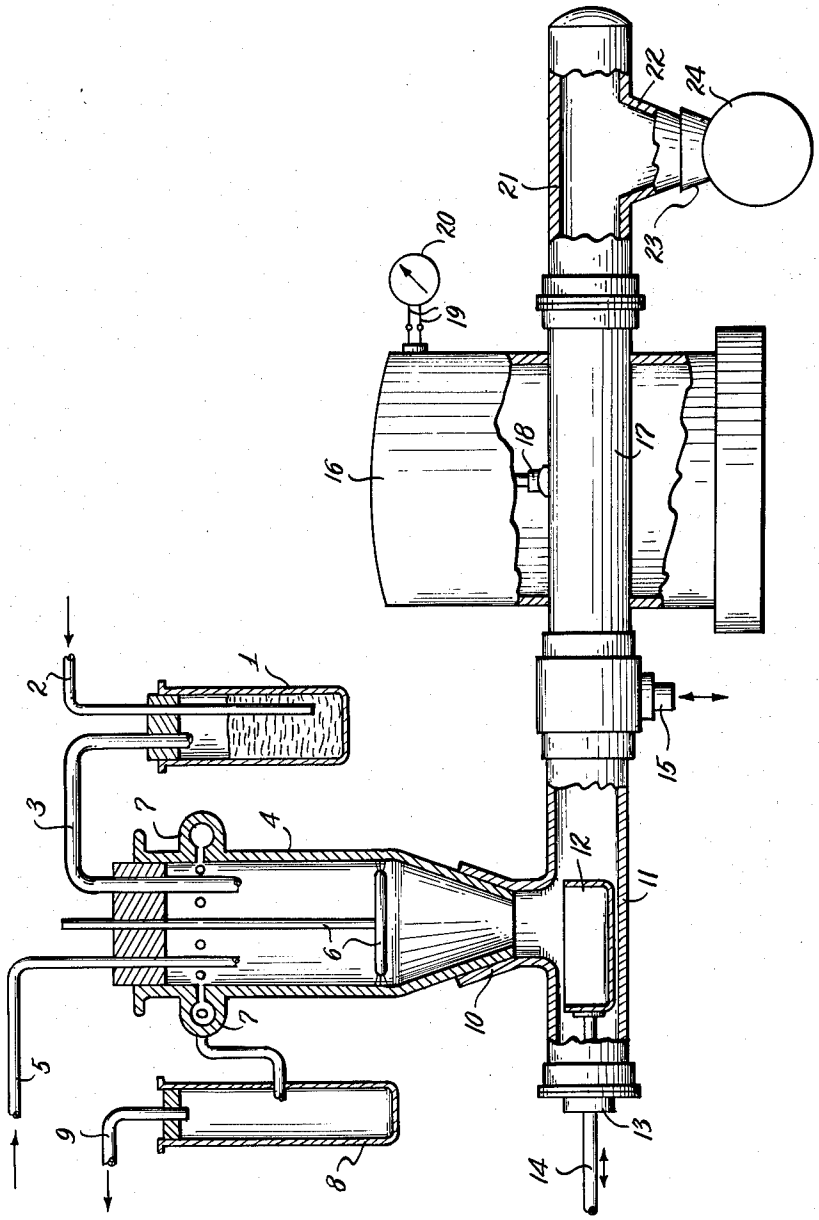
June 21, 1966 B. BERGHAUS ET AL 3,257,296

PROCESS FOR OBTAINING METALS BY FUSION ELECTROLYSIS

Filed May 8, 1964



INVENTORS

BERNHARD BERGHAUS
MARIE STAECHE

BY Bacon & Thomas

ATTORNEYS

United States Patent Office 3,257,296 Patented June 21, 1966

3,257,296

PROCESS FOR OBTAINING METALS BY FUSION ELECTROLYSIS

Bernhard Berghaus, Grand Hotel Dolder, Zurich, Switzerland, and Marie Staesche, Mattenstrasse 31, Wettingen, Aargau, Switzerland

Filed May 8, 1964, Ser. No. 366,109
18 Claims. (Cl. 204—64)

This application is a continuation-in-part of copending applications Serial No. 54,356, filed September 7, 1960, now abandoned, and Serial No. 81,735, filed January 10, 1961. The former application is a continuation-in-part of Serial No. 27,153, filed May 5, 1960, now abandoned, which in turn is a continuation-in-part of Serial No. 827,070, filed July 14, 1959 now issued on June 2, 1964 as Patent No. 3,135,675.

The present invention relates to a process for obtaining metals by fusion electrolysis and more particularly to a process of obtaining metals from their halides.

It is generally known that metals which are used industrially, can only in very rare cases be mined in pure form. For example, at places where large meteors have fallen, the deposit consists for the most part of pure metals. The greatest part of the metals used industrially at present are prepared by more or less complicated production processes from metal compounds found in ore or salt deposits.

The cost involved in such production processes plays a very substantial if not a decisive role in the price of the metal. Thus, for example, the price of aluminum in the middle of the previous century was somewhat on the order of the price of gold, and was attributable to the cost of the process of production.

But even today in the era of great technical production of metals, the production cost per ton of metal is greater in by far the most cases, than the cost of other raw material. It has, therefore, always been the object of professional people working in this field to lower those production costs as much as possible.

Now science, particularly chemistry and physical chemistry, offer many routes of metal recovery which all proceed from the raw material, the metal compound, to the production of the pure metal. Of these methods a great number are eliminated from the very beginning, because the necessary process steps cannot be carried out economically given the present state of technology, and indeed not just on the ground that each step of the process is uneconomical but in most cases because these processes produce intermediate compounds, the further treatment of which is attended with considerable difficulties.

