially fragmentary, without the ordered arrangement of crystal lattices. Evaporation may be accomplished by heating a metal wire in a very high vacuum - 10^{-4} millimeter of mercury - by means of an electric current or external source of heat. At a sufficiently high vacuum the metal will tend to evaporate and diffuse toward an article to be coated. Since the article is much cooler than the metal source, the metal will condense, thus forming the coating. The physical condition and adherence of the deposit is affected by the presence of gases, as well as the distance between the evaporating source and the receiving surface, and by the temperature.

Sputtering. A second new development involving a high vacuum technique for coating metals with aluminum

is sputtering⁽⁴⁴⁾. Very little is known about the mechanism of the sputtering reaction, but it is believed that when an arc is struck between two pieces of the same metal in a high vacuum, radicals or ions of the metal are liberated from the surface. These ions or radicals seem to have a charge which may be attracted to the cathode by impressing a negative potential upon it. The electrically created radicals migrate to the cathode which is the article to be coated with the metal at the arc. The vacuum needed for this work is in the range of 1 to 300 microns.

Sputtered metal coatings do not oxidize easily and they are remarkably stable and chemically pure.

Fused Salt Electrolysis

The electrochemistry of fused salts presents many problems that are not involved in the use of aqueous solutions. The temperature is a very critical property when dealing with molten salts, while it is of only minor importance with aqueous solutions⁽¹⁾. Chemical side reactions and corrosion problems are much more prevalent when molten salts are used as electrolytes.

Conductivity. Molten salts are good conductors of electricity⁽¹⁾. A comparison of the conductivities of molten salts and those of aqueous solutions in Table I indicate that they are much larger for the molten salts but are in the same range. Conductivity increases almost linearly with increase in temperature except at very high temperatures where conductivity lags behind temperature increase. In most cases the effect of temperature can be accounted for by the decrease thereby produced in the viscosity of the melt.

The conductivity of fused salt mixtures fall below the calculated values according to the law of mixtures and in some cases fall below the conductivity of any of the pure components.

Measurement of conductivity of fused salts may usually be accomplished by regular methods. Mantzell⁽⁴⁶⁾ and Yamoyuti and Siskdo⁽⁸⁶⁾ published methods of measuring conductivities of fused salts and fused salt mixtures.

Faraday's Laws and Fused Salts. Richards and Stull⁽⁶³⁾ and Lorenz and Helfenstein⁽⁴⁵⁾ have defended the application of Faraday's laws to electrolysis of fused salts. However, the causes of low current efficiency in aqueous solutions are accelerated in molten

TABLE I

A Comparison of the Specific Conductivities of Molten Salts a Few Degrees Above Their Melting Points and Aqueous Solution Conductivities at 18 °C

Molten Salt	Temperature, °C	Specific Conductivity, rho/cu cm
NaNO ₃	318	1.022
KNO ₃	393	0.645
CaCl ₂	800	1.900
K ₂ CO ₃	900	1.950
ZnCl ₂	300	0.00186
PbCl ₂	528	1.596
NaCl	850	3.500
Aqueous Salt Solution	Concentration, normality	Specific Conductivity, rho/cu cm
NaCl	4	0.197
AgNO ₃	1	0.068
CuSO ₄	1	0.025
Na ₂ CO ₃	2	0.079

Allmand, A. J. and H. J. T. Ellingham: "The Principles of Applied Electrochemistry," p. 26. Edward Arnold Co., London, England, 1931.

salt baths. Velocity of diffusion and of chemical reaction are both much greater. Therefore, unless anodic and cathodic products are carefully isolated from one another, from the action of the electrolyte and from the air the yields will be much less than those calculated by Faraday's laws.

The chief causes of low cathode efficiency are: volatility of the electrolyte due to the high temperature, diffusion of the anode products, formation of metal fog and action of the atmosphere⁽⁴⁵⁾.

Metal Fog. Lorenz⁽⁴⁵⁾ noticed a property of molten salts that tends to decrease current efficiency and cause deviation from Faraday's laws. If a metal, such as zinc or lead, is melted under one of its fused salts, as lead chloride or zinc chloride, the salt will be unaffected at low temperatures, but at higher temperatures the molten metal seems to volatilize and form an equilibrium mixture with the fused salt. This phenomenon may be also produced by adding a small amount of a reducing agent to the bath. While the amount of metal included in the bath is not great, it tends to adversely affect the yield, since the metal in the "fog" form is not susceptible to chemical attack. It is believed that these fogs are colloidal in nature, but the forces that regulate their actions are not thoroughly understood.

Voltage in Fused Salts. In aqueous solutions the electromotive force of cells depend upon the concentration of the electrolyte⁽⁶⁷⁾. With pure fused salts, concentration does not enter the picture, and therefore, the primary electromotive force depends only on the nature of the electrodes, electrolyte and the temperature. In pure fused salts the electromotive force and the decomposition potential are essentially the same. In a mixture of salts, the electromotive force depends upon the concentration of the salt corresponding to the metal used as the cathode.

Anode Effect. In the electrolysis of fused salts, it frequently happens that the voltage rises suddenly and the amperage decreases and a hissing sound is heard from the cathode⁽⁴²⁾. The anode appears to glow owing to the formation of innumerable little spark discharges. This phenomenon is known as the anode effect.

During the normal course of electrolysis, gas bubbles are constantly escaping at the anode in a smooth and regular order. When the anode effect occurs the gases form a film around the anode which holds the molten electrolyte away from the surface. The anode effect is particularly noted with high current densities. It may be made to disappear by removal of the gas layer, which may be done by stirring, raising the anode or reversing the current.

Concentration Polarization. At high current densities the voltage does not increase linearly with the current density⁽¹⁾. This phenomenon is due to the exhaustion of ions near the cathode in aqueous solutions and can be extended to explain the same phenomenon in fused salts, if the idea of ions is extended to include fused salts. Temkin⁽⁶⁹⁾ and Walden⁽⁷⁵⁾ have shown both experimentally and mathematically that ionization should be extended to molten salts.

Electrochemistry of Aluminum.

Some information as to the behavior of aluminum salts and ions in the presence of an electric current was available. Consideration was also given to the ability of aluminum to resist corrosion.

Electroplating on Aluminum. For over thirty years the electrodeposition of other metals onto aluminum surfaces has remained one of the concerns of the electroplating industry. During this time many processes have been patented, but only in recent years have satisfactory methods been established⁽⁵⁰⁾.

Satisfactory plating on aluminum has been produced largely by two methods⁽⁵⁰⁾. One consists of electrochemical oxidation of the aluminum and plating upon the oxide film, while the second involves the use of a sodium

zincate dip. This dip imparts a zinc film to the aluminum, which subsequently may be plated with other metals.

Aluminum as an Anode. Aluminum has a high affinity for oxygen, quickly forming a protective oxide film upon exposure to an oxygen-bearing atmosphere⁽⁵²⁾.

While this film is ordinarily only about 0.0000005 inch thick, it effectively prevents further attack unless removed or penetrated by chemical or mechanical action. Advantage has been taken of this phenomenon in the finishing of aluminum⁽²⁵⁾. The various oxide finishes are obtained by treating the aluminum to be coated anodically in various electrolytes in such a manner that a thin, inert and durable aluminum oxide coating is obtained on the metal surface. The film formed is very hard and offers excellent abrasion and corrosion protection to the underlying metal. Some of these films are clear and transparent, while others are colored in varying degrees of brown, gray and silver.

The method of anodic film formation is not complicated. In anodizing, the aluminum is made the anode, and electrolytes capable of yielding oxygen on electrolysis are used. Examples of electrolytes include chromic, sulfuric, phosphoric and boric acid⁽²⁵⁾.

While advantage has been taken of this anodizing principle for decoration and protection of aluminum, it must be remembered that this property can also be extremely disadvantageous⁽²⁵⁾. In attempts to electrodeposit aluminum onto other metals, it is helpful to use an aluminum anode so that a source of aluminum, other than the electrolyte, will be present for the electrodeposition. Since an aluminum oxide coating will not conduct electricity, great care must be taken to insure that the electrolyte employed will not release oxygen at the anode upon electrolysis⁽⁵²⁾. An aluminum anode must be highly polished before being placed into service to remove the oxide coating that it might have picked up from the atmosphere. The affinity of aluminum for oxygen is so great, in fact, that the surface reactivity of the metal may be greatly reduced after only seconds exposure to oxygen.

Properties of Aluminum Coated Surfaces. Since an electrodeposit bonds with and closely adheres to the base metal, the surface of the base metal has essentially the same properties as the electrodeposited material⁽²¹⁾. Therefore, properties of aluminum would apply, in general, to those surfaces coated with aluminum.

Upon exposure to the atmosphere, aluminum quickly forms a protective oxide film⁽⁵²⁾. This film serves as a preventive for further atmospheric attack. In some cities, where there is a high concentration of sulfur dioxide or chlorine from industrial areas, there may be some corrosion of aluminum⁽⁵⁸⁾. Sea spray will attack aluminum if the metal is in direct contact with the salt water. Atmospheric corrosion can be effectively eliminated by the use of certain aluminum alloys.

Aluminum is resistant to attack by some chemicals, but is readily attacked by others⁽²⁾. In general, the following information with regard to the behavior of aluminum in contact with other metals may be followed: neutral solutions are less corrosive to aluminum than are acidic or basic solutions; in the presence of an electrolyte, the electrical contact of aluminum with heavy metals, such as copper, iron, nickel, lead, etc produces galvanic corrosion of aluminum; aluminum is more resistant to the action of oxidizing substances than to that of reducing substances; the halogen salts of the alkali metals are more active in producing attack on aluminum than are most other neutral salts of these metals; and the simultaneous presence of dissolved heavy metal compounds and halogen salts is likely to cause severe attack of the aluminum.

Electrodeposition of Aluminum

Electrodeposition of aluminum is one of the difficult problems of the electroplating industry. The first article describing attempts to solve this problem was published in 1802⁽⁴⁹⁾. The methods that have been studied for electroplating aluminum may be arbitrarily classified into four systems: from aqueous solutions, from nonaqueous solutions of inorganic salts, from nonaqueous organic liquid solutions and from fused mixtures.

Aqueous Solutions. In 1854, Wohler⁽⁸⁵⁾ was unable to obtain aluminum from a solution of cryolite in an aqueous solution of sodium hydroxide. About this same time, Deville⁽²⁰⁾ attempted to use other aluminum salts in aqueous solution without success.

Thomas and Tilley⁽⁷¹⁾ in 1855 electrolyzed a solution of freshly precipitated alumina or alum in a solution of potassium cyanide and claim to have deposited aluminum. Corbelli⁽¹⁶⁾ said in 1858 that he deposited aluminum by electrolyzing a mixed solution of alum, aluminum sulfate and calcium or sodium chloride in aqueous solution. Gore⁽³³⁾ claims in 1854 to have electrodeposited aluminum on copper from warm, dilute

solution of potassium alum, from a concentrated solution of aluminum acetate and from a cold, filtered solution of pipeclay in hydrochloric acid. Bertrand⁽⁵⁾ in 1876 used an aqueous solution of ammonium aluminum chloride to deposit aluminum on copper.

Numerous patents have been granted for electro-deposition of aluminum from aqueous solution^(26,31,49,79).

Wohler⁽⁸⁵⁾, Deville⁽²⁰⁾, Nickles⁽⁵³⁾, Fischer⁽²⁷⁾, Mierzinsky⁽⁵¹⁾, Hampe⁽³⁷⁾, Winkler⁽⁸¹⁾ and Sprouge⁽⁶⁵⁾ have challenged these methods of depositing aluminum. Wade and coworkers⁽⁷⁴⁾ in 1940 have shown that hydrogen is discharged at the cathode at a lower potential than aluminum. The reason for the failure of attempts to deposit aluminum from aqueous solution was based on this phenomenon.

Tucker and Thompson⁽⁷²⁾ claimed to have produced a suitable method for electrodeposition of aluminum by carrying on the electrolysis in an aluminum chloride paste in which the cathode was rotated at 20,000 revolutions per minute.

P. Marino⁽⁴⁷⁾ obtained a patent for electrolyzing an aqueous solution of sodium pyrophosphate to which had been added ten per cent phosphoric acid and from five to ten per cent sulfanilic acid, while Q. Marino⁽⁴⁸⁾

patented a process using an aqueous ammonia solution of aluminum tartrate, paratartrate and oxalate. Aluminum was used as the anode in all of these processes.

Liquid Inorganics. Two teams of investigators^(8,66) in 1930 and 1934 respectively, failed to obtain aluminum from the electrolysis of liquid ammonia solutions of aluminum salts.

Fused Mixtures. In 1808, Davy⁽¹⁸⁾ tried to electrolyze molten alumina, but because of the weakness of the current available, he obtained no aluminum. Bunsen⁽¹⁰⁾ first obtained aluminum by electrolysis of a fused bath of sodium aluminum chloride contained in a partitioned, porcelain crucible and using carbon electrodes. At low temperatures the aluminum was obtained as a gray powder, but by working at high temperatures the aluminum was found in small beads. Sodium chloride was used as a flux in this process. Deville⁽²⁰⁾ decomposed sodium aluminum chloride by electrolysis at about the same time. He used a porcelain crucible fitted inside a fireclay crucible. The fireclay cover was cut to admit a strip of platinum to serve as the cathode and a porous cell which contained the carbon anode. Chalelier⁽¹⁴⁾ patented a similar process whereby an anode of carbon and alumina was used.

Mellor(49) mentions other systems that have been studied for the electrodeposition of aluminum which include: cryolite and sodium chloride, molten cryolite, alkali chloride and alum, aluminum fluoride and alkaline earth metal salts, aluminum phosphate and aluminum borate. No evidence of success was indicated for these systems.

Wade and coworkers(74) employed a system of 20 mol per cent sodium chloride, 14 mol per cent potassium chloride and 66 mol per cent aluminum chloride in a study of deposition and decomposition potentials of a number of chlorides. Platinum was used as the reference electrode. Aluminum was found to deposit as a smooth surface at a potential of 2.02 volts and at a current density of 1.25 amperes per square decimeter. Dendritic aluminum was deposited at a potential of 2.17 volts and the same current density. Samples of these two deposits were easily removed from the cathode by scraping with a dull blade. X-ray examination and comparison with pure aluminum confirmed their identity as the pure metal.

Pink and Solanki(26) investigated containers for electrolyzing a mixture of aluminum chloride and sodium chloride. The possibility of obtaining aluminum metal was also investigated. From a system of aluminum-sodium chloride, aluminum was obtained in crystalline form

using a nickel crucible as cathode and a carbon rod as anode.

Plotnikov, et al⁽⁵⁹⁾ claims to have produced a satisfactory surface of aluminum on copper from a bath containing aluminum chloride and sodium chloride in a two to one ratio at 220 to 250 °C. Cathode current density was one ampere per square decimeter.

Wehrman and Yntema⁽⁷⁷⁾ studied the alkali-aluminum bromide series for deposition potentials of various metals. Aluminum bromide-potassium bromide had a decomposition potential of 1.61 volts which was more electronegative than that of any other metal studied. In the study of the addition of chlorides to the bromide series, a system of 66 mol per cent aluminum chloride, 20 mol per cent sodium bromide and 14 mol per cent potassium bromide was investigated. The decomposition potential was 1.71 volts. Deposits of aluminum similar to those deposited from the chloride baths were found.

Chittum⁽¹⁵⁾ patented a process for depositing aluminum on copper from a fused aluminum chloride-lithium chloride bath. A current density of 0.2 ampere per square centimeter was used.

In a number of studies by Wade, et al⁽⁷⁴⁾, Skobets and Kanetskii⁽⁷⁴⁾ and Plotnikov, et al⁽⁷⁴⁾ the electro-deposition series of a number of metals was studied.

In every case aluminum was found to be more electro-negative than any of the other metals except the alkalis. The order, as reported by Wade, with platinum as the reference electrode in an aluminum chloride, sodium chloride, potassium chloride bath was hydrogen, cobalt, nickel, copper, iron, zinc, manganese and aluminum.

Von Zeerleder⁽⁷³⁾ patented a process for depositing a dense coating of aluminum alloy in the presence of a metal other than iron that was more electropositive than aluminum, such as lead. A mixture of halide and alkaline earth metal salts was used as the electrolyte.