The professional people active in the field of metal production have more intensively studied the remaining processes, which according to their view, are the only ones permitting economical performance and have highly refined each detail of these routes of recovery. So there is today a definite production process for the recovery of each individual metal of the principally used metals, which process is individually regarded as the most economical.

By way of example, the production of aluminum is carried out in the following manner:

The basic material available bauxite $Al_2O_3 \cdot nH_2O$ (n=1, 2 or 3) with impurities of ferric hydroxide $Fe(OH)_3$ is ground, boiled in caustic soda solution and the resulting aluminate solution is separated by filtration from the undissolved ferric hydroxide. The aluminum is then recovered from the filtrate in the form of precipitated aluminum hydroxide ($Al(OH)_3$) by introducing CO_2 according to the following reaction:

$$2NaAlO_2 + CO_2 + 3H_2O \rightarrow Na_2CO_3 + 2Al(OH)_3\downarrow$$

The resulting intermediate product $Al(OH)_3$ is converted by calcining into aluminum axide (Al_2O_3) from which the pure aluminum is recovered by means of the fusion electrolysis of a melt consisting of about 10% Al_2O_3 and 90% cryolite (Na_3AlF_6), the aluminum collecting in the box which forms the cathode.

The disadvantages associated with this fusion electrolysis such as the evaporization of the electrolyte, the necessary expenditure of about 20 kilowatt hours per kilogram of aluminum and a temperature of the melt of about 950° C. necessary for carrying out the fusion electrolysis, were regarded as unavoidable conditions, since apparently any significant improvement in these characteristics of fused liquid electrolysis could not be attained in any direct manner.

As in many parallel cases in technology fundamental research is required to make an improvement of conditions previously regarded as permanent since any other solution appears insurmountable. Basic research does not start out with the purpose of improving one or more of the conditions previously considered as insurmountable, but disregards the prejudices of the technical world—that namely the processes used constitute an optimum in respect to economy—and seeks and tests fundamentally new processes even when these processes reach a point where further treatment of the resulting intermediate product in accordance with previously valid conceptions is attended with such expense that these processes from the very beginning have previously been eliminated as being uneconomical for extended technical use or large scale production.

In such a search for new processes of metal production, the inventor proceeded from the known fact that the separation and refining of most metals may be accomplished at comparatively small expense from the halides of the metals, and that further the natural deposits of compounds of some metals are already in the form of halides so, for example, besides the chlorides of the alkali metals sodium and potassium, the halides of magnesium, magnesium chloride and magnesium bromide are likewise recoverable from salt beds, which metal today is gaining more and more importance as a raw material.

This viewpoint appeared at first however to offer only small prospect since it was considered established that these metal halides would either not decompose during fusion electrolysis at all or only at considerable expense since the halogen atoms are relatively firmly bound to the metal.

The problem underlying the invention was therefore to find a method with small technical expense of decomposing by fusion electrolysis the metal halides and other naturally occurring or easily obtained metal compounds, and thereby obtain the pure metal.

According to the invention this problem of obtaining metals by fusion electrolysis, is solved in that there are added to the melt before and/or during the electrolysis one or more electrolytic additives which consist of addition compounds of nitrogen-hydrogen compounds with metal salts of the group consisting of halides, nitrates, nitrites, chlorates and perchlorates of the light and transition metals Al, Mg, Be, Ca, Ti, Zr, Hf, Th, V, Nb, Ta, Mo, U, Ce, or an additive resulting from a heat treatment in an inert, protective atmosphere.

Preferably there will be used as electrolytic additive a product consisting of a metal chloride-ammonia addition compound or a product derived therefrom. It is particularly preferable to use as an electrolyte additive, an addition compound of the salt of the metal to be recovered or a modified product derived therefrom. It is further preferable to use as an electrolytic additive such an addition compound or product derived therefrom, in which on one molecule of the metal salt, the smallest possible

number of molecules of the additive material is attached.

Suitably, in the use of the addition compounds as electrolyte additives, they are introduced with the exclusion of air or in an oxygen-free protective gas atmosphere.

In the recovery of aluminum in accordance with the process of the invention by means of fusion electrolysis of an electrolyte consisting essentially of an alkali metal aluminum halide and up to 10% aluminum oxide, an electrolyte additive is added, suitably an ammonia addition compound of an aluminum halide and preferably consisting of aluminum chloride or a decomposition product derived therefrom.

In the recovery of aluminum in accordance with the process of the invention by fusion electrolysis there is used an electrolyte consisting essentially of only alkali metal aluminum chloride, as electrolyte additive preferably an ammonia addition compound of aluminum chloride or a stable decomposition product thereof.

In the recovery of titanium in accordance with the process of the invention by fusion electrolysis, there is used preferably an electrolyte consisting essentially of an alkali metal titanium fluoride and as an electrolyte additive an ammonia addition compound of a titanium halide, preferably titanium chloride or a stable decomposition product derived therefrom.

In many cases it can also be of advantage to use as an electrolyte additive an addition compound of a salt of a metal other than the metal to be recovered or a stable decomposition product derived therefrom or a mixture of addition compounds of salts of the metal to be recovered and other metals or stable decomposition products derived therefrom, or also addition compounds of salts of several different metals to be recovered or stable decomposition products derived therefrom.

Especially it is advantageous to use as an electrolyte additive a product obtained by heat treating an addition compound at a temperature above 400° C.

Particularly advantageous is to use as an electrolyte additive a heat stable product of an addition compound heated to a selected temperature over 400° C. and maintained at this temperature until evolution of decomposition products terminates. It is further an advantage, if there is used as electrolyte additive, a product derived from a heat treatment of an addition compound in a stream of protective gas.

Preferably the electrolyte additive is added to the electrolyte in small percentage proportion, preferably between 0.2 and 5% by weight.

For production of electrolyte additives according to the invention the metal salts are preferably metal halides or initial materials containing metal halides such as compounds of a metal and iodine, bromine, fluorine or chlorine. Among these preferred metal halides and raw materials containing metal halides, again the metal chlorides or raw materials containing metal chlorides are preferred, such as $AlCl_3$, $BeCl_2$, $MgCl_2$, $TiCl_4$. In addition, certain other metal salts or raw materials containing metal salts can be transformed into suitable electrolyte additives according to the method of the invention, particularly metal nitrites and raw materials containing metal nitrites, such as $Cu(NO_2)_2$, metal nitrates and raw materials containing metal nitrates, such as $Cu(NO_3)_2$, $Ca(NO_3)_2$, $Zn(NO_3)_2$ and $Cd(NO_3)_2$, metal chlorates and raw materials containing metal chlorates, such as $Cu(ClO_3)_2$, $Zn(ClO_3)_2$ and $Cd(ClO_3)_2$ and metal perchlorates or raw materials containing metal perchlorates, such as $Cu(ClO_4)_2$ and $Cd(ClO_4)_2$.

The addition compound which serves as the additive is preferably produced in such a manner that the metal salt or the raw material containing the metal salt and the substances to be added to it to form the addition compound are introduced into a reaction vessel in very fine dispersion and in such a manner as to ensure an intimate contact of the smallest particles of the two reactants, by way of example in such a manner that the two reactants

are supplied to the reaction vessel by two coaxial nozzles. In most cases it will be necessary, owing to the instability in air of the intermediate metal salt addition products obtained in the first step of the method, for a protective gas atmosphere free from oxygen to be provided in the reaction vessel.

Of particular advantage is a very fine distribution of the metal salt or of the raw material containing the metal salt in an oxygen-free carrier gas which cannot react with the salt and which simultaneously can act as a protective gas for the addition compound formed in the reaction vessel, e.g. a rare gas such as argon or molecular nitrogen.

The metal salt or the raw material containing the metal salt is preferably dispersed in the carrier gas in the form of vapour, this dispersion being obtained, by way of example, in such a manner that the carrier gas is passed, in the form of gas bubbles, through the metal salt or the raw material containing the metal salt in the liquid state and heated to evaporation temperature.

The substance designed for addition should preferably be a gas within the temperature range suitable for the performance of the method and should further naturally be in very fine dispersion. Ammonia gas is suitable as a substance for addition to the metal salt, though other nitrogen-hydrogen compounds such as hydrazine, hydroxylamine and organic amines also form addition compounds suitable for performance of the instant invention.

Addition compounds also referred to herein as the intermediate product within the meaning of the present invention are understood to be complex combinations of metal salts and an integral member of N–H units possessing characteristic heat effects and are generally capable of isobaric decomposition to lower N–H values.

Of the known addition compounds the following examples are representative of those suitable for the method of the present invention:

LiCl.4,3,2,1-NH_3
LiI.4,3,2,1-NH_3
$CaCl_2$.8,4,2,1-NH_3
$CaBr_2$.8,6,2,1-NH_3
CaI_2.8,6,2,1-NH_3
$CaCl_2$.2-N_2H_4
$Ca(NO_3)_2$.8,4,1-NH_3
$MgCl_2$.6,4,2-NH_3
$BeCl_2$.12,6,4,2-NH_3
$BeCl_2$.2-N_2H_4
$AlCl_3$.14,9,7,6,5,3,1⅙,1-NH_3
$CdCl_2$.6,5,4,3,2,1-NH_3
$CdBr_2$.6,4,3,2-NH_3
CdI_2.6,4,2-NH_3
LiBr.4,3,2,1-NH_3
$ZnCl_2$.6,5,4,2-NH_3
$ZnBr_2$.6,2-NH_3
ZnI_2.6,2-NH_3
$ZnCl_2$.2-N_2H_4
$ZnBr_2$.2-N_2H_4
$ZnCl_2$.2-NH_2OH
$Zn(NO_3)_2$.6,4,3-NH_3
$Zn(NO_3)_2$.3-N_2H_4
$Zn(ClO_4)_2$.X-NH_3 (X not determined)
$CdBr_2$.2-NH_2OH
CdI_2.2-NH_2OH
$Cd(ClO_3)_2$.6,4-NH_3
$CdCl_2$.2-N_2H_4
$CdBr_2$.2-N_2H_4
CdI_2.2-N_2H_4
$CdCl_2$.2-NH_2OH
$GaCl_3$14,7,6,5,3,1-NH_3
$GaBr_3$.14,7,6,5,3,1-NH_3
GaI_3.20,13,9,7,6,5,1-NH_3
$InCl_3$.15,7,5,3,2,1-NH_3
$InBr_3$.15,(14),7,5,3-NH_3
InI_3.21,(20),13,9,7,5,2-NH_3
$In(NO_3)_2$.6,4,3-NH_3
$In(ClO_3)_2$.X-NH_3 (X not determined)
$AsCl_3$.7,4,2-NH_3
$AsBr_3$.3-NH_3
AsI_3.NH_3
2AsI_3.9-NH_3
$FeCl_3$.12,6-NH_3
$FeBr_3$.6-NH_3
$FeCl_2$.10,6,2,1-NH_3
$Cd(ClO_4)_2$.6,4-NH_3
$Cd(NO_3)_2$.6,4-NH_3
$Cd(NO_3)_2$.3-N_2H_4
TlCl.3-NH_3
$TlCl_3$.3-NH_3
$TlBr_3$.3-NH_3
$TiCl_4$.8,6,4-NH_3
$ThCl_4$.18,12,7,6,4-NH_3
$ThBr_4$.20,14,10-NH_3
$In(NO_3)_2$.3-N_2H_4
$In(ClO_4)_2$.X-NH_3 (X not determined)
$SbCl_3$.2,1-NH_3
$SbCl_5$.6,4,3-NH_3
$TeCl_4$.6,5,4,3-NH_3
$MoCl_3$.6-NH_3
UCl_4.12,8-NH_3
$FeBr_2$.6,2,1-NH_3
FeI_2.6,2-NH_3
$FeCl_2$.2-N_2H_4