Plotnikov and Kolita⁽⁶⁰⁾ claimed that additions of calcium salts to a bath containing aluminum and sodium chloride improved the conductivity of the bath and the deposit.

Czechralski and Milchljczyk⁽¹⁷⁾ patented a method of depositing aluminum from fused aluminum halides.

Peacock⁽⁵⁷⁾ patented a process for producing aluminum from a very high temperature bath of aluminum-potassium-sodium fluoride. The deposits were weak and had to be compacted by cold rolling.

Organic Systems. Since the organic systems have been thoroughly covered in a companion thesis⁽⁵⁵⁾, these subjects have been omitted from this literature review.

III. EXPERIMENTAL

The experimental work on this thesis was divided into sections corresponding to the seven systems investigated. Under each section a literature review pertaining to that system, the materials and apparatus used, method of procedure, data and results and discussion of results was presented.

Purpose of Investigation

The purpose of this investigation was to study the possibilities of using the inorganic molten salt systems aluminum chloride - alkali chloride, aluminum fluoride - alkali fluoride, aluminum sulfide - alkali sulfide, aluminum cyanide, aluminum fluoborate, aluminum formate and aluminum thiocyanate as electrolytes for the electrodeposition of aluminum.

Plan of Experimentation

The general plan of experimentation of the electrodeposition of aluminum from molten inorganic salt mixtures was to study various systems of aluminum and alkali metal salts with the view of finding a mixture with a

low viscosity and melting point at a temperature below the melting point of aluminum, 660 °C.

The systems were studied by literature reviews and experimentation.

Literature Review. The literature was searched for information relative to each system selected. Methods of preparation for the chemicals involved, commercial availability of such chemicals, corrosion problems relative to these chemicals, physical properties of the pure chemicals and any specific data on the mixtures of the components were the topics which were of concern to the investigator for each system.

Experimental Work. Many of the systems selected were eliminated by the literature review and were not submitted to experimental study.

When a probable system was found, the first step in the investigation was to obtain the chemicals necessary either commercially or by synthesis. Methods of preparation found in the literature were used where necessary and available.

The second step in the study of each system was to determine the melting range of a mixture of the components of the system. The course of action for this determination was governed by the physical properties of the

materials involved. In most cases, however, determinations were made in a glass container heated by an oil bath. Various ratios of the component materials were fused together and the melting range of the resulting mixture determined. Several of the systems were eliminated at this point in the investigation because of excessively high melting points or for various other reasons more fully explained in the discussions.

The third step in the investigation was to determine the electrical conductivity of the fused mixture. This was done by using platinum electrodes at a fixed distance apart and applying varying potentials across these electrodes. The current that passed through this circuit was measured.

The fourth step was the determination of the corrosive effect of the bath on aluminum metal. Sample strips of aluminum were dipped into the molten bath for varying lengths of time, removed and visually examined for corrosive action.

The fifth step was to try to electrodeposit aluminum from the salt mixture. Electrodes of aluminum as anode and copper as cathode were normally used. Varying

current densities were applied for varying lengths of time at constant temperatures. The electrodes were examined physically and chemically for the presence of aluminum.

The sixth step in the investigation was to determine the properties of any aluminum deposit that was obtained and to submit the bath to such other tests that were deemed necessary. Since no suitable system was found, this sixth step was not taken.

Evaluation of Results. The results obtained from the studies were evaluated by tabulation; graphical interpretation, where suitable, and discussion.

CHLORIDE SYSTEM

The electrodeposition of aluminum from halides and particularly from chlorides had been studied to a considerable degree by other investigators. However, since this was the only inorganic system that had ever successfully served as an electrolyte for the deposition of aluminum, it seemed to be a good starting point from which to become acquainted with the experimental study of the subject.

Literature Review

Much of the literature review for the chloride system has been previously presented in the general literature review, page 30 to 33. Several patents (26,31,78) have been granted for electrodeposition of aluminum from molten chlorides. Russian investigators (17,59,60) have done considerable work on the system, but the principle source of information on the chloride system has been the work of Wade and coworkers (74). This investigation was very detailed giving conditions and a thorough summary of results. Wade used an electrolyte consisting of 66 mol per cent aluminum chloride, 20 mol per cent sodium chloride and 14 mol per cent potassium chloride in a fused bath at 160 °C. A glass cell was used to contain the fused mixture which was heated by means of an external oil bath. Electrodes of the "projector type" carbon as anode and platinum as cathode were used. The cathode current density was 1.25 amperes per square decimeter when operated at optimum conditions.

The results obtained by Wade were similar to those reported by other investigators. A spongy deposit of aluminum was found on the cathode. This deposit could be removed very easily by scraping with a dull blade. Upon examination of the deposit, it was found to consist

of dendritic structure at current densities above 1.5 amperes per square decimeter and very fine crystals at lower current densities.

Materials

The following materials were used in the investigation of the chloride system for the electrodeposition of aluminum:

Acid, Hydrochloric. CP, lot No E407014.

Obtained from General Chemical Co., New York, N. Y. Used in preparation of cleaning solution for electrodes.

Acid, Nitric. CP, lot No E405005. Obtained from General Chemical Co., New York, N. Y. Used in cleaning solution for electrodes.

Acid, Sulfuric. CP, lot No E406026. Obtained from General Chemical Co., New York, N. Y. Used in cleaning solution for electrodes.

Alcohol, Ethyl. Absolute. Obtained through Virginia Alcoholic Beverage Control Board from U. S. Industrial Alcohol Company, Baltimore, Md.

Aluminum Chloride. CP, anhydrous, lot No E 137. Obtained from General Chemical Co., Phillipsburg, N. J. Used as electrolyte component.

Aluminum Chloride. CP, anhydrous, lot No 72245. Obtained from J. T. Baker Chemical Co., Phillipsburg, N. J. Used as electrolyte component.

Aluminum Chloride. CP, anhydrous, sublimed, lot No 500119. Obtained from Fisher Scientific Company, Pittsburgh, Pa. Used as electrolyte component.

Aluminum Metal. Commercial grade, 0.040 inch thick, sample No 35414040. Manufactured by Reynolds Metal Corp., Louisville, Ky. Used as material for making aluminum anodes.

Aluminum Wire. Brown and Sharpe gage No 14. Obtained from Fisher Scientific Company, Pittsburgh, Pa. Used to connect aluminum anodes to source of electricity.

Copper Metal. Strip, commercial grade, 1/32 inch thick. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used to make copper cathodes.

Copper Wire. Brown and Sharpe gage No 18. Obtained from Fisher Scientific Company, Pittsburgh, Pa. Used to connect copper cathodes to source of electricity.

Oil, Motor. S. A. E. No 40. Obtained from Esso Standard Oil Co., Bayway, N. J. Used as heating material in oil bath.

Platinum Metal. CP. Purchased from Fisher Scientific Company, Pittsburgh, Pa. Used for electrodes.

Potassium Chloride. Crystal, Code No 2150, lot No 0226. Obtained from General Chemical Co., New York, N. Y. Used as component of electrolyte.

Sodium Chloride. USP, lot No 43213. Obtained from Merck and Co., Rahway, N. J. Used as electrolyte component.

Sodium Hydroxide. CP, pellets, lot No 461988. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used to make five per cent test solution for testing aluminum deposits.

Apparatus

The following apparatus was used in the chloride investigation of the electrodeposition of aluminum:

Ammeter. Direct Current, 0-1.5, 0-3, 0-30 ampere ranges, model No 28, serial No 194093. Manufactured by Weston Electrical Instrument Co., Newark, N. J. Used to measure current in electrolysis circuit.

Balance, Analytical. Capacity 500 grams, chainomatic. Manufactured by Seederer-Kohlersch

Co., Inc., Jersey City, N. J. Used to weigh samples and electrodes.

Balance, Beam. Capacity 600 grams. Obtained from Eimer and Amend, New York, N. Y. Used for weighing chemicals for electrolyte.

Batteries, Wet Cell. Model No 1724AN, 24 volts. Manufactured by Delco-Remy Division, General Motors Corp., Anderson Indiana. Used as a source of direct current.

Beakers. Pyrex, 250 milliliter, tall, Available from Fisher Scientific Co., Pittsburgh, Pa. Used for electrolytic cells.

Furnace, Muffle. Type FD 204C, serial No 34928, 110 volt, 30.9 amperes. Manufactured by Hoskins Electric Co., Detroit, Mich. Used for heat treating aluminum deposits.

Glassware. Miscellaneous, laboratory, including beakers, evaporating dishes, glass tubing, flasks, etc. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used for various purposes in connection with experimental work.

Heater, Autemp. Variable temperature, 115 volt AC. Manufactured by Eimer and Amend, New York, N. Y. Used to heat oil bath for electrolyte.

Microscope. Dissecting, serial No 176495.
Manufactured by Spencer Lens Co., Buffalo, N. Y.
Used to examine electrodeposits.

Oil Bath. Capacity one quart, galvanized iron,
brazed joints. Made in Chemical Engineering Shops,
Virginia Polytechnic Institute. Used as container
for oil for heating electrolytes.

Oven. Drying, electric utility, model No
OV - 8, serial No 8-270, 115 volt, 5 amperes, AC.
Manufactured by Modern Electric Laboratories,
Chicago, Ill. Used to dry apparatus and chemicals.

Rheostat. Slide wire, 125 ohm, 3 ampere.
Obtained from Phipps and Bird, Inc., Richmond, Va.
Used to control voltage and amperage in electro-
lysis circuit.

Rheostat. Variable, 110 volts, 30 - 15 ampere,
AC, type No X41692. Obtained from Eimer and Amend,
New York, N. Y. Used to control muffle furnace.

Thermometer. Laboratory, mercury in glass,
0-400 °F. Obtained from Fisher Scientific Company,
Pittsburgh, Pa. Used for measuring temperature of
oil bath and electrolyte.

Voltmeter. Direct current, 0-3, 0-14, 0-120
volt ranges, model No 489. Manufactured by Weston
Electrical Instrument Co., Newark, N. J. Used for
measuring voltage in electrolysis circuit.

Methods of Procedure

The procedure used in this investigation was to repeat the work as published in the literature and to extend the available data where possible.

The Electrolyte. The electrolyte used was a mixture of 66 mol per cent aluminum chloride, 20 mol per cent sodium chloride and 14 mol per cent potassium chloride. In these proportions an eutectic was formed having a melting point of approximately 145 °C. In the initial fusion the sodium and potassium chlorides were dried thoroughly in an oven at 120 °C for twenty-four hours. The two salts were carefully mixed, the correct amount of anhydrous aluminum chloride added and the mixture transferred to a 250-milliliter beaker as quickly as possible to minimize the amount of moisture picked up by the salts. The beaker was tightly stoppered, vented through a drying tube and placed in an oil bath. The temperature of this bath was increased slowly by means of an electric hotplate until the temperature of the chloride mixture was approximately 165 °C at which point it was held constant until the contents of the beaker were completely melted. Care was taken to keep the salt mixture stoppered, since the aluminum chloride volatilized below 2.5 atmospheres. Since this pressure

could not be obtained in glassware, a certain amount of aluminum chloride was lost by condensation on the sides of the beaker and on the stopper, but no accounting was made for this loss. A diagram of the type apparatus used for this work is shown in Figure 1.

The Electrodes. The literature recommended the use of a platinum cathode and a graphite anode. In a test using these electrodes, the graphite anode disintegrated, because of a reaction with the binding material, and the platinum color was so near to that of aluminum that any of the metal deposited could not be easily recognized. After further tests, an aluminum anode and a copper cathode were chosen for the electrodes.

Current Density. In a second aspect, the actual procedure used did not agree with that recommended by the literature. A current density of 1.25 amperes per square decimeter based on the cathode surface area was given in the standard procedure. In this investigation, a current density of 0.833 amperes per square decimeter was found to give the best results.

Electrodeposition. The mixture was heated to a constant temperature of 170 °C, the electrodes were lowered into the molten bath and the potential was

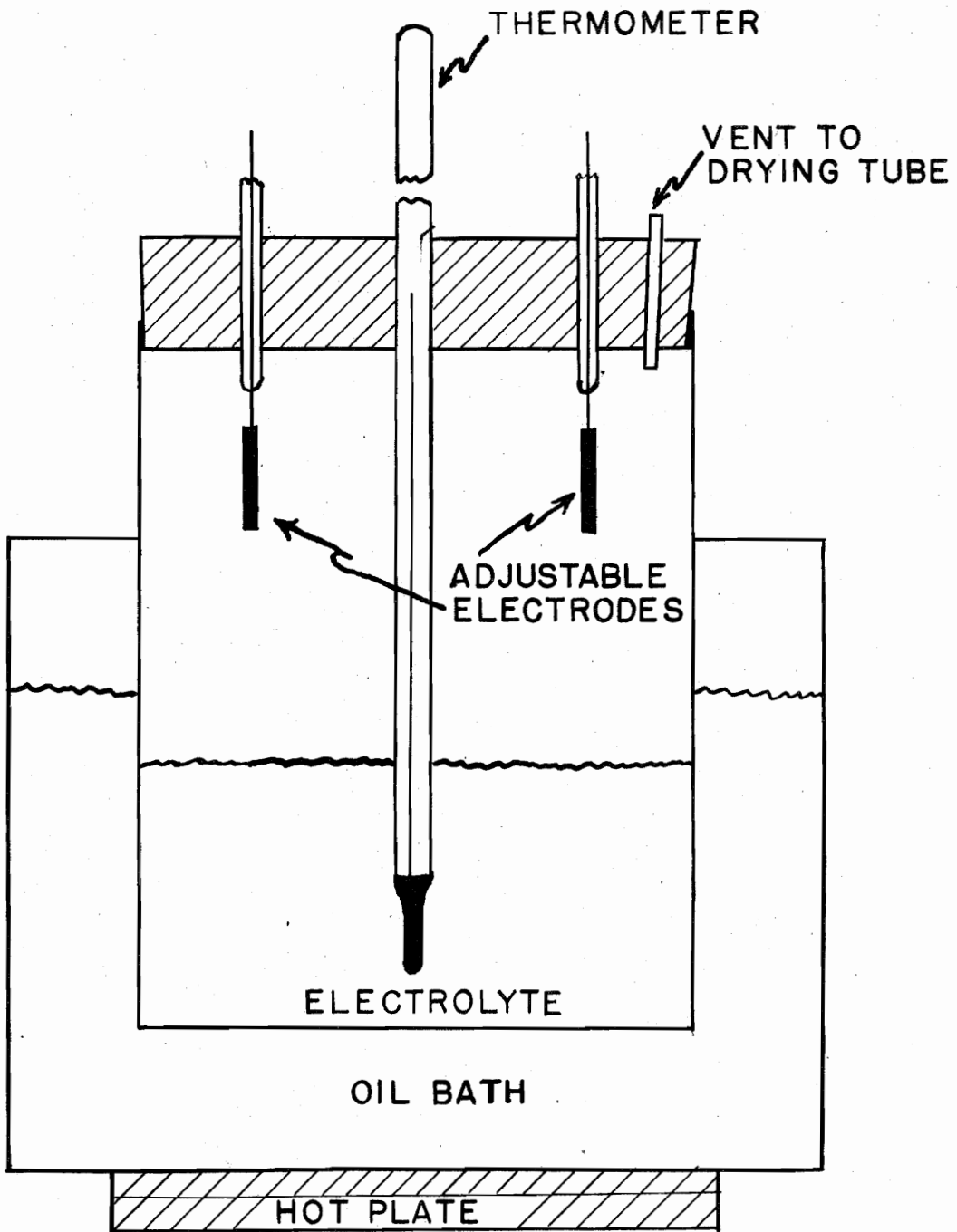


FIGURE 1. DIAGRAM OF CELL USED FOR THE ELECTRODEPOSITION OF ALUMINUM FROM A SYSTEM OF ALUMINUM CHLORIDE, SODIUM CHLORIDE AND POTASSIUM CHLORIDE.

applied from a direct current source through a circuit as shown in Figure 2. The resistance was adjusted until the current density for that particular test was obtained. The electrolysis was carried out for a specific length of time for each test in the range of from thirty minutes to five hours. Upon completion of the test, the electrodes were removed from the electrolyte and examined visually and chemically for aluminum. The visual examination was made with a surface microscope, while the chemical test consisted of applying a five per cent solution of sodium hydroxide to the electrode to see if a reaction occurred with the surface. Aluminum is rapidly soluble in sodium hydroxide while copper is not.