The number of molecules of the substance designed for addition to a molecule of the metal salt or of the raw material containing metal salt will then essentially depend

on the temperature at which this addition is performed. Accordingly, the temperature should be selected in accordance with the number of molecules desired for addition to a metal salt molecule. In order to provide the temperature selected for the performance of the method, the heat released in the exothermic formation process of the addition compounds will preferably be employed at least in part during the addition reaction. In addition, extraneous sources of heat acting on the reaction point may be employed to produce the temperature selected for the performance of the method.

The temperature required for the performance is preferably obtained by keeping the supply of metal salt or the raw material containing the metal salt at a temperature depending on the heat supplied by the exothermic formation process (e.g. $TiCl_4$ for the formation of $TiCl_4.8NH_3$ at minus 20° C. to 0° C. for the formation of $TiCl_4.6NH_3$ at plus 20° C., and for the formation of $TiCl_4.4NH_3$ at plus 80° C. to plus 90° C.) and delivering the raw material to the reaction vessel at this temperature.

The process is advantageously performed at such a temperature that the number of the molecules of the substance selected for addition added to a molecule of the metal salt or the raw material containing the metal salt is as small as possible and that the quantity of the addition substances required per unit volume of the metal salt or the raw material containing the metal salt is kept at a minimum. In this connection it should be pointed out that electrolyte additive is produced by heat treatment of the addition compound for such a period that the separation of the decomposition products of the added substances and the halogen removed from the metal at the end of the processing period has reached its boundary value depending on the operating temperature in this second step and consequently ceases. The final heat treated electrolytic additive obtained is independent of the number of molecules originally added to a molecule of the metal salt and such various integral addition compounds when heat treated according to the second step of the method apparently possess the same composition.

Furthermore, the first step of the method is preferably performed in such a manner that the stoichiometric quantities of metal salt or raw material containing the metal salt supplied to the reaction vessel per unit time on the one hand, and the substances designed for addition to said salt on the other are adjusted in accordance with the number of molecules to be added to the former volume at the temperature selected so that they may fully react with one another.

It is furthermore advantageous to so adjust the formation of the addition compound from the metal salt or the raw material containing the metal salt on the one hand, and the substances designed for addition on the other in respect to their mutual chemical action that the addition compound forming the reaction product is a solid substance and will therefore precipitate.

The heat treatment of the addition compound is carried out at a temperature corresponding to the desired degree of stabilization of the final product, the said degree of stabilization being determined mainly by the desired stability of the final product in respect to air, humidity and other atmospheric influences.

The intermediate products should preferably be subjected to a treatment, in the second step, of a duration designed to ensure that the separation of the decomposition products of the addition substances and the halogens removed from the metal salt of the intermediate product reaches, at the end of the treatment period, its boundary value dependent on the processing temperature, and will therefore cease.

With addition compounds unstable in air, the second step of the method must also be performed in an oxygen-free protective gas atmosphere.

From the decomposition products separating from the intermediate product composed of the added substances and the halogens removed from the metal, the substances used for addition may advantageously be recovered by treatment with appropriate chemicals and be recirculated to the first step of the process for the formation of further addition compounds. By way of example, in the case of NH_3 to be added to metal chlorides, the separated products from the second step are passed into lime milk $Ca(OH)_2$, and NH_3 is thereby recovered.

The stable calcined final product or metal salt addition intermediate products are preferably employed as additions to the melt in the fusion electrolysis production of this metal and this offers great advantages. Particularly advantageous electrolyte additives are the final intermediate products produced from ammonia and a metal halide of a light metal such as aluminum, magnesium, beryllium and titanium. These, of course, will be employed as additions to the melt in the fusion electrolytic production of the metal in question.

By way of example, ammonia addition compounds of $AlCl_3$ obtained by the method according to this invention will be suitable as such or after heat treatment according to the second step as additions to a melt containing approximately 10% Al_2O_3 and 90% $NaAlF_6$ for the fusion electrolysis employed to produce aluminium. A further example is presented by the ammonia addition compounds of $TiCl_4$ obtained according to the method of the invention, which are excellently suited as additions to a melt containing approximately 5% $K_2Ti_1F_6$ and 95% other salts, the additive likewise being either in the form of an addition compound or stable heat treated product derived therefrom according to the second step of the process, in the fusion electrolysis of titanium.

The intermediate products or final products of a metal of the group comprising vanadium, tin, hafnium, zirconium, thorium, uranium, tantalum, boron, molybdenum, tungsten, niobium and cerium obtained by the method according to this invention are examples of further substances perfectly suitable as electrolyte additives to the melt in the fusion electrolysis for the recovery of the named metal.

Furthermore, electrolyte additives according to this invention may advantageously be employed as additions to the melt in the fusion electrolysis for the production of another metal, e.g. electrolyte additives obtained from a salt of zirconium may be added to the melt in the fusion electrolysis for the production of titanium. This is of advantage particularly when the metal of the heat treated addition salt is designed to become an alloying constituent of the metal contained in the solution. In this case, the volume added should advantageously be so selected that the corresponding alloying constituent percentage desired is contained in the metal produced by fusion electrolysis. In addition, it may be of great advantage, e.g. with an alloy consisting of a base metal and a plurality of alloying constituents, to employ as electrolyte additives various intermediate addition products or their corresponding final decomposition products obtained from the salts of several metals, e.g. from all or a portion of the metals used as alloying constituents, by the method according to this invention. By way of example, the additives are added in quantities corresponding to the metal content of the final alloying percentages, to the solution in the fusion electrolysis for the production of, e.g., the base metal. Additions obtained only from the salts of the alloying metals, and, furthermore, an addition obtained from the salt of the base metal may be employed.

When intermediate products not stable in air are employed as additions to the melt, they must be supplied to the solution in the absence of air, i.e. while an oxygen-free protective gas is employed.

The substances recited as additions to the melt are preferably employed in a small percentage of the melt, which is normally between 0.2 and 5%. Naturally, this does not apply to the case above disclosed when certain alloying percentages are to be obtained because the quantity

of the substance added is determined by the alloying percentage desired.

The substances employed as additions to the melt may very advantageously be employed to lower the temperature of the electrolyte and the melting temperature of the solution, to reduce evaporation of the solution and to increase the conductivity of the electrolyte and, furthermore, to reduce the consumption of electrical energy per unit weight of the metal produced.

The method according to this invention is described in greater detail in reference to the description of a device for the performance of the said method and of several examples illustrative of the method. In the drawing

FIG. 1 shows a laboratory-type device by means of which an addition compound is obtained from metal halides in the liquid state and a heat treatment performed of this addition compound.

In the arrangement shown in FIG. 1, the vessel **1** contains a metal halide, e.g. titanium tetrachloride in the liquid state. Supplied through the tube **2** is a carrier gas, by way of example molecular nitrogen, which must be carefully purified of oxygen. The carrier gas rises, in the form of gas bubbles, to the surface of the liquid metal halide heated to evaporation temperature and is accordingly enriched with a mist of this metal chloride while it rises. The temperature of the metal halide is so selected that the desired number of molecules are added, in the reaction with the substances designed for addition, to a molecule of the metal halide. By way of example, in the addition of ammonia to titanium tetrachloride at a temperature of the liquid titanium tetrachloride of minus 20° C. to 0° C. 8 molecules ammonia are added to a molecule of titanium tetrachloride; at a temperature of plus 20° C., 6 molecules ammonia, and at a temperature between plus 80° C. and 90° C., 4 molecules ammonia. Through the tube **3** this metal halide dispersed in the carrier gas in the form of vapour passes into the reaction vessel **4**. The reaction vessel **4** is further supplied, through the tube **5**, with ammonia gas which will immediately form a solid addition compound with the finely dispersed metal halide supplied, the said compound becoming visible, in the case of titanium tetrachloride, as a yellow turbidity and conglomerating soon into loose flakes at the wall and in the funnel-type lower portion of the reaction vessel **4** so as to be passed downward from time to time by means of the scraper **6**. The surplus gases (molecular nitrogen and ammonia) are removed via the annular tube **7** communicating with the interior of the reaction vessel **4** via openings, and pass first into the collecting chamber **8** where particles of the addition compound formed which may have been carried along, can be deposited. The surplus gases will then emerge from the settling chamber **8** through the tube **9**.

The reaction vessel **4** is connected to the transverse glass or plexiglass tube **11** by means of tapered neck portion **10** of sufficient width and taper so as to mate with the funnel-type lower portion of vessel **4**. Arranged at one end of plexiglass tube **11** is a gas-tight stuffing box **13** and push rod **14**. Steatite boat **12** is longitudinally slidable in the tubes and may be slid into steatite tube **17** disposed in oven **16** by means of rod **14** across the slide **15** between tubes **11** and **17**. At the position where the steatite boat **12** is placed for the heat treatment in the steatite tube **17**, a thermocouple element **18** is located which indicates the available temperature at this point by means of the instrument **20** connected to element **18** via the lines **19**. At its other end, the steatite tube **17** is again connected, in gas-tight connection, with the delivery device formed of glass or plexiglass, which is here composed, by way of example, of the tube **21** with the funnel **22** and the conical ground member **23** to which the neck of the flask **24** communicates in gas-tight relationship.

Prior to the experiment, the device is evacuated to at least one mm. Hg pressure and checked for tightness. It is then filled with dry ammonia gas through the tube **5**. Subsequently, the metal halide finely dispersed in the carrier gas is supplied to the reaction vessel **4** through the tube **3** and the product obtained collects in the steatite boat **12** located in the left-hand part of the tube **11**. The boat is then shifted slowly to the right by means of the rod **14** attached to it until completely filled. The boat is thereupon moved further to the right over the slide **15** to the center of the oven **16** and there heated after the slide **15** has been closed. After reaching the desired temperature, the substance is kept at such temperature for, e.g., one hour. After a certain amount of cooling so as to protect the tube **21**, the boat **12** is moved into the tube **21**, tilted and emptied into the flask **24**. During the entire heating and cooling process, ammonia gas is passed through the oven via the tube **17**. The surplus ammonia gas and the heating products obtained are removed by means of an absorbing device not shown, and the ammonia gas is cycled to vessel **4**.