Heat Treatment. It has been possible in certain types of plating to increase the covering power of the deposit by breaking down the crystal structure of the plate by sintering in an electric furnace. It was believed that this procedure was worth consideration in the study of the crystal formations found on the cathode after electrodeposition from the aluminum chloride system.

Five samples were prepared for this study by electroplating at a current density of 0.833 ampere per

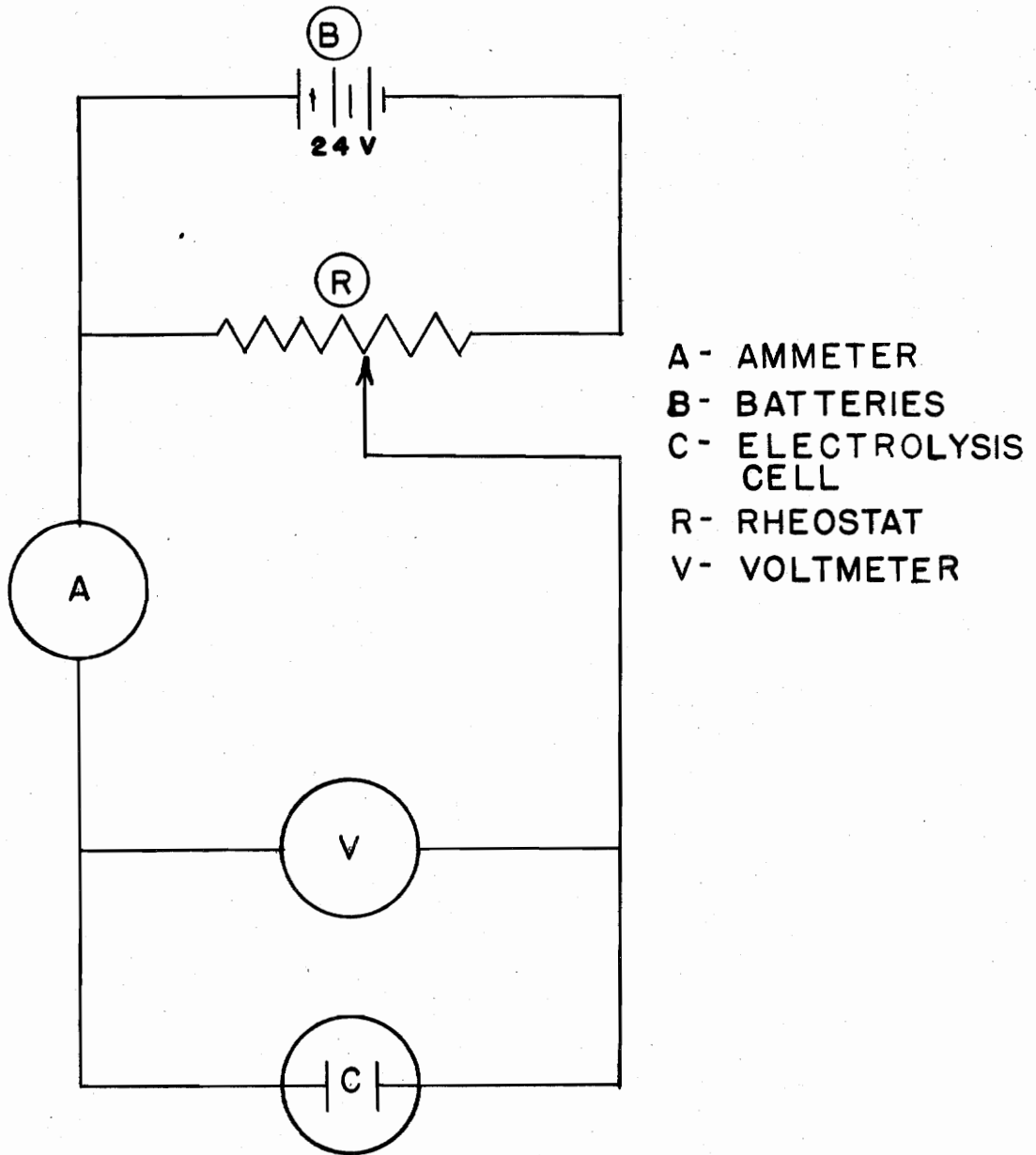


FIGURE 2. ELECTRICAL DIAGRAM OF CIRCUIT USED FOR THE ELECTRODEPOSITION OF ALUMINUM FROM A SYSTEM OF CHLORIDES

square decimeter from an aluminum chloride-sodium chloride-potassium chloride bath at 170 °C using a copper cathode and an aluminum anode. The electrodes had a total area of approximately ten square centimeters. The first sample of copper, plated with aluminum, was placed in a porcelain dish in an electric furnace and the temperature was gradually increased to 550 °C, as measured by a chromel-alumel thermocouple. The second aluminum-coated strip was placed in the electric furnace at 1000 °C and held there for one minute. Tests three and four were similar to one and two except that the samples were surrounded by an inert atmosphere of nitrogen. Sample number five was kept for comparison and control.

Four strips of copper similar to those used in the previous tests were dipped into molten aluminum and then heat treated in an electric furnace. Sample number one was dipped into the aluminum in an atmosphere of air and was gradually heated from 25 to 550 °C, while sample number two was heated for one minute at 1000 °C after having been dipped in an atmosphere of air. Samples three and four were treated similarly except that the dipping was done in an atmosphere of nitrogen. The protection given to the copper by the

aluminum coating was compared with that which was applied by electrolysis.

Data and Results

A summary of the data collected and the results obtained for electrodeposition from a system including aluminum chloride may be found in Table II.

The results obtained from the experiments on heat treating samples of copper that had been coated with aluminum are tabulated in Table III.

Discussion of Results

The chloride system still remains the only inorganic fused salt bath from which aluminum can be deposited with any semblance of satisfaction. The quality of the deposit obtained was very poor indeed, lacking adherence and continuity. The greatest single disadvantage of the chloride bath seemed to be its extreme sensitivity to water or atmospheric moisture. Since this difficulty was the nature of the compound, there seemed to be little point in continuing investigation of a system that was so limited.

Addition Agents. In certain other electroplating systems, success has been had with addition of certain

TABLE II

Attempts to Electrodeposit Aluminum from a System of
Aluminum Chloride, Potassium Chloride and Sodium Chloride

TABLE II

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Attempts to Electrodeposit Aluminum from a System of Aluminum Chloride, Potassium Chloride and Sodium Chloride

Test No.	Cathode	Anode	Average EMF, volts	Average Current, amperes	Average Temp. °F	Current Density, amps/dm ²	Time of Operation, hours	Results
1	Pt	Carbon	2.3	0.25	314	1.50	3.5	No aluminum. Black deposit that dissolved in HCl on cathode. Anode disintegrated.
2	Pt	Al	---	---	314	----	0.5	Unable to secure usable voltage.
3	Pt	Al	2.3	0.25	314	1.50	3.5	No aluminum. Suspected contamination with water
4	Cu	Al	1.0	0.195	308	1.25	0.5	Oxide film formed on anode causing current to drop to zero.
5	Cu	Al Pt	0.185	1.5pt 0.8Al	315	1.25	3.5	Spongy black to copper color deposit on cathode. Deposit easily removed by rubbing with finger. Microscopic examination showed tiny particles of silver material.
6	Cu	Al	0.65	0.10	320	0.675	4.0	Dendritic aluminum crystals on one side of cathode. Spongy in nature, easily removed.
7	Cu	Al	0.65	0.05	320	0.337	3.5	No deposit
8	Cu	Al	0.37	0.05	320	0.337	3.25	No deposit
9	Cu	Al	1.30	0.20	305	1.25	3.0	No deposit
10	Cu	Al	0.55	0.10	314	0.675	3.5	Granular deposit of aluminum.
11	Cu	Al	0.90	0.081	290	0.833	2.0	Poor yield of granular aluminum coating.
12	Cu	Al	1.25	0.12	306	0.833	4.0	Very poorly adherent aluminum coating.
13	Cu	Al	0.90	0.12	320	0.833	5.0	Granular aluminum.
14	Cu (2)	Al	1.25	0.24	304	0.833	4.5	Granular aluminum.
15	Cu (2)	Al	1.05	0.24	300	0.833	5.0	Granular aluminum, some dendrites.

TABLE III

Results from Heat Treating Strips of Copper
Coated with Aluminum

TABLE III
Results from Heat Treating Strips of Copper
Coated with Aluminum

Sample No.	Treatment	Time, min	Temperature, °C	Atmosphere	Description of surface after heating
1	Electroplated	40	Slowly increased to 550 °C from 25 °C.	Air	Crystal structure on the surface unchanged. Metal deposit could be removed by washing with water. Five per cent sodium hydroxide solution reacted only slightly with surface. At surface, a change in color had occurred. Surface film very adherent, not being removed by file or sandpaper. No scale on copper where aluminum was present, oxide on other parts of sample.
2	Electroplated	1	1000	Air	Same properties as sample number one. Penetration apparently greater than in sample one.
3	Electroplated	40	Slowly increased to 550 °C from 25 °C.	Nitrogen	Deposited aluminum still reacted vigorously with sodium hydroxide. Similar in other aspects to first sample. No copper oxide present.
4	Electroplated	1	1000	Nitrogen	Same as sample number three. Penetration apparently greater.
5	Dipped	40	Slowly increased to 550 °C from 25 °C.	Air	Base metal oxidized and made brittle, no change in color at surface.
6	Dipped	1	1000	Air	Same as sample number five.
7	Dipped	40	Slowly increased to 550 °C to 25 °C.	Nitrogen	No oxide. No change in color at surface. Apparently no reaction.
8	Dipped	1	1000	Nitrogen	Same as sample number seven.

Electroplated at a current density of 0.853 ampere per square decimeter from a bath of 66 mol per cent aluminum chloride, 20 mol per cent sodium chloride and 14 mol per cent potassium chloride for three hours.

compounds to the bath, which compounds seem to break up crystals formations and cause the plate to be brighter and smoother. It was thought that this procedure might have been helpful in the case of the chloride system. No experimentation was carried out on this phase of the work since the addition agents would not overcome the basic fault of the chloride bath - sensitivity to moisture. The type addition agent that might be satisfactory cannot be definitely stated, since there is no satisfactory theory of the behavior of addition agents. Trial and error with the large molecule organics seemed to be the best approach.

Heat Treatment. When a sample of copper was electroplated with aluminum and subsequently heated in an electric furnace, a distinct change in color was noticed at the surface. The deep copper color was lightened to a shade similar to gold. Commercial alloys of copper and aluminum are available that have this same color; therefore, it was believed that an alloy had been formed on the surface between aluminum and copper. This alloy was very adherent, being removed only by prolonged scraping with a metal file. This type of surface alloy has been produced in several other ways, especially on steel where the process is known as calorizing, but there

were no references in the literature to heat treating copper that had been electroplated with aluminum.

Samples of copper similar to those used in the previously mentioned test were dipped into molten aluminum and subsequently heat treated under the same conditions as the aluminum plated pieces. In every case, there was no alloy formed and where oxygen was present in the atmosphere, the base became very brittle and covered with the black oxide of copper.

Comparison of these two experiments gave a definite indication that during heat treatment, aluminum electrodeposited from a chloride bath onto copper provided better protection from oxidation to the copper than aluminum applied by dipping the copper piece into a molten bath of aluminum.

Recommendations

The following recommendations are made for future work on the chloride system for the electrodeposition of aluminum:

If no other suitable method for the electrodeposition of aluminum can be found, then additional work should be done with anhydrous aluminum chloride by designing apparatus that would be air and moisture tight.

Under the previously mentioned condition, addition agents of the high molecular weight organic type should be investigated with the aluminum chloride bath.

Limitations

The limitations under which the experimental work on the electrodeposition of aluminum from a molten salt system including aluminum chloride were as follows:

An electrolyte consisting of 66 mol per cent anhydrous aluminum chloride, 20 mol per cent sodium chloride and 14 mol per cent potassium chloride in a temperature range of 300 to 400 °F was used. Electrodes of aluminum, platinum and graphite as the anode and copper and platinum as the cathode were employed. The current density was varied from 0.625 to 1.50 amperes per square decimeter for electrolyses of from thirty minutes to five hours.

The tests on the deposits were limited to visual observation and chemical reaction of the deposit with five per cent sodium hydroxide solution.

Conclusions

An exploratory investigation of the system aluminum chloride, potassium chloride, sodium chloride as an

electrolyte for the electrodeposition of aluminum led to the following conclusions:

1. A poorly adhering aluminum plate can be obtained on copper at a current density of 0.833 ampere per square decimeter by means of a fused bath consisting of 66 mol per cent aluminum chloride, 20 mol per cent sodium chloride and 14 mol per cent potassium chloride.

2. A mixture of 66 mol per cent aluminum chloride, 20 mol per cent sodium chloride and 14 mol per cent potassium chloride has a melting point of approximately 145 °C and a fluid viscosity low enough to be used as an electrolyte in the temperature range 155 to 170 °C.

3. An aluminum deposit from an aluminum chloride, sodium chloride, potassium chloride bath has the appearance of a spongy growth. It is very poorly adherent, being easily removed by rubbing with the finger.

4. When a piece of copper that was coated with aluminum by electrodeposition from a chloride bath was heat treated in an electric furnace at 550 and 1000 °C an alloy of copper and aluminum was formed on the copper surface.

5. Aluminum chloride baths or baths containing aluminum chloride are not satisfactory for the commercial electrodeposition of aluminum because of their extreme sensitivity to water or moisture.

CYANIDE SYSTEM

The possibility of using aluminum cyanide as an electrolyte for the electrodeposition of aluminum was investigated entirely by literature review.

Literature Review

The literature was investigated for information about aluminum and alkali cyanides to determine the possibilities of using these agents for electrolytes in the electrodeposition of aluminum.

There were no literature references that gave evidence that aluminum cyanide exists. Williams⁽⁸⁰⁾ states that aluminum cyanide does not appear to have a separate existence. Anderson and Forbes^(3,29,30) have prepared a number of inorganic cyanides, thiocyanates and cyanates, but there was no reference to aluminum cyanide in the work of these authors. The American Cyanamid Company⁽⁴⁰⁾ had no evidence of the existence of aluminum cyanide.

Anderson and Forbes⁽²⁹⁾ prepared boron cyanide which is in the same group in the periodic table as aluminum, but were unable to determine any of its

properties or characteristics because of its instability and extreme deliquescence.

Sodium and potassium form stable cyanides that have very high melting points; potassium cyanide, 635 °C and sodium cyanide, 564 °C⁽³⁶⁾. Potassium cyanide decomposes at a temperature slightly above its melting point or at approximately 700 °C.

Anderson and Forbes⁽³⁰⁾ had a violent explosion while investigating chromyl cyanide.

Discussion of Results

Since there was no evidence that an aluminum cyanide existed, an attempt was made to correlate the knowledge of existing cyanides with their position in the periodic table to try to predict the possibility of an aluminum cyanide being formed. In the same group as aluminum, the only compound that forms a cyanide is boron. The properties of this compound have not been identified because of its extreme deliquescence. Since sensitivity to moisture was one of the difficulties with the aluminum chloride system, it seemed that it would be unsuitable to use a cyanide system because of the probable decomposition of the aluminum cyanide upon exposure to moisture.

In the same period as aluminum, the elements on either side of aluminum form cyanides. Sodium cyanide in group one is a common and stable compound, while silicon cyanide in group four is stable, but not easily isolated. Magnesium cyanide, in group two, is unknown however. Other elements in group two but in different periods from aluminum form stable cyanides, as calcium cyanide, cadmium cyanide, barium cyanide. Other elements in adjacent periods and groups to aluminum that form cyanides include potassium and germanium. However, since the tendency for compounds of the same group to form similar compounds is much stronger than for compounds of like or closely adjacent periods, it seemed that existence of aluminum cyanide could not be predicted and if it did exist, it would probably be extremely unstable.