At approximately 200° C. white vapours of mostly ammonium chloride (NH_4Cl) begin to escape. If the temperature is held constant, the formation of a gas comprising ammonium chloride will stop after some time and a product of yellow-to-orange colour is obtained which is, however, largely stable to atmospheric moisture. On further heating additional ammonium chloride is formed. If the temperature is kept constant, evolution of gas again ceases but is resumed when the temperature is raiesd further. It has been found that ammonium chloride is formed in not inconsiderable quantities even at 1100° C.

The product in the boat depending on the temperature selected will be yellow, orange, brown, black or, at very high temperatures, brown with a bronze cast. The stability in atmospheric humidity and even to water treatment increases at higher temperatures without noticeable reduction of the chemical activity. A product calcined at temperatures as high as 1100° C. will still evolve a gas comprising NH_4Cl and products treated at 1300° C. will still react with acids and exercise the improved effects as an additive for fusion electrolysis.

Behind the boat (towards the outlet) in the tube **17** there will always be located a batch of yellow, orange or brown colour which is composed mainly of ammonium chloride. On the average it will still contain up to about 2% of the metal of which the halide was the starting material in the process.

The boat **12** in the tube **11** may also be replaced by a conveyor and compressing worm driven via a shaft **14** which conveys the loose product coming from the vessel **4** through the wide neck **10** in the direction towards the closed slide **15** forcing it against the same. This conveyor and compressing worm enables the loose product to be compacted into a tablet immediately in front of the slide and accordingly to be compressed. After opening the slide **15**, this tablet may then be moved into the tube **17** in the oven **16** in a suitable manner and withdrawn from the oven after termination of the heating and cooling cycle. The use of such a pre-compacted tablet enables the throughput per unit time to be increased.

In the processing device disclosed above, the heating oven **16** may also be replaced by a device for dielectric high-frequency heating of the product. Heating of the addition compounds obtained in a glow or gas discharge vessel is also possible, care being taken to ensure the substances to be treated and heated as uniformly as possible.

By treatment of an addition compound as described above the metal content of the final product is higher than that of the starting addition compound and the nitrogen content of the end product as determined by the Kjeldahl method is substantially less than that of the corresponding nitride, and the halogen content as determined by titration is less than 10%.

The treatment when carried out in a flowing gas atmosphere, more particularly an oxygen free gas stream such as ammonia gas, permits the easy removal of the evolved gas comprising ammonium halide. The sublimated am-

monium halide can also be separated from the treated material in other ways; for instance, by suitably guiding the heat flow, it is possible to ensure that the sublimated ammonium halide precipitates at a point sufficiently far removed from the region of sublimation.

When a flowing gas atmosphere is used, the gas is preferably recovered after leaving the treatment space and recycled to the treatment space, so that the gas stream therefore moves in a closed circuit. Ammonia may with advantage be released, by chemical reaction, from the ammonium halide sublimated during the treatment; this ammonia is then additionally supplied as treatment gas to the reaction chamber during the formation of the addition compound. This possibility is of course available only in cases in which the treatment is carried out in the ammonia atmosphere which is preferably used.

In general, in the present method it is extremely important that the treatment of the addition compounds of metal halide with ammonia should take place in an atmosphere free from oxygen. If oxygen is present even in a small quantity in the gas atmosphere, then metal hydroxides or oxychlorides or oxyamines are formed from the addition compounds during the heat treatment and cannot be further decomposed.

Tests have also shown that in the presence even of very small quantities of oxygen in the treatment gas atmosphere the conversion of the addition compounds during the heat treatment does not proceed in the same way as in the method according to the invention, and that when the treatment is otherwise the same the end products produced are substantially different, in their essential characteristics, from the end products produced in an atmosphere completely free from oxygen. For instance, when used as an electrolyte additive these end products produced in an atmosphere that is not completely free from oxygen do not have the above-mentioned improving effects on the conductivity and the temperature.

Generally, the colour of the end products that are made is sufficient to show whether the treatment atmosphere has been sufficiently free from oxygen or whether the treatment atmosphere contained residues of oxygen that had not been removed. For instance, when addition compounds of titanium chloride with ammonia are treated in a gas atmosphere that is not completely free from oxygen, the end products obtained generally have a bluish or violet lustre, whereas treatment in an atmosphere completely free from oxygen under conditions that are otherwise the same produces a dull black colour. This difference in colour is sufficient to show clearly the great extent to which the formation of the end products is affected even by very small quantities of oxygen.

A further important factor in carrying the present method into effect is that care must be taken to ensure that the ammonium halide which is produced in the heat treatment of the addition compound of metal halide with ammonia and which sublimates from the material being treated, is removed from the sublimation zone. If this is not done, then it is possible that the sublimated ammonium halide may precipitate for instance on a wall located above the region of sublimation and fall back from this wall into the material being treated, so that after the conclusion of the treatment the material obtained will be a worthless mixture containing ammonium halide, the required end product and also perhaps complex compounds of these two materials or their components.

The best way of removing this sublimated ammonium halide from the sublimation zone is to carry out the treatment in a flowing gas atmosphere which continuously removes the sublimated ammonium halide from the region of sublimation until the halide finally precipitates at a sufficiently cool point on the path of flow. The use of a flowing ammonia gas atmosphere is particularly advantageous, because the ammonia gas favours the progress of the treatment and promotes the formation and sublimation of the ammonium halide. But in the case of treatment in a flowing gas atmosphere care must be taken to ensure that the speed of flow and also the increase in temperature during the heating of the substances under treatment, are kept so small that the gas flow will take away only the ammonium halide that is formed and will not also take away the substances under treatment. In regard to this it is to be observed that if the rise in temperature is too rapid, the large heat flow that is thereby produced will cause removal of the treated material by the flowing gas stream, and such removal will also take place if the speed of flow of the gas atmosphere itself is too high.

The treatment itself proceeds in such a manner that the starting material is first heated slowly and continuously. possibly, detachment of ammonia molecules from the addition compound of a metal halide with ammonia used as starting material first takes place at temperatures that are still relatively low, if the starting material used is an addition compound in which the number of ammonia molecules added on to a metal halide molecule is such that detachment can still take place, i.e. it may be that as the temperature rises the first thing that occurs is that the next lower possible addition compound of ammonia with the metal halide in question is formed. But the question of whether this detachment actually occurs in this form is not of importance for the present method, since the conversion of the starting material into the required end product begins with the separation of ammonium halide, and this separation begins at temperatures that are above the temperature range within which this detachment would proceed. In reference to this, however, it is noteworthy that both the composition of the end product obtained by the treatment and also the action of this product on suitable reagents are independent of the number of ammonia molecules added on to a metal halide molecule in the starting material. For instance, the end product claimed when $TiCl_4 \cdot 6NH_3$ is used as the starting material, is the same as when $TiCl_4 \cdot 4NH_3$ is used. In this connection it is to be observed that in general it is advisable to use as the starting material an addition compound in which as few ammonia molecules as possible are added on to a metal halide molecule, because on the one hand such starting materials are easier to handle since they are not so unstable, when subjected to the action of the atmosphere, as is a corresponding starting material with a larger number of ammonia molecules added on to a metal halide molecule, and because on the other hand this relatively lower ammonia content of the starting material permits the quantity of gas circulating in the cyclic process to be reduced.

When a certain temperature, which is about 200° C. for instance when addition compounds of titanium chloride and ammonia are the starting material, is reached, the corresponding ammonium halide, which is NH_4Cl in the case of addition compounds of $TiCl_4$ with NH_3, begins to separate from the material under treatment. If a particular treatment end temperature is maintained, this separation of ammonium halide ceases after a certain time, when the end product produced has reached a composition characteristic of this treatment end temperature. Further separation of ammonium halide will occur only if the treatment temperature is raised.

Now, in the present method the treatment temperature is gradually raised to an end temperature which, when maintained until the separation of ammonium halide ceases, and will give an end product of which the metal content is higher than that of the addition compound used as starting material but lower than that of the corresponding metal nitride, and of which the nitrogen content as determined by Kjeldahl's method is substantially less than that of the corresponding metal nitride, and of which the halogen content as determined by titration is less than 10%.

When the treatment temperature is higher, the metal content of the end product approximates more closely to that of the corresponding metal nitride, whereas the nitro-

gen content of the end product as determined by Kjeldahl's method and the halogen content of this product as determined by titration, become less when the treatment temperature is higher, and decrease to small percentages, and even to fractions of one percent when the treatment temperatures are very high.

The nature of the bonds between the molecules and atoms of the substances contained in the end products obtainable by means of the present method, has not been determined. But it is not necessary to know this in order to carry the present method into effect, since experiments have shown that this method can be reproduced at any time and leads in every case to the same end product when the same starting materials and protective gas atmosphere are used and the duration of treatment and the end temperature are the same.

The present method of treating addition compounds of ammonia is therefore a defined process which is applicable to all known addition compounds of ammonia with metal halides and which gives reproducible end products which are substantially more stable when exposed to the action of the atmosphere, more particularly when exposed to air and moisture, than the starting materials.

The following examples are given by way of illustration of the heat treatment step of the invention.

Example 1

An addition compound with NH_3, having the composition $TiCl_4 \cdot 6NH_3$, was made from $TiCl_4$ and this compound was heated in a tube furnace with careful exclusion of air. The whole operation was carried out under ammonia as a protective gas. The samples were each treated for an hour at a temperature of about 700° C., and afterwards introduced into a test container, also under ammonia. The excess NH_3 was driven off by H_2 and the final product obtained, which was very stable and did not react when exposed to air or to moisture, was tested for Ti, N and Cl. If the compound is heated only to about 400° C., a yellow-brown end product is obtained, which is also substantially more stable than the starting product. If the compound is heated to temperatures above 600° C., a dull black end product is obtained; analysis shows that this product, inter alia, contains Ti, N and Cl. This product is largely stable in the presence of air and water; it is light, but when shaken it immediately settles again without forming dust. During the heating process a substance consisting mainly of NH_4Cl in large crystals settles on the cold parts of the container. The product obtained at temperatures of not less than 600° C. contains black and also red-brown flakes some of which, have a metallic lustre and which call to mind the description of TiN. The higher the treatment temperature, the higher is the proportion of these constituents. The average titanium content, however, amounts to only 60 to 70% Ti, and the titanium content of the lustrous flakes is 72 to 75% Ti, whereas pure TiN contains 77.4% Ti.

The treatment can also be carried out by heating at subatmospheric pressure.

When the treatment end temperature is about 700° C., the product obtained by the present method is largely stable in the presence of air and water but is still very reactive. With a small amount of HNO_3 it changes at 80 to 100° C. into a greenish-white substance, possibly $TiNNO_3$, which is also stable in the presence of air and is particularly easily soluble in sulphuric acid. A corresponding sulphate is formed by reaction with a small quantity of sulphuric acid. Small percentages of the abovementioned products will dissolve in metal salt melts, such as NaCl, alkali compounds, alkaline earth metal chlorides, Na_2TiF_6, K_2TiF_6 and others, and this results in a substantial lowering of the melting point of the metal melt.