There was a possibility that an eutectic melting point for potassium and sodium cyanides could be found. If this were the case the electrodeposition might be carried on without an aluminum salt in the electrolyte, using an aluminum anode as a source of the metal. Aluminum cyanide might exist as a transition compound momentarily in a fused mixture such as this when electric current was passed,

decomposing at the cathode and depositing the aluminum,

Another possibility of using a cyanide system would be employment of other aluminum salts with the alkali cyanides, such as chlorides, carbonates, oxide or fluoride. Investigation of these systems might reveal a suitable electrolyte for the electrodeposition of aluminum.

Upon further examination of the literature, however, it was found that cyanides may decompose to form the highly toxic hydrocyanic acid and in some cases may form explosive mixtures. These dangers seemed to make this system impractical for further investigation.

Recommendations

The following recommendation for use of a cyanide system for the electrodeposition of aluminum is made:

If adequate ventilation can be obtained, systems of potassium and sodium cyanides with aluminum compounds such as the carbonate, oxide, chloride and fluoride as solutes should be studied for the electrodeposition of aluminum.

Conclusions

Based on the literature survey on the use of a cyanide system for the electrodeposition of aluminum, the following conclusions were made:

It is improbable that aluminum cyanide exists.

The health and safety hazards of the cyanide system indicate that a study of this system is impractical.

FLUORIDE SYSTEM

The fluoride system was investigated by literature review and experimentation.

Literature Review

Peacock⁽⁵⁷⁾ patented a process for producing elemental aluminum from a very high temperature bath containing aluminum fluoride, potassium fluoride and sodium fluoride. The deposits were easily removed unless compacted by cold rolling.

Two references were found that indicated that aluminum fluoride and potassium fluoride formed an eutectic mixture that melted below the melting point of aluminum, 660 °C. Pushin and Baskov⁽⁶¹⁾ report that potassium fluoride and aluminum fluoride have

an eutectic mixture containing 40 mol per cent aluminum fluoride and 60 mol per cent potassium fluoride which melts at 568 °C. Fedotiev and Timofeev⁽²⁴⁾ report an eutectic at 45 mol per cent aluminum fluoride and 55 mol per cent potassium fluoride that melts at 575 °C.

Materials

The following materials were used in the investigation of the fluoride system for the electrodeposition of aluminum:

Aluminum Fluoride. CP, lot No 400119. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used as a component of electrolyte.

Copper-Aluminum Alloy. Composition 92 per cent copper and 8 per cent aluminum, sample No A188543. Extruded bar, five inches in diameter. Manufactured by Ampco Metal Co., Inc. Milwaukee, Wisconsin. Used to make crucible and thermocouple protection tube.

Graphite. Rod, 2 inch diameter, LG plain "Acheson" graphite, 99.9 per cent pure carbon. Obtained from National Carbon Company, Niagara Falls, N. Y. Used to make crucible.

Graphite. Rod, 1/2 inch diameter, LG plain "Acheson" graphite, 99.9 per cent pure carbon. Obtained from National Carbon Co., Niagara Falls, N. Y. Used to made thermocouple protection tubes.

Nitrogen. Dry, oil pumped, cylinder No 224774. Obtained from Air Reduction Sales Co., Richmond, Virginia. Used to create inert atmosphere around crucible.

Potassium Fluoride. Anhydrous granular, Code No 2113, lot No Fo58. Obtained from General Chemical Co., New York, N. Y. Used as a component of electrolyte.

Apparatus

The following equipment was used in the investigation of the fluoride system as an electrolyte for the electrodeposition of aluminum:

Batteries. Dry cell, "Eveready", 1.5 volt direct current. Manufactured by National Carbon Co., Niagara Falls, N. Y. Used as a source of E. M. F. for potentiometer.

Furnace. Crucible, 10.0 amperes, 115 volt alternating current, type FD204, serial No 34119. Manufactured by Hoskins Manufacturing Co., Detroit, Mich. Used to heat electrolyte.

Galvanometer. Serial No 570-201. Manufactured by G. M. Laboratories, Inc. Chicago, Illinois. Used with potentiometer and thermocouple.

Rheostat. Variable, 115 volt AC, 11.9 to 5 amperes. Obtained from Eimer and Amend Co., New York, N. Y. Used to regulate temperature of crucible furnace.

Standard Cell. Cadmium, serial No 392006, 1.0185 volts. Manufactured by Epperly Laboratories Inc., Newport, R. I. Used as a source of standard electromotive force with potentiometer and thermocouple.

Thermocouple. Iron-Constantan. Wire manufactured by Hoskins Manufacturing Co., Detroit, Mich. Fused and calibrated in V.P.I. Chemical Engineering Shops. Used for measuring temperature of electrolyte.

Valve. Pressure reduction, Ox-weld type, H-R-67, serial No R4656372. Manufactured by V. G. and C. Corp., New York, N. Y. Used to reduce pressure on nitrogen supply line.

Methods of Procedure

The following experimental methods were used in the investigation of a system of aluminum and potassium fluorides as a possible electrolyte for the electro-deposition of aluminum.

Determination of Melting Point. The initial melting tests for this system were made using a machined graphite crucible of approximately 100-milliliter capacity. A mixture of 45 mol per cent aluminum fluoride and 55 mol per cent potassium fluoride was placed in this crucible. The crucible was subsequently placed in a furnace and the temperature gradually increased to the maximum available in the furnace or approximately 950 °C. The temperature of the fluoride mixture was measured at regular intervals by means of an iron-constantan thermocouple in a graphite protection tube. The mixture was held at the maximum temperature for approximately thirty minutes. The crucible was removed and the mixture visually examined. The temperature was plotted against time.

A second test was performed using a crucible machined from an alloy of 8 per cent aluminum and 92 per cent copper. The previously mentioned procedure was repeated using the same ratios of aluminum and potassium fluorides.

A third test was made in which the crucible and the fluoride mixture were surrounded by an atmosphere of nitrogen. This was accomplished by constructing a seal for the top of the crucible furnace. Nitrogen gas was passed into the furnace expelling the oxygen and air through such leaks as were present in the bottom of the furnace. Nitrogen was continually added so as to insure freedom from contamination by atmospheric oxygen.

Using the nitrogen atmosphere as previously mentioned, three tests were made in which the ratio of aluminum fluoride to potassium fluoride was changed. The ratios used were 45 to 55 mol per cent, 42 to 58 mol per cent and 40 to 60 mol per cent. The basic procedure as previously reported was used to determine the melting point.

Data and Results

A summary of the tests made on the fluoride system for the electrodeposition of aluminum is shown in Table IV. A mixture of fluoride with a melting point below 360 °C was not found in any of these tests.

TABLE IV

Summary of the Tests Performed on a System of Aluminum Fluoride and Potassium Fluoride as an Electrolyte for the Electrodeposition of Aluminum.

Test No.	Crucible	Composition, mol per cent		Remarks
		AlF ₃	KF	
1	Graphite	45	55	Melting point not reached, crucible visibly attacked by fluoride vapor.
2	Alloy - 92 per cent copper, 8 per cent aluminum.	45	55	Melting point not reached, crucible oxidized by atmospheric oxygen. Resulting copper oxide dissolved in fluoride paste causing blue color.
3	Alloy - 92 per cent copper, 8 per cent aluminum.	45	55	Nitrogen atmosphere around crucible, no fluoride corrosion or oxidation. Melting point not reached at 950 °C.
4	Alloy - 92 per cent copper, 8 per cent aluminum.	42	58	Melting point not reached at 950 °C.
5	Alloy - 92 per cent copper, 8 per cent aluminum.	40	60	Melting point not reached at 950 °C.

Discussion of Results

The results of the tests on a system of aluminum fluoride and potassium fluoride as an electrolyte for the electrodeposition of aluminum were negative since no mixture of these materials could be found that melted below the melting point of aluminum, 660 °C.

There seemed to be no satisfactory explanation for the discrepancy between the literature and the findings of this investigation in regard to the formation of an eutectic mixture of aluminum and potassium fluorides that melts at approximately 575 °C. One possible explanation might be that the melting temperature of both aluminum fluoride and potassium fluoride had to be reached before they were miscible. While the melting point of potassium fluoride, 880 °C, was below the maximum temperature, 950 °C, that could be reached with the furnace available, the melting point of the aluminum fluoride, 1040 °C, was not reached. It was the usual case, however, for one salt to be soluble in the liquid of the second, and therefore, the melting point of only one of the components need be reached to form an eutectic mixture. No furnace was available for securing higher temperatures from which atmospheric oxygen could be excluded.

In the first test in which a graphite crucible was used, the graphite was attacked by the fluoride vapor

and the graphite protection tube was cut in half at the level of the mixture in which the tube was inserted.

The use of a crucible machined from an alloy of 92 per cent copper and 8 per cent aluminum effectively eliminated the fluoride corrosion problem but in turn instituted a problem of its own. At temperatures above 350 °C, the copper in the alloy oxidized very rapidly because of atmospheric oxygen, causing copper oxide scale to contaminate the fluoride mixture. Even in its "pasty" or unmelted state, the fluoride took on the blue characteristic color of copper. This difficulty was eliminated in future tests by heating the crucible in a nitrogen atmosphere. While this was satisfactory for laboratory scale investigations, the cost of the nitrogen would make this procedure impractical in commercial processes.

The extremely high melting temperature of the fluoride system even at the eutectic temperature, combined with the corrosive action of the fluoride on most materials seemed to eliminate this system from consideration as an electrolyte for the electro-deposition of aluminum.

Recommendations

On the basis of the experimental work done on the fluoride system for the electrodeposition of aluminum, the following recommendations are made:

A furnace capable of producing temperatures above the melting point of aluminum fluoride, 1040 °C, should be employed to fuse the two components together before testing for the eutectic melting point.

Limitations

The limitations under which the experimental work on a system of aluminum and potassium fluorides was done for the electrodeposition of aluminum were as follows:

The materials used were aluminum fluoride and anhydrous potassium fluoride. The ratios at which melting tests were made were 45 to 55, 42 to 58 and 40 to 60 mol per cent aluminum fluoride to mol per cent potassium fluoride. The maximum temperature to which the mixtures were heated was 950 °C.

Conclusions

An exploratory investigation of the system aluminum fluoride-potassium fluoride as an electrolyte for the electrodeposition of aluminum led to the following conclusions:

1. Mixtures of potassium fluoride and aluminum fluoride in the ratios of 45 to 55, 42 to 58 and 40 to 60 mol per cent aluminum fluoride to mol per cent potassium fluoride melt initially at temperatures above 950 °C.

2. Graphite was attacked by fluoride vapors and therefore, was not suitable as a container for the mixture.

3. An alloy of aluminum and copper consisting of eight per cent aluminum was not appreciably attacked by potassium and aluminum fluorides at 950 °C in an atmosphere of nitrogen.

SULFIDE SYSTEM

Aluminum sulfide has a melting point that is greater than the melting point of aluminum, but the alkali polysulfides melt under 400 °C. Therefore, there was a possibility that a system of alkali polysulfide and aluminum sulfide might melt at a temperature that would be satisfactory for use as an electrolyte for the electrodeposition of aluminum.

Literature Review

There were no literature references to the use of and alkali-aluminum sulfide electrolyte at a temperature below the melting point of aluminum.

Rontgen and Borchers⁽⁶⁴⁾ electrolyzed a mixture of 40 per cent sodium chloride and 60 per cent aluminum sulfide at 700 °C. Elemental aluminum was obtained. This process was claimed to have many economic advantages over the present commercial method of producing aluminum. Khazanov and Belyaev⁽⁴¹⁾ electrolyzed aluminum sulfide in a solvent of 70 per cent sodium chloride and 30 per cent sodium aluminum fluoride at 800 °C. They claim a high current efficiency for the production of elemental aluminum.

Thomas and Rule⁽⁷⁰⁾ studied the composition and melting points of the systems, sodium sulfide-sulfur and potassium sulfide-sulfur. Melting point data and composition relationships are shown in Figure 3 and 4. Table V, page 76, compares the physical data for the two systems studied and gives the values obtained in the investigation. The curves of temperature versus composition show that potassium sulfide and sulfur have an eutectic melting composition corresponding to a molar ratio of 3.5 sulfur to 2.0 potassium. The melting point of this composition was found to be 142 °C. On increasing the sulfur content of the compounds, the melting temperature increased until a fairly stable melting point of approximately 189 °C was found for components with

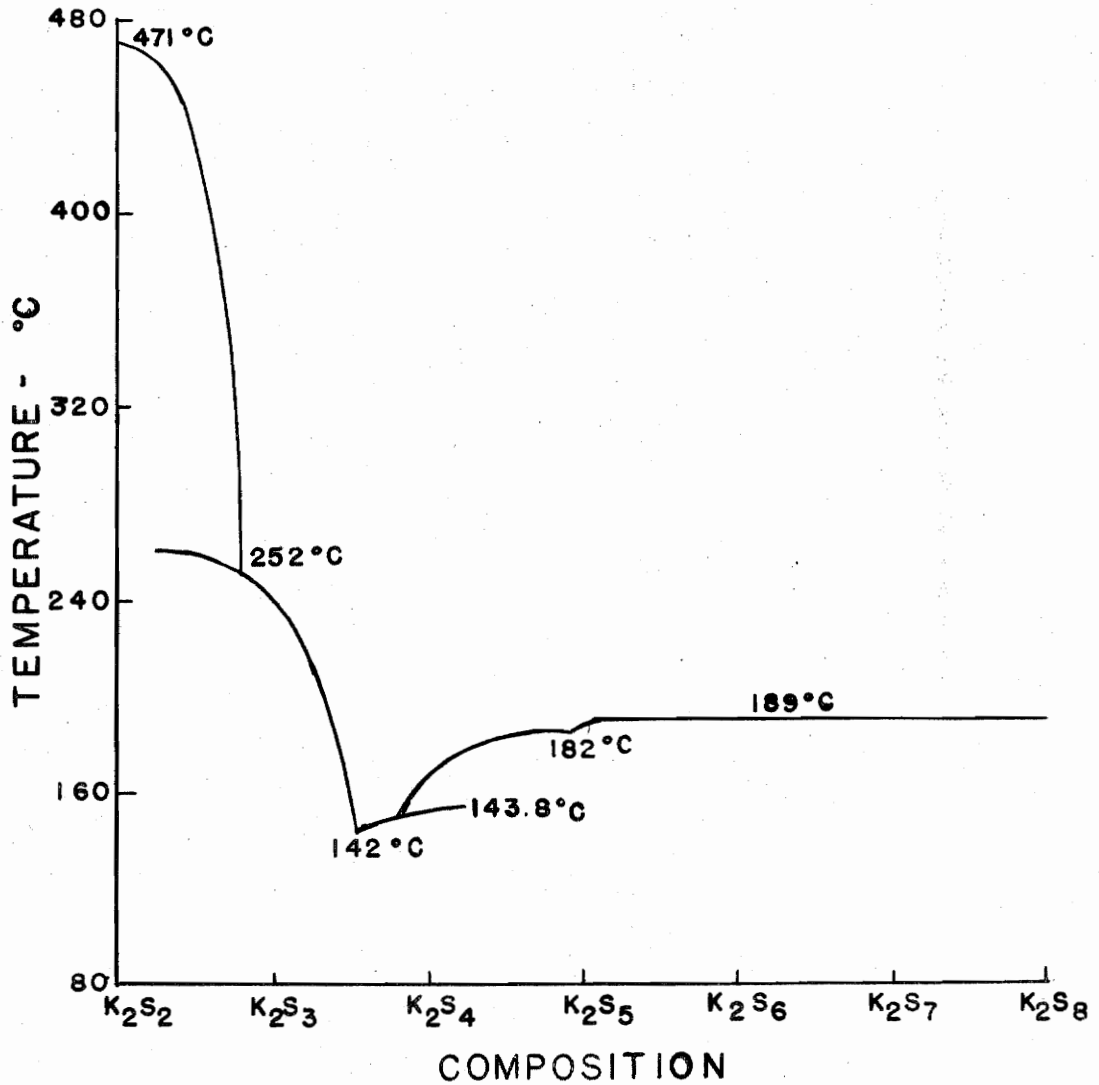


FIGURE 3. FREEZING POINT CURVE FOR THE BINARY SYSTEM POTASSIUM SULFIDE-SULFUR

THOMAS, J.S. AND A. RULE: THE POLYSULFIDES OF ALKALI METALS, *JOUR. AMER. CHEM. SOC.*, III, 1063 (1917).

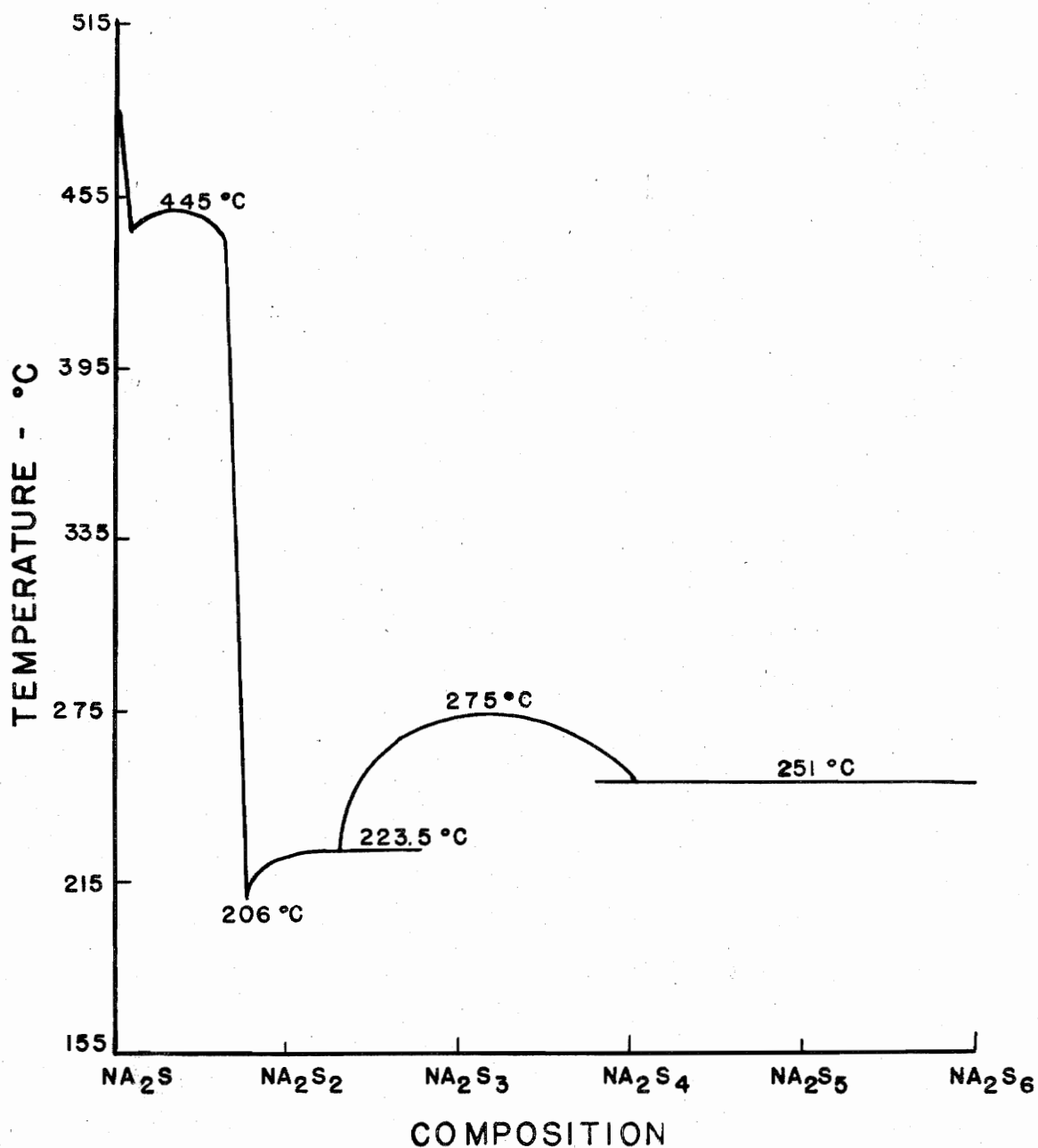


FIGURE 4. FREEZING POINT CURVE FOR THE BINARY SYSTEM SODIUM SULFIDE - SULFUR

THOMAS, J. S. AND A. RULE: THE POLYSULFIDES OF THE ALKALI METALS, JOUR. AMER. CHEM. SOC., 111, 1063 (1917)

the molar ratios of 2.0 potassium to from 5.0 to 8.0 sulfur. Sodium sulfide and sulfur showed a similar relationship, but the melting points for all of the sodium mixtures were found to be about 65 °C higher than those of the corresponding potassium compositions.

Mellor⁽⁴⁹⁾ indicates that sulfur exhibits a direct relationship between viscosity and temperature up to a maximum and then exhibits an inverse relationship. The location of this maximum point will depend upon the treatment that the sulfur has received in the initial melting stage. If the material were fused at a high temperature, the viscosity maximum would be higher than for material that was melted initially at a very low temperature. This "memory" feature made the viscosity of molten sulfur rather unpredictable except that it followed certain trends as shown in Figure 5, which is the viscosity-temperature plot for a typical sample of sulfur. Most substances exhibit inverse viscosity relationships with temperature.

Preliminary experiments by Thomas and Rule⁽⁷⁰⁾ indicated that glass and porcelain were satisfactory containers for molten sulfur and sulfides provided that the temperature did not exceed 400 °C.

TABLE V

Comparison of Melting Points for Potassium and Sodium Polysulfide Compounds

Compound or Eutectic	Melting Temperature	
	Sodium, °C	Potassium, °C
Disulfide	445	471
Di-tri-eutectic	206	250.9
Trisulfide	223.5	252
Tri-tetra eutectic	222.6	-----
Tetrasulfide	275	145.0
Tetra-penta eutectic	247.8	143.4
Pentasulfide	251.8	206.0
Penta-hexa eutectic	-----	182.9
Hexasulfide	-----	189.0
Saturated Solution	249.6	188.1

Thomas, J. S. and A. Rule: The Polysulfides of Alkali Metals, J. Amer. Chem. Soc., 111, 1063 (1917).

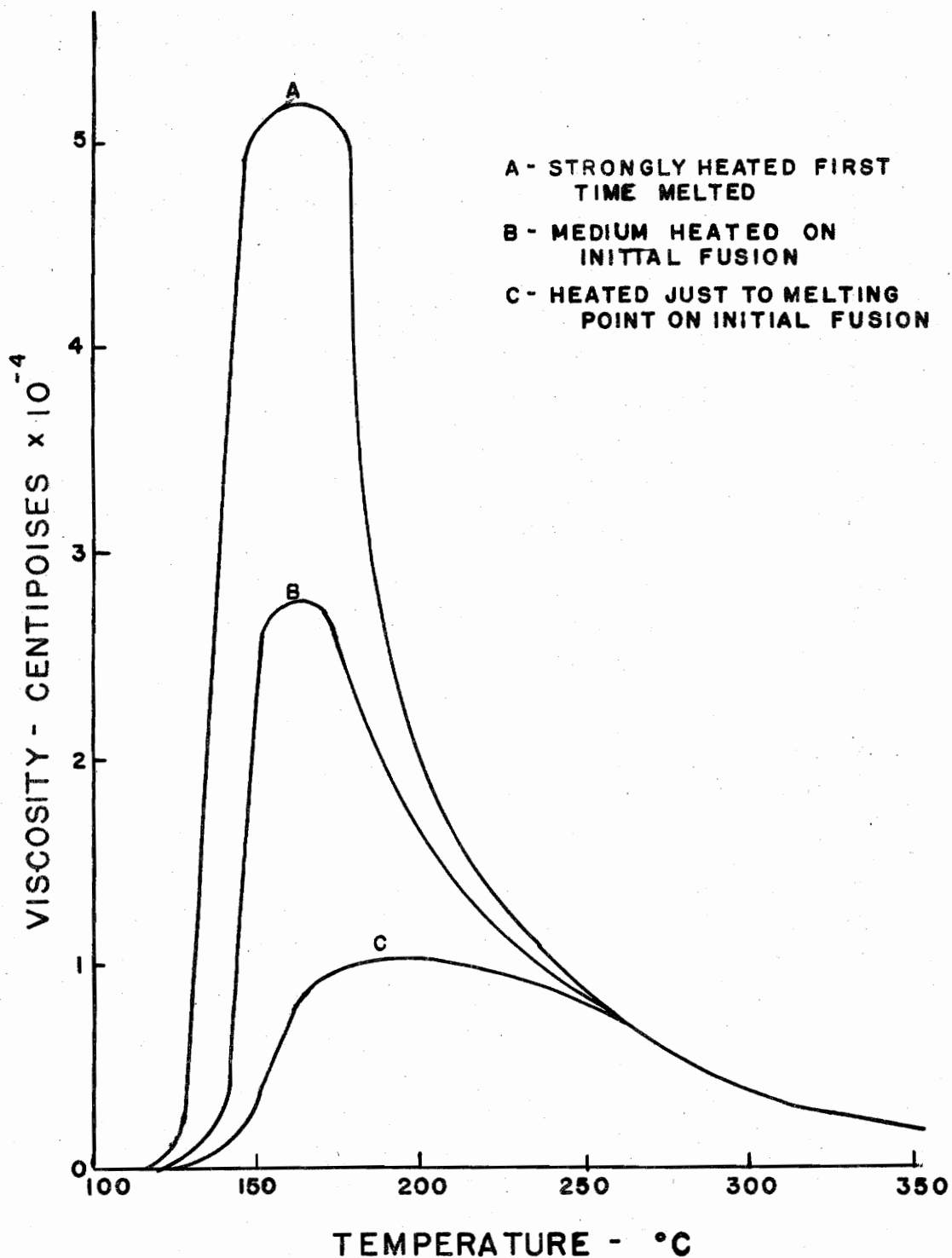


FIGURE 5. EFFECT OF PREVIOUS TREATMENT ON VISCOSITY-TEMPERATURE RELATION OF SULFUR

MELLOR, J. W.: "A COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY," VOL. X, P. 66. LONGMANS GREEN AND SON, LONDON, ENGLAND, 1924.

Materials

The following materials were used in the experimental work on the sulfide system as an electrolyte in the electrodeposition of aluminum:

Acid, Hydrochloric. CP, lot No E407014.

Obtained from General Chemical Co., New York, N. Y. Used in the analysis of aluminum sulfide.

Aluminum Metal. Commercial grade, 0.040 inch thick, sample No 35414040. Manufactured by Reynolds Metal Corp., Louisville, Ky. Used as material for making aluminum electrodes.

Aluminum Wire. Brown and Sharpe gage No 14. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used to connect aluminum anodes to source of electricity.

Ammonium Hydroxide. Concentrated, lot No. E432219. Obtained from General Chemical Co., New York, N. Y. Used in analysis of aluminum sulfide.

Carbon Disulfide. Technical, Code No 1553, lot No G044J. Obtained from General Chemical Co., New York, N. Y. Used to clean electrolyte from electrodes.

Copper Metal. Strip, commercial grade, 1/32 inch thick. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used to connect copper cathodes to source of electricity.

Copper Wire. Brown and Sharpe Gage No 18. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used to connect copper cathodes to source of electricity.

Mercury Metal. CP, lot No 38. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used in nitrogen supply line to indicate flow.

Nitrogen. Dry, oil pumped, cylinder No 224774. Obtained from Air Reduction Sales Co., Richmond, Virginia. Used to create inert atmosphere around electrolyte.

Platinum Metal. CP, 0.015 inch thick. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used for electrodes.

Potassium Sulfide. Fused, lot No 800869. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used as component of electrolyte.

Sulfur. USP. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used as electrolyte component.

Apparatus

The following equipment was used in the experimental work on the electrodeposition of aluminum from a sulfide system:

Ammeter. Direct current, 0 to 1.5, 0 to 3 and 0 to 30 ampere ranges, model No 28, serial No 194093. Manufactured by Weston Electrical Instrument Co., Newark, N. J. Used to measure current in electrolysis circuit.

Balance. Analytical, capacity 500 grams, chainomatic, Manufactured by Seederer-Kohlbusch Co., Inc., Jersey City, N. J. Used to weigh samples of sulfide for analysis.

Balance. Beam, capacity 600 grams, 0.1 gram divisions. Obtained from Eimer and Amend, New York, N. Y. Used for weighing materials for electrolytes.

Beaker. Glass, 250-milliliter, tall, pyrex. Available from Fisher Scientific Co., Pittsburgh, Pa. Used as container for electrolyte.

Crucible. Porcelain, glazed, 100-milliliter. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used in analysis of aluminum sulfide.

Furnace. Crucible, 10.9, 115 volt alternating current, type FD204, serial No 34119. Manufactured by Hoskins Manufacturing Co., Detroit, Mich. Used to heat electrolytes.

Generator. Direct current, 25 volt, model No 30 USN, serial No 79155. Manufactured by Burke Electric Co., Erie, Pa. Used as a source of direct current.

Heater. Autemp, variable temperature, 115 volt alternating current. Manufactured by Eimer and Amend, New York, N. Y. Used to heat samples in analysis of aluminum sulfide.

Milliammeter. Direct current, 0 to 500 milli-ampere range, model No 643, serial No 215493. Manufactured by Weston Electrical Instrument Co., Newark, N. J. Used to measure current in electrolysis circuit.

Motor. Electric, induction, 220 volt, 3 phase, 60 cycle alternating current, 8 ampere, type KH, 3 horsepower, serial No 4207. Manufactured by Mechanical Appliance Corp., Milwaukee, Wisconsin. Used to drive direct current generator.

Rheostat. Variable, 110 volt, alternating current, 11.5 to 5 amperes. Obtained from Eimer and Amend, New York, N. Y. Used to regulate temperature of crucible furnace.

Rheostat. Slide wire, 125 ohm, 3 ampere. Obtained from Phipps and Bird, Inc., Richmond, Va. Used to control voltage and amperage in electrolysis circuit.

Rheostat. Variable, 172 ohms, air cooled, unlabeled. Obtained from War Surplus, U. S. Army. Used as field resistance for generator.

Thermometers. Laboratory, mercury in glass, 0-360 °C. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used for measuring temperature of electrolytes.

Valve. Pressure reduction, Ox-weld type H-r-67, serial No R4656372. Manufactured by V. G. and C. Corp., New York, N. Y. Used to reduce pressure on nitrogen supply line.

Voltmeter. Electronic, model 209A, serial No 6-13232. Manufactured by Hickok Electrical Instrument Corp., Cleveland, Ohio. Used to measure voltage in electrolysis circuit.

Voltmeter. Direct current, 0 to 3, 0 to 7.5 and 0 to 30 volt ranges, model No 489. Manufactured by Weston Electrical Instrument Corp., Newark, N. J. Used to measure voltage in electrolysis circuit.

Methods of Procedure

In the investigation of the electrodeposition of aluminum from a system of molten sulfides, the following procedures were used:

Preparation of Electrolyte. In Figure 3, page 73, it was shown that sulfur and potassium sulfide form an eutectic at approximately 142 °C. The initial step in this investigation was to confirm this melting point. Ten grams of fused potassium sulfide and 13.8 grams of sulfur, corresponding to a 2 to 3.5 molar ratio, were placed in a 100-milliliter beaker which was closed with a cork stopper. A thermometer was inserted through a hole in this stopper as were two glass tubes. The beaker was placed in a furnace and heated slowly. Dry nitrogen gas was passed in and out of the beaker through the glass tubes that were mentioned previously. The nitrogen was used to provide an inert atmosphere and thus prevent oxidation. At intervals of one minute the temperature and time were recorded. Figure 6 shows a diagram of the apparatus used in this determination, whereas Figure 7 presents a photograph of the equipment arranged for electrolysis.