Example 2

The addition compound $TiCl \cdot NH_3$ representing a solid loose product is annealed under an inert gas at a temperature of 500° C. After a 2 hour heat treatment a solid compound is obtained which is substantially stable against the effects of air and humidity. About 0.5 g. of this heat treated product is mixed with 50 g. Na_2TiF_6=salt. The mixture is heated and becomes current conductive at 610° C. In a parallel embodiment with Na_2TiF_6=salt without an addition substance, the current conductivity will appear only at about 712° C. The mixture melts at about 719° C. while the melting point in the parallel embodiment without an addition substance will be at 780° C. On electrolyzing the melted mixture, metallic Ti as well as Na will be formed after some 100 minutes of testing; a combustion of the Na takes place at the surface of the liquefield product, while the Ti forms a precipitate at the cathodic electrode consisting of sheet-iron.

Example 3

The addition compound $TiCl \cdot NH_3$ was annealed for an hour under a protective gas NH_3 at a temperature of 1000° C. and a black powder was produced as a decomposition product which, practically, was completely stable against the effects of air and humidity. 0.59 g. of this powder was mixed with 60 g. Na_2TiF_6, and 50 g. of this mixture were electrolyzed. Conductivity begins at 658° C. The melting process begins at 688° C. and is completed at 704° C. The electrolysis of this mixture produces separated titanium, while separation of Na has not been observed.

Example 4

The addition compound $TiCl \cdot NH_3$ was annealed for 1 hour under NH_3 as protective gas and at a temperature of 1300° C. A dark shining powder, bronzelike on the surface, was produced as a decomposition product which, practically, is completely steady against air and water. 0.538 g. of this powder was mixed with 50 g. Na_2TiF_6 and electrolyzed. Current passage begins at 560° C. and the mixture melts at 708° C. During electrolysis Ti is separated, a separation of Na has not been observed.

Example 5

The additive substance was produced in the same manner described in Example 3 from an addition compound $TiCl \cdot NH_3$ and added to the Na_2TiF_6 in the quantity described therein. During electrolysis it has been observed that an impoverishment of the liquefield product takes place after a few hour's treatment and that the current strength is reduced and correspondingly the voltage requirement for the maintenance of a determined current strength increases. After a current decrease from 127 ma. at a temperature of the liquefied material at 729° C., 3.5 g. Na_2TiF_6 were added to the liquefied product. A current increase to 118 ma. resulted therefrom, but already 30 minutes later the current was again down at 50 ma. 50 g. of the mixture from 60 g. Na_2TiF_6 and 0.59 g. of this additive were then added to the liquefied material, whereupon, 15 minutes later, a current increase to 165 ma. was obtained so that electrolysis could be carried on at a sufficient current strength for 3 more hours.

Example 6

A mixture similar to the one illustrated in Example 3 was produced and electrolyzed. After a longer time, an impoverishment similar to the one in Example 5 was observed and the current decreased to 85 ma. (at 13.15 h.). 5 g. of a mixture of Na_2TiF_6 and about 2% of an addition compound $TiCl \cdot NH_3$ were then added to the liquefied material. In order to avoid a decomposition of the unsteady addition compound, the preparation and addition of this substance ought to be effected under a protective gas. The mixture having been added, a current increase was observed, though, about 1 hour later, its action was already exhausted. The attempt by adding directly the addition compound $TiCl \cdot NH_3$ to the liquefied material in absence of a protective atmosphere did how-

ever not influence the current passage as the addition compound, without being able to penetrate the liquefied material, evaporized already on the surface.

It is substantially more advantageous to employ the heat treated addition products as the additives in fusion electrolysis. This procedure will now be discussed in greater detail in reference to examples of titanium and aluminum production.

In the fusion electrolysis for the production of titanium which is commonly used, the solution consists of approximately 5% of an alkali titanium fluoride, e.g. Na_2TiF_6, and of approximately 95% other salts such as NaF and CaF_2, and KCl, NaO and SrF_2. This fusion electrolysis is performed at a voltage of approximately 3 volts and a solution temperature between 700° C. and 750° C., and produces a power efficiency corresponding to tetravalent titanium of approximately 80%.

In fusion electrolysis including the electrolyte additives according to this invention, a solution consisting of almost 100% alkali titanium fluoride may be employed. If fractions of one percent up to several percent, preferably approximately 1% of a final product obtained by means of heat treatment of an ammonia addition compound of titanium tetrachloride are added to such a solution using a titanium anode and a cathode formed of copper, nickel, steel or the like, voltages of below 1 volt, preferably between 0.5 and 0.7 volt, will produce pronounced separation of extremely coarse crystalline titanium at the cathode, which largely exceeds the titanium quantities dissolved at the anode and therefore originates in the solution. The addition substances here operate as crystal nuclei around which the monocrystals of the metal contained in the solution will form. The temperature of the solution, depending on the quantity of the substance added, will be around 700° C. to 730° C. and it is therefore substantially lower than the melting temperature of the pure alkali titanium fluoride which is at approximately 870° C. for Na_2TiF_6. At the same time a power efficiency of between 90 and 95% is obtained on the basis of monovalent titanium. Instead of using the final heat-treated product, addition of the addition compound not subjected to heat treatment, i.e. the intermediate product, may be employed with the same results. In this case, however, the quantities added must be increased, in accordance with the lesser titanium content of the untreated addition compound, so that the same titanium content is present in the addition. The quantities to be added here range between 1% and 10% preferably 3% approximately. Without the addition of either the heat treated additive