A second test was made using ten grams of potassium sulfide and 20.4 grams of sulfur. This mixture

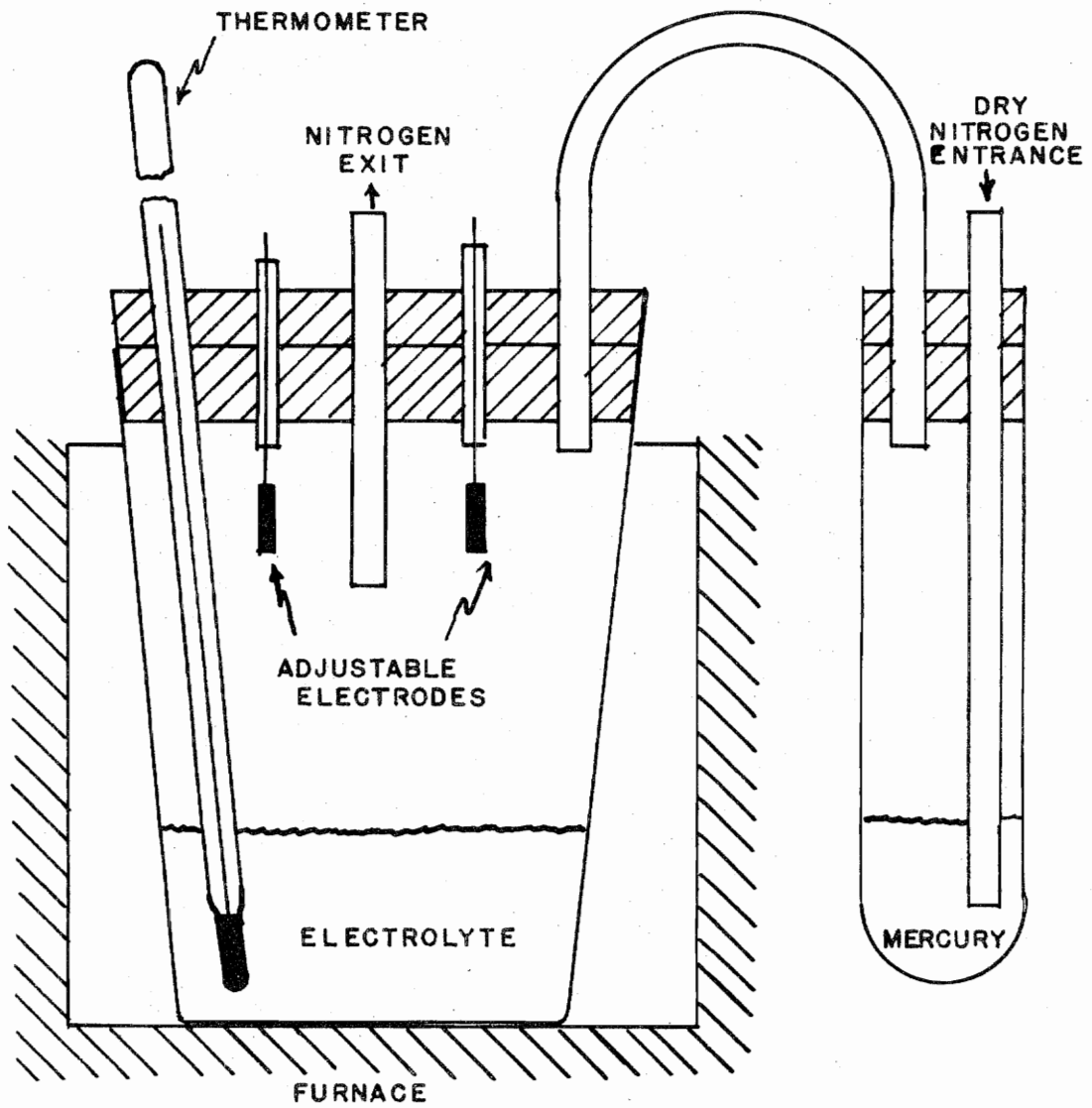


FIGURE 6. DIAGRAM OF CELL FOR ELECTROLYTIC STUDY OF A SYSTEM OF ALUMINUM POLYSULFIDE AND POTASSIUM POLYSULFIDE



FIGURE 7. PHOTOGRAPH OF APPARATUS ARRANGED FOR ELECTROLYTIC STUDY OF ALUMINUM POLYSULFIDE AND POTASSIUM POLYSULFIDE SYSTEM

corresponded to a molar ratio of two potassium to eight sulfur. The procedure as previously mentioned was repeated.

After complete fusion of the sulfide and sulfur, the bath was allowed to cool and additions of finely divided, solid aluminum polysulfide were made. The mixture was then remelted. The initial test included 10 weight per cent aluminum polysulfide which was fused at 300 °C. After 30 minutes, the cell was removed from the furnace and the mixture allowed to cool. The melting point of this system was determined.

Additional mixtures containing 20 and 30 weight per cent aluminum sulfide in a potassium polysulfide solvent were fused and the melting points determined.

Electrodeposition. A study of the conductivity of a mixture of 70 weight per cent K_2S_8 and 30 weight per cent Al_2S_7 was made by electrolyzing the mixture at various potentials and observing the current passed. Platinum electrodes two centimeters square at a distance of three centimeters apart were used.

An investigation to determine if aluminum could be electrodeposited from the polysulfide mixture was the next step in the procedure. An electrolyte containing 70 weight per cent K_2S_8 and 30 weight per cent Al_2S_7

was used. A polished aluminum anode two centimeters square and a copper cathode also two centimeters square were used. A current density of 2.5 amperes per square decimeter was employed. The mixture was electrolyzed for three hours.

The copper cathode was replaced with a platinum strip, two centimeters square, and the electrolysis was repeated for three hours at the same current density.

A third test with an aluminum anode and platinum cathode was made at a current density of 5.0 amperes per square decimeter. The anode was weighed on an analytical balance before beginning the electrolysis. After two and one-half hours the electrodes were removed and carefully cleaned in carbon disulfide and water and reweighed.

Analysis of Aluminum Sulfide. The aluminum polysulfide as received, was of technical grade. A test was performed to determine the number of sulfur molecules present in the compound. Two samples of 0.5 gram each were weighed and placed into 250-milliliter beakers. To each of these beakers 100 milliliters of distilled water and 25 milliliters of concentrated hydrochloric acid were added and the solution allowed to stand overnight. Additional distilled water was added and the solution

boiled for one hour, then filtered and allowed to cool. The mixture was made just alkaline with ammonium hydroxide and the precipitate was filtered through quantitative filter paper. The residue was ignited for two hours, cooled and weighed. It was reignited for one hour and reweighed. The aluminum content of the original sample was calculated directly. The sulfur content was calculated by difference.

Volt-Ampere Curve. The decomposition or volt-ampere curve for 30 weight per cent aluminum polysulfide and 70 weight per cent potassium polysulfide was studied. A cell similar to that used for the electrodeposition, and a circuit such as shown in Figure 2, page 46, were employed. A vacuum-tube voltmeter that could be read to 0.01 volt and an ammeter that could be read to 0.1 ampere were used. Two pieces of platinum foil, two centimeters square, placed three centimeters apart served as the electrodes. The temperature was held constant at 300 °C.

The cell potential was varied in increments of 0.1 volt in the range of 0 to 30 volts, 0.2 volt in the range of 3 to 4 and 6 to 7 volts and 0.4 volt in the range of 4 to 6 volts. Corresponding currents were read and recorded for each voltage. Three sets of data were obtained, the first with increasing potential

the second with decreasing potential and the third with increasing potential. A plot of cell potential versus current was made.

Data and Results

The data and results for the electrodeposition of aluminum from a system of potassium polysulfide and aluminum polysulfide are presented in this section.

Melting Curves. Data for the melting curves of potassium sulfide, sulfur and aluminum polysulfide mixtures are presented in Table VI and these curves are shown in Figure 8. Curves for mixtures of potassium sulfide and sulfur corresponding to a molar ratio of two potassium to three and one-half sulfur, potassium sulfide and sulfur in a ratio of two potassium to eight sulfur, 10 weight per cent aluminum polysulfide and 90 weight per cent potassium polysulfide, 20 weight per cent aluminum polysulfide and 80 weight per cent potassium polysulfide, and 30 weight per cent aluminum polysulfide and 70 weight per cent potassium polysulfide were plotted.

Figure 9 shows the correlation between the amount of aluminum polysulfide and the melting range for the resulting mixture.

The melting ranges obtained for the various mixtures were: 174 to 176 °C for $K_2S_{3.5}$, 187 to 190 °C for K_2S_8 .

TABLE VI

Data for the Melting Point Curves of Mixtures of
Aluminum Sulfide, Potassium Sulfide and Sulfur

Time, minutes	Temperatures				
	$K_2S_{3.5}$ °C	K_2S_8 °C	90% K_2S_8 10% Al_2S_7 °C	80% K_2S_8 20% Al_2S_7 °C	70% K_2S_8 30% Al_2S_7 °C
0	130.0	125.0	150.0	120.0	149.0
1	133.0	130.0	151.0	128.0	157.0
2	136.0	131.0	153.0	128.0	167.0
3	138.5	134.0	154.0	145.0	183.0
4	140.5	138.0	155.0	153.0	191.0
5	143.0	141.0	157.5	161.0	198.0
6	145.3	145.0	159.0	169.0	203.0
7	147.5	148.0	160.0	177.0	215.0
8	149.5	151.0	164.0	183.0	220.0
9	152.0	154.0	166.0	188.0	228.0
10	155.3	159.0	-----	195.0	232.0
11	158.3	161.0	-----	201.0	236.0
12	160.0	163.0	-----	206.0	240.0
13	162.0	165.0	-----	214.0	243.0
14	163.5	167.0	175.0	212.0	246.0
15	165.0	168.0	-----	215.0	250.0
16	167.5	169.0	176.0	210.0	256.0
17	168.5	179.0	-----	211.0	262.0
18	170.0	184.0	180.0	213.0	266.0
19	171.5	185.0	-----	217.0	273.0
20	172.2	187.0	187.0	222.0	276.0
21	173.5	188.0	-----	222.0	278.0
22	174.0	189.0	192.0	233.0	283.0
23	175.0	189.0	-----	240.0	-----
24	175.0	190.0	197.0	245.0	-----
25	175.3	189.0	-----	251.0	-----
26	176.5	189.0	195.0	255.0	-----
27	177.5	189.0	-----	259.0	-----
28	178.0	190.0	198.0	263.0	-----
29	179.0	191.0	-----	266.0	-----
30	179.5	191.5	198.0	269.0	-----
31	-----	-----	-----	272.0	-----
32	-----	-----	200.0	274.0	-----
33	-----	-----	-----	277.0	-----
34	-----	-----	202.0	281.0	-----
35	-----	-----	-----	284.0	-----
36	-----	-----	204.0	-----	-----

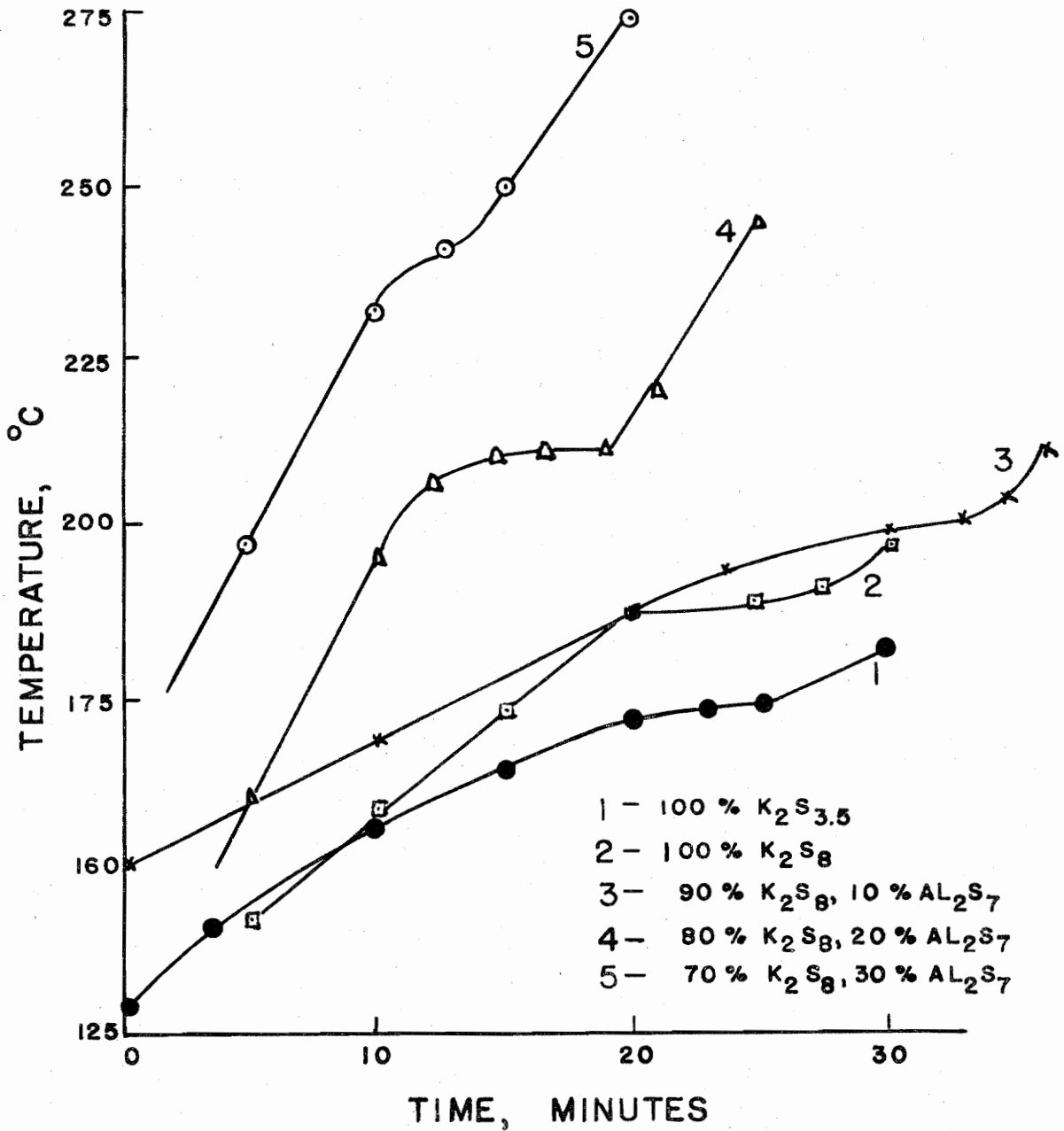


FIGURE 8. HEATING CURVES FOR VARIOUS MIXTURES OF ALUMINUM POLYSULFIDE, POTASSIUM SULFIDE AND SULFUR

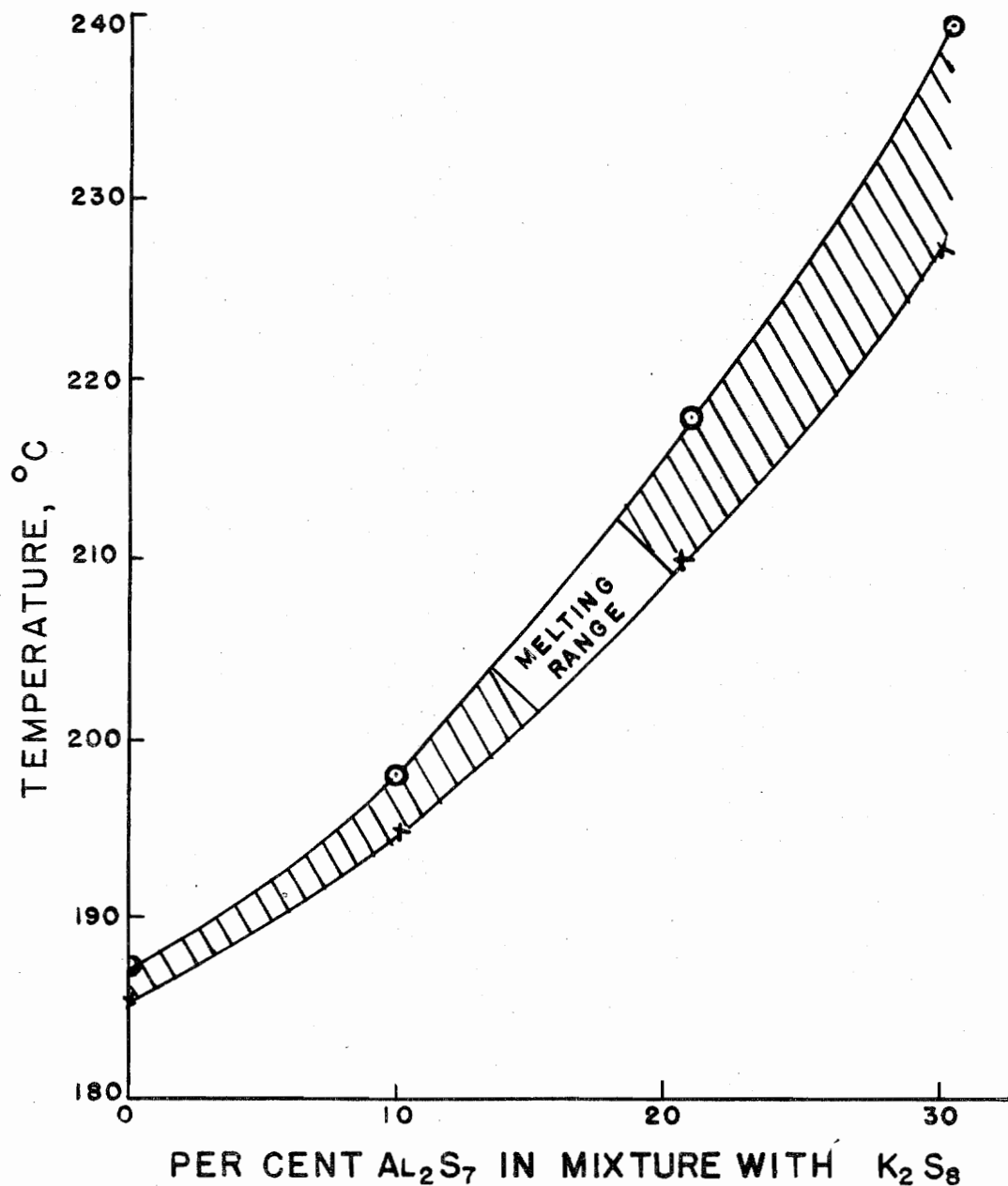


FIGURE 9. MELTING RANGE OF MIXTURES OF ALUMINUM POLYSULFIDE AND POTASSIUM POLYSULFIDE.

195 to 198 °C for 10 per cent Al_2S_7 and 90 per cent K_2S_8 , 210 to 218 °C for 20 per cent Al_2S_7 and 80 per cent K_2S_8 , and 228 to 240 °C for 30 per cent Al_2S_7 and 70 per cent K_2S_8 .

Electrodeposition. Three tests of the electrolysis of aluminum polysulfide bath failed to produce a trace of aluminum. In the test using a copper cathode, the copper was severely attacked by the electrolyte. The three tests made were, (a) aluminum anode-copper cathode in 30 per cent aluminum polysulfide and 70 per cent potassium polysulfide as electrolyte for three hours at a current density of 2.5 amperes per square decimeter, (b) aluminum anode-platinum cathode in same electrolyte at a current density of 5.0 amperes per square decimeter for two and one-half hours, and (c) aluminum anode-platinum cathode in same electrolyte at current density of 2.5 amperes per square decimeter for three hours.

Voltage-Current Curve. The voltage-current curve for 30 weight per cent aluminum polysulfide and 70 weight per cent potassium polysulfide at 300 °C is given in Figure 10, and the data for this curve are presented in Table VII.

TABLE VII

Data for Voltage-Current Curve for 30 per cent Aluminum Polysulfide and 70 per cent Potassium Polysulfide at a Temperature of 300 °C, Using Platinum Electrodes

Potential, volts	Current, amps	Potential, volts	Current, amps	Potential, volts	Current, amps
0.05	0.005	2.00	0.190	5.60	0.430
0.10	0.012	2.10	0.200	5.80	0.425
0.20	0.025	2.20	0.210	6.00	0.410
0.30	0.030	2.30	0.220	6.20	0.415
0.42	0.040	2.40	0.225	6.40	0.450
0.50	0.050	2.50	0.230	6.60	0.470
0.60	0.067	2.60	0.240	6.80	0.625
0.70	0.075	2.70	0.250	7.00	0.700
0.82	0.080	2.80	0.260	7.50	0.755
0.91	0.090	2.90	0.265	7.00	0.695
1.00	0.120	3.00	0.275	6.75	0.580
1.10	0.120	3.20	0.285	6.50	0.465
1.20	0.145	3.40	0.310	6.25	0.430
1.30	0.145	3.60	0.325	6.00	0.400
1.40	0.148	3.80	0.335	5.75	0.425
1.50	0.150	4.00	0.350	5.25	0.440
1.60	0.155	4.40	0.380	5.00	0.430
1.70	0.160	4.80	0.420	4.75	0.410
1.80	0.165	5.20	0.440	4.50	0.400
1.90	0.170	5.40	0.440	4.25	0.360

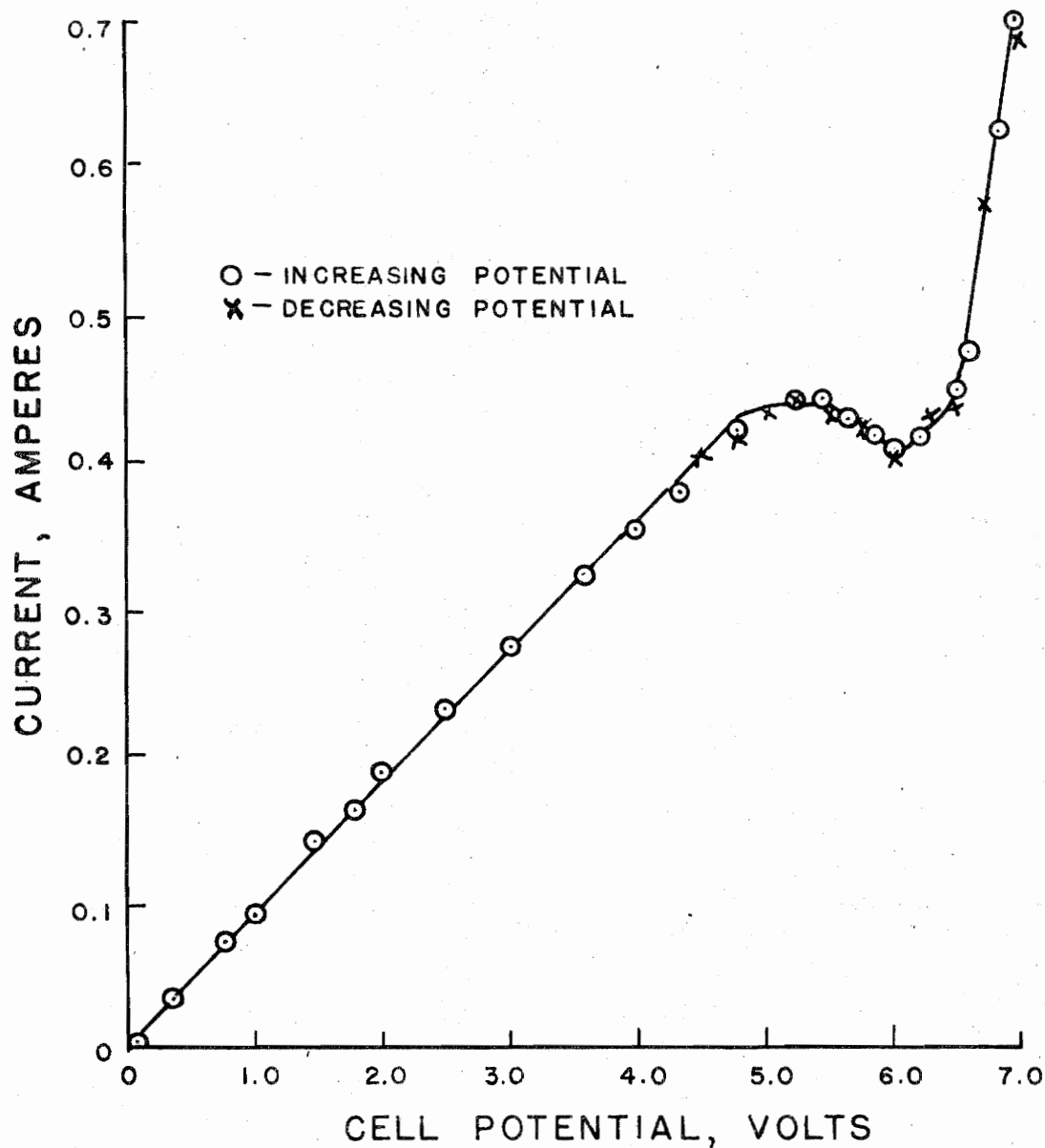


FIGURE 10. CURRENT-VOLTAGE CURVE FOR 30 WEIGHT PER CENT ALUMINUM POLYSULFIDE AND 70 WEIGHT PER CENT POTASSIUM POLYSULFIDE AT 300°C, USING PLATINUM ELECTRODES

Discussion of Results

The following discussion applies to the electro-deposition of aluminum and related tests from a system of aluminum polysulfide and potassium polysulfide:

Electrolyte. Observation of the electrolyte showed that the mixture melted to a smooth, brown liquid, but did not freeze at the same temperature. Supercooling took place to a remarkable extent, confirming the observations of Thomas and Rule⁽⁷⁰⁾ with the potassium polysulfides. On occasion the mixture would solidify in what may have been an amorphous state which, upon standing for several days, suddenly crystallized with a large increase in volume. This increase was often so sudden that the container was shattered.

As may be seen from the melting curves, Figure 8, page 91, there was no sharp melting point, but rather there was what has been called a melting range. The absence of a definite melting point is frequently found when studying mixtures⁽⁸⁷⁾. Also, uneven heating of the material because of the low thermal conductivity of the sulfides might account for the lack of a sharp melting point. Another factor that might have caused the melting point to be obscured was that these mixtures were constantly changing in composition from loss of sulfur as a vapor.

Since a sharp melting point could not be obtained and since the temperature desired for this work was not necessarily the melting point but the point at which the viscosity was satisfactory for electrodeposition, a melting range was selected based on the melting curves and upon visual observation of the melt. The viscosity of the melt at any temperature within this range would be satisfactory for the use of the material as an electrolyte.

During the heating of the electrolyte, sulfur fumes were evolved. The higher the temperature, the more sulfur lost. This fact helped to explain the discrepancy between the literature and actual observations for the formation of an eutectic between sulfur and potassium sulfide at 142°C . If the literature and Figure 3, page 75, be consulted, it may be seen that a very small loss in sulfur would cause a relatively large increase in temperature. This would not be true with the mixtures that contained greater than five sulfur molecules. By starting the addition of aluminum polysulfide to the mixture of K_2S_8 it was unlikely that sufficient sulfur would be lost to cause any appreciable change in the melting temperature.

One big difficulty with the electrolyte was the necessity of keeping an inert atmosphere present at all times. Oxidation occurred very rapidly at the temperatures involved. Nitrogen was very satisfactory for providing this atmosphere.

The analysis of the aluminum polysulfide used in the electrolyte indicated a composition corresponding to two mols of aluminum and seven mols of sulfur. It must be remembered, however, that polysulfide compounds are not consistent throughout the supply and this formula can be considered only as an average of the actual composition.

Decomposition Potential Curve. From electrochemical theory(88) there are three possible types of electrode reactions. These three types of electrode reactions can be shown by current-voltage, also called decomposition voltage, curves. Two of these curves, when plotted, appear as straight lines, while the third takes the form of an elongated "S". An electrolysis in which the anode is dissolving in the electrolyte and metal is correspondingly being deposited at the cathode will give a straight line through the origin. This same linear relationship occurs when there is no dissolution or deposition of metal at either electrode,

but when complimentary oxidation and reduction reactions are occurring at the anode and cathode, respectively. A broken current-voltage curve occurs when reactions are occurring at the cathode and anode that are not complimentary of each other. In this case a decomposition potential for the system may be obtained. In addition to these three fundamental types of curves, there are combinations of the three curves that are caused by combinations of the reactions.

In the electrolysis of the sulfide system a straight line was obtained for the first portion of the curve to approximately 5.2 volts, a distinct break was found between 5.2 and 6.2 volts and a straight line was found from 6.2 to 7.0 volts. Since there was no loss or gain in weight of the platinum electrodes, the reactions occurring to cause the lower straight line portion must have been oxidation and reduction of the electrolyte. The actual reaction would be difficult to determine since so little is known about polymerization of sulfides, but an example of the reaction that might occur is:

At anode:



At cathode:



The break that occurs in the voltage-current curve at 5.2 volts may be postulated as a change in the electrode reactions. When the cell potential is increased to 5.2 volts, the electrode potentials reach a value which permits stable formation of another compound, at the electrode surface. The dip in the curve may be accounted for by assuming that in this region the new reaction conditions are becoming stabilized. When the reaction is occurring at every point on the electrode, the plot of current versus voltage resumes as a straight line.

This phenomenon has been observed by Littler and Tarter(89), who have discussed reasons for a change in electrode reaction in electrolysis of copper from a hydrochloric acid solution. In their work, it was shown that there were two tendencies for reaction at the anode, as illustrated by the following equations:



At low current densities, the first tendency predominated, suppressing the second, and therefore the voltage-current curve appeared as a straight line thru the origin.

As the current density was increased, however, the second tendency became more important, which resulted in a dip in the voltage-current curve. When the current density

was increased further, the second tendency became predominate, suppressing the first and giving a straight line on the current-voltage plot. When the current density was decreased, exactly the reverse occurred, and the points on the voltage-current curve could be retraced. Over the range of this experiment, the cathode reaction was constant.

The electrolysis of the sulfide system cannot be an exact analogy to the copper in hydrochloric acid electrolysis, since it was shown that no metal was dissolving or plating out at the electrodes. Therefore, it was believed that the two tendencies might have been both due to oxidation or reduction of the electrolyte at either cathode or anode. It is not possible to identify the reactions that were occurring in the sulfide system, since so little is known about the polysulfides.

Recommendations

On the basis of the data obtained in the investigation of a system of potassium polysulfide and aluminum polysulfide as electrolyte for the deposition of aluminum, the following recommendations are made:

The addition of some suitable carrier salt, such as sodium chloride, to the mixture of aluminum polysulfide

and potassium polysulfide should be investigated to determine if this salt would increase the conductivity and act as a flux in the decomposition of the aluminum polysulfide to give elemental aluminum.

Aluminum polysulfide should be used in conjunction with other inorganic salts to try to find a system that would have a low melting point and not be sensitive to oxidation. Some salts that might be tried, include chlorides, carbonates, phosphates and oxides of the alkali metals.

Limitations

The limitations of this investigation of the electrodeposition of aluminum from a system of aluminum polysulfide and potassium polysulfide were as follows:

Electrodeposition was attempted from a system of 30 weight per cent aluminum polysulfide and 70 weight per cent potassium polysulfide at 300 °C. Current densities of 2.5 and 5.0 amperes per square decimeter were used. Time of electrolysis was from 2.5 to 3.0 hours, and the electrodes were aluminum for the anode and copper and platinum for the cathode. The distance between these electrodes was from 3.0 to 3.5 centimeters.

Conclusions

An exploratory investigation of system of aluminum polysulfide and potassium polysulfide as an electrolyte for the electrodeposition of aluminum at 300 °C led to the following conclusions:

1. Aluminum polysulfide is soluble in molten potassium polysulfide.
2. Electrodeposition from a system of aluminum polysulfide and potassium polysulfide must be carried on in an inert atmosphere to prevent oxidation.
3. Mixtures of aluminum polysulfide and potassium polysulfide have a suitable viscosity for use as electrolytes at 195 to 198 °C for 10 weight per cent aluminum polysulfide and 90 weight per cent potassium polysulfide, 210 to 218 °C for 20 weight per cent aluminum polysulfide and 80 weight per cent potassium polysulfide, and 228 to 240 °C for 30 weight per cent aluminum polysulfide and 70 weight per cent potassium polysulfide.
4. No aluminum was obtained at a platinum cathode after electrolysis of 30 weight per cent Al_2S_7 and 70 weight per cent K_2S_8 at a current density of 2.5 and 3.0 amperes per square decimeter for three hours.

FLUOBORATE SYSTEM

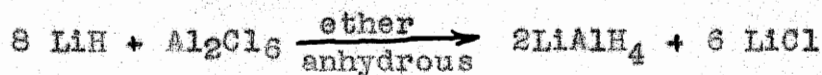
Systems containing aluminum fluoborate were considered as electrolytes for the electrodeposition of aluminum. No experimental work was carried out on these systems, but the following information was available from the literature.

Literature Review

Preparation of the chemicals involved and some information as to the reactions of these systems during electrolysis are presented in this literature review.

Preparation of Aluminum Fluoborate. Berzelius⁽⁶⁾ prepared aluminum fluoborate by reacting freshly precipitated aluminum hydroxide with fluoboric acid. The resulting solution was evaporated to dryness slowly. The derived compound contained water of crystallization to an unknown degree. Upon heating, the fluoborate decomposed, giving off water and fluoboric acid and leaving a residue of aluminum borate. Berzelius⁽⁷⁾ was unable to produce anhydrous aluminum fluoborate.

In connection with work on boron hydrides, Bauer⁽⁴⁾ mentions a method for preparing anhydrous aluminum fluoborate. This reaction proceeds as follows:



Discussion of Results

In work done by Chao⁽¹³⁾ it has been found that in a borate electrolyte there was no aluminum recovered at the cathode. Instead, the aluminum reduced the boron to give a cathode coating assumed to be a boride of aluminum. It was believed that a similar reaction would occur with the fluoborate.

The preparation of anhydrous aluminum fluoborate was not considered to be a simple process, since the resulting products in the synthesis contained a mixture of aluminum and lithium fluoborates. The separation of these compounds would be difficult. There was a possibility that these compounds need not be separated, but there was no information available on the melting range of mixtures of these two components.

Further work was postponed on the fluoborate system since time did not permit obtaining the supplies necessary for the preparation of the aluminum fluoborate.

Recommendations

The following recommendations for further work on the electrodeposition of aluminum from a system of fluoborates are based on study of the literature available:

An attempt should be made to synthesize anhydrous aluminum fluoborate as described in the literature.

If the necessary chemicals can be prepared the fluoborate system should be studied to determine the type of electrochemical reactions occurring at the electrodes.

Limitations

The work on the fluoborate system for the electrodeposition of aluminum was limited to study of the literature available.

Conclusions

Since no experimental work was performed on the electrodeposition of aluminum from a fluoborate system, no quantitative conclusions can be drawn.

FORMATE SYSTEM

A molten salt system containing aluminum formate was considered as an electrolyte for the electrodeposition of aluminum. This system was investigated by literature review only.

Literature Review

Aluminum formates exist in two known forms, normal and basic. Both forms are stable and may be prepared easily⁽⁷⁰⁾.

Basic aluminum formate may be prepared by dissolving freshly precipitated aluminum hydroxide in formic acid and evaporating until a scum appears. Upon cooling, the formate precipitates from the solution as a white solid⁽⁷⁹⁾.

Normal aluminum formate is a by-product of the basic variety. This compound may be synthesized by evaporating basic aluminum formate in an excess of formic acid⁽⁷⁹⁾.

Farben⁽²³⁾ has secured a patent for preparing aluminum formate by heating clay to glowing below 1000 °C with twenty to sixty per cent formic acid. The formula of the salt that was derived by this method was not given.

No reference to the use of aluminum formate as an electrolyte in any electrolysis reaction appears in the literature.

Discussion of Results

Since no quantitative data from the work on the formate system was obtained, this discussion is based on the data available in the literature relative to this compound.

Both forms of aluminum formate, basic and normal, contain water of hydration. No information as to the behavior of this water during an electrolysis is available, but it was believed that the water would be removed only when the formate decomposed to aluminum oxide. Since water in hydrates decomposes to give hydrogen at the cathode, work with a compound that was stable only with water of hydration seemed impractical.

Assuming that the water was driven off when the compound was heated and aluminum oxide was left, the system would be useless as an electrolyte for the electrodeposition of aluminum because of the high melting point and poor conductivity of aluminum oxide.

Because of these undesirable factors, the aluminum formate system was eliminated from consideration as an electrolyte for the electrodeposition of aluminum.

Recommendations

There are no recommendations for the use of aluminum formate as an electrolyte for the electro-deposition of aluminum.

Limitations

The work on the formate system was limited by the availability and reliability of the literature from which the information for this work was gathered.

Conclusions

Based on the literature review made on the use of aluminum formate as an electrolyte for the electro-deposition of aluminum the following conclusions were made:

Aluminum formate is not stable upon loss of the water of hydration by heating.

Aluminum formate would not be suitable as an electrolyte for the electrodeposition of aluminum because of the presence of water of hydration.

THIOCYANATE SYSTEM

Aluminum thiocyanate was considered as an electrolyte for the deposition of aluminum.

Literature Review

The literature was reviewed for material relative to the preparation and properties of aluminum thiocyanate.

Preparation of Aluminum Thiocyanate. Parrett⁽⁵⁶⁾ indicates that aluminum thiocyanate may be prepared by the reaction of aluminum oxide with thiocyanic acid. No other references to this compound were found in the literature.

Preparation of Thiocyanic Acid. Since neither aluminum thiocyanate nor thiocyanic acid were commercially available, the literature was reviewed for methods of preparation of the acid so that it might be used in the preparation of the aluminum compound.

Brooker and Keyes⁽⁹⁾ prepared thiocyanic acid by distilling a mixture of a metal thiocyanate and dilute sulfuric acid under reduced pressure. They also produced the acid by passing dry hydrogen sulfide through mercuric thiocyanate. Fischer and Schiebe⁽²⁸⁾ mentioned

a third method of preparation that consisted of direct mixing of potassium thiocyanate and potassium hydrogen sulfate in a stream of hydrogen gas at about forty millimeters pressure.

Properties of Thiocyanic Acid. Thiocyanic acid is a colorless volatile liquid that melts at about 5 °C and rapidly decomposes at room temperatures. It is only slightly poisonous.

Discussion of Results

The thiocyanate system seemed to show considerable promise, since the literature⁽⁵⁶⁾ indicated that the compound was nondeliquescent, which was an unusual and desirable property of an aluminum compound. The system was abandoned for the present, however, because time did not permit preparing the aluminum thiocyanate.

Recommendations

Based on the data available in the literature the following recommendations are made for future work on the thiocyanate system for the electrodeposition of aluminum:

An attempt should be made to synthesize aluminum thiocyanate by the methods given in the literature and the properties of this compound should be studied for possibility of using this material for the electro-deposition of aluminum.

Limitations

The investigation of the thiocyanate system for the electrodeposition of aluminum was limited to study of the literature available.

Conclusions

No quantitative conclusions can be drawn since no experimental work was done on the electrodeposition of aluminum from a thiocyanate system.

IV. DISCUSSION OF ALL SYSTEMS

Since 1808 work has been done on the electro-deposition of aluminum and to date no method that provides a corrosion resistant coating has been found. Much of the past research, however, has been aimed at the recovery of elemental aluminum rather than the obtaining of an aluminum coating on other surfaces.

Aluminum provides adequate protection from most types of atmospheric corrosion, is relatively inexpensive and is potentially one of the most plentiful of metals. Aluminum also has the ability to form surface alloys with other metals when heated to high temperatures, decreasing the formation of scale on the basic metal. Jet engines and other equipment that operate at high temperatures require protection such as provided by surface alloys. If a suitable method for coating with aluminum were available, development of surface alloys would be furthered, and one more step would be taken in the elimination of corrosion.

Some types of aluminum coating, such as sputtering, painting, spraying and thermal evaporation have been developed, but none of these are suitable for use in alloy formation or completely fill the need for formation

of a corrosion resistant surface. Electrodeposition, in general, provides surfaces that are more uniform, compact and adherent than do any of the other methods of coating. Also, electrodeposits may be applied in an infinite series of thickness. It is difficult to compare the various methods of applying surfaces, since each has advantages for some applications. Electrodeposition, however, is probably the most versatile. It is suitable for providing decorative coatings, for providing corrosion resistant coatings and for replacement of worn surfaces. The equipment required for electrodeposition is not as elaborate as that needed for sputtering or thermal evaporation and would therefore, probably be less expensive. Economic factors, other than equipment cost, that enter into the selection of a method of applying a metal coating are durability, maintenance cost and cost of replacement. Aluminum electrodeposition, when available, will probably provide the best and most economical method of coating.

There seem to be several reasons for the difficulty encountered in plating aluminum onto other metals. The affinity of aluminum for oxygen may result in the formation of a nonconductive oxide layer on anodes,

often stopping the electrolysis completely. Secondly, aqueous solutions probably cannot be used as electrolytes for the electrodeposition of aluminum, since water has a lower decomposition potential than the potential required to exceed the overvoltage of aluminum.

Consequently, the water decomposes first, releasing hydrogen at the cathode and interfering with the deposition of aluminum, if not eliminating it entirely. Thirdly, aluminum compounds, in many cases, are susceptible to hydrolysis in the presence of atmospheric moisture. This hydrolysis introduces water as a contaminate to the electrolyte, which upon electrolysis may decompose and promote passivity of the anode.

When every operation must be carried out in an inert atmosphere, the usefulness of a method for electrodeposition of aluminum would be seriously limited because of the excessive expense and production problems thereby introduced.

Since electrolysis of aqueous solutions seems impractical, two other choices for methods of electrodeposition of aluminum are available; electrolysis of fused salts or of liquid organic solutions.

Considerable work has been done by other investigators attempting to electrodeposit aluminum, principally with the aluminum and alkali halide fused salts.

These halide baths, while they were suitable for producing dendritic, loosely adherent aluminum on the cathode, were undesirable because of sensitivity to moisture, passivity, anode effect and low efficiency.

When comparing the work of previous investigators one fact that stands out is the formation of dendritic aluminum from every system from which the metal has ever been deposited. This phenomenon seems to indicate that the solution of this problem in electrodeposition might not be the discovery of a new system, but rather the development of a new technique that would smooth out the aluminum coating. The usual method for accomplishing this is to make additions of some inert substance that seems to prevent the formation of large metal crystals, but consideration should be given to procedures such as, periodic reversal of the current and superposition of alternating current on direct current to accomplish this aim. No work has been done with the addition agents in aluminum electrolysis, since no electrolyte has been found that did not have serious limitations.

In the investigations undertaken in this thesis, the most promising system seemed to be the thiocyanate. Although no experimental work was carried out on this

system, the literature indicated that the aluminum thiocyanate was nondeliquescent, which was an unusual and desirable property for an aluminum compound. While the difficulties encountered in the synthesis of the chemicals for this system may be great, the investigation of the thiocyanates may provide a solution to the problem of electrodeposition of aluminum.

Work on the sulfide system was seriously hampered by the necessity of working in an inert atmosphere with the sulfide electrolyte. Unless a system can be found, in which the mixture is not sensitive to oxygen, aluminum sulfide will probably not be suitable for commercial applications as a constituent of a plating bath. The further use of the polysulfides as solvents for aluminum sulfide is discouraged, since the complexity of these compounds introduces many variables into the electrolysis.

The fluoborate and cyanide systems were eliminated from future consideration since both systems were limited by sensitivity to decomposition in the presence of moisture. In fact, aluminum cyanide is probably so sensitive to decomposition that it has never been isolated.

The fluoride system was eliminated from study because of its extremely high melting point. Aluminum fluoride is not susceptible to moisture and by virtue of this property might be worthy of future consideration. It must be remembered, however, that molten fluorides are extremely corrosive to many substances.

In summary, the electrodeposition of aluminum will be solved when a system that is insensitive to moisture and oxidation is found or when a new procedure for electrolysis is developed that will smooth out and strengthen deposits of aluminum that may now be produced from fused chloride electrolytes and certain organic liquid solutions.

V. CONCLUSIONS

An exploratory investigation of the possibility of using the inorganic molten salt systems aluminum chloride-alkali chloride, aluminum sulfide-alkali sulfide, aluminum fluoride-alkali fluoride, aluminum fluoborate, aluminum formate, aluminum thiocyanide and aluminum cyanide as electrolytes for the electrodeposition of aluminum at temperatures below the melting point of aluminum, 660 °C, led to the following qualitative conclusions. Quantitative conclusions are listed with the discussion for each system.

1. Poorly adherent, crystalline aluminum may be deposited on a copper surface from an electrolyte of aluminum chloride, sodium chloride and potassium chloride.

2. A system of potassium and aluminum fluorides could not be found that melted below the melting point of aluminum.

3. No aluminum was obtained from the electrolysis of a system of aluminum and potassium sulfides.

4. Fluoborate and formate systems could not be found in the anhydrous state.

5. In a literature review, aluminum thiocyanate showed promise as an electrolyte for the deposition of aluminum.

6. A system of cyanides proved to be impractical because aluminum cyanide could not be synthesized and because of the toxicity of the chemicals involved.

VI. SUMMARY

In order that further steps could be taken in the attempt to defeat corrosion, it was desirable to find a method for electrodepositing aluminum on other metal surfaces.

To meet this need, an investigation was conducted to attempt to find an electrolyte that would be suitable from the field of molten inorganic aluminum and alkali salts.

The principal work by other investigators on the electrodeposition of aluminum has been with aqueous solutions which have proved unusable and with fused alkali-aluminum halide mixtures that have produced crystalline, poorly adherent aluminum coatings.

In the present investigation, seven inorganic, fused salt systems were studied. These systems were chloride, fluoride, cyanide, sulfide, thiocyanate, formate and fluoborate. No electrolyte was found that gave a compact, adherent aluminum deposit.

Investigation of a fused electrolyte containing 66 mol per cent aluminum chloride, 20 mol per cent sodium chloride and 14 mol per cent potassium chloride at 160 °C produced poorly adherent, dendritic aluminum deposits on a copper cathode at a current density of

0.833 ampere per square decimeter. This coating formed a surface alloy between aluminum and copper when electroplated pieces of copper were heat treated in an electric furnace at 550 °C for 45 minutes and at 1000 °C for one minute. The piece treated at 1000 °C seemed to have deeper penetration of the aluminum.

Ratios of 45 to 55, 42 to 58 and 40 to 60 mol per cent aluminum fluoride to potassium fluoride failed to produce a composition that would have a low viscosity at a temperature below the melting point of aluminum, 660 °C.

A fused bath of 70 weight per cent potassium sulfide, K_2S_8 , and 30 weight per cent aluminum sulfide, Al_2S_7 , did not yield aluminum after electrolysis at current densities of 2.5 and 5.0 amperes per square decimeter for three hours at a temperature of 300 °C and using platinum electrodes. A plot of cell potential versus current for the sulfide system indicated oxidation and reduction of the electrolyte with ultimate passivity of the anode.

Systems of cyanide, fluoborate and formate proved to be impractical because of the difficulty in handling or obtaining the chemicals involved.

Aluminum thiocyanate showed promise as an electrolyte but limitation of time prevented experimental work on this system.

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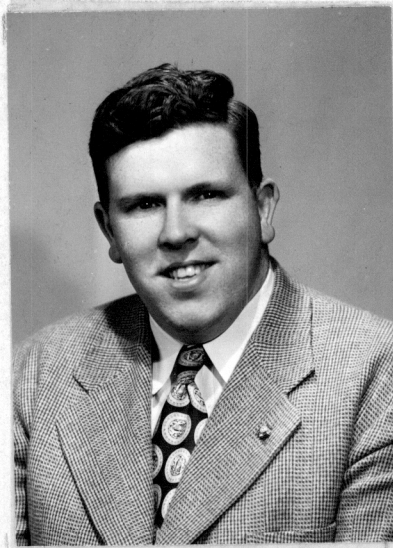
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IX. VITA



Robert Lee Scott was born in Roanoke, Virginia on October 15, 1926. His early education was obtained in the public school system of that city, graduating from Jefferson Senior High School in February, 1945.

Immediately after graduation, he served two years in the United States Army. Fourteen months of this time was spent overseas in the Philippines and Korea. He was discharged in December, 1946 as a Staff Sergeant.

In February, 1947 he started his college education when he enrolled as a pre-engineering freshman at

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He was awarded a fellowship sponsored by the V. P. I. Research Foundation for research in electrochemistry in June, 1950. While holding this fellowship, work was pursued leading to a Master of Science degree in Chemical Engineering in June, 1951.

The author is a member and past president of Alpha Phi Omega, national service fraternity; associate member of the Society of Sigma Xi; member of the V. P. I. Science Club; and member of Phi Lambda Upsilon, national chemistry and chemical engineering honor society.

A handwritten signature in cursive script, appearing to read "Robert A. Heath". The signature is written in dark ink and is positioned in the lower right quadrant of the page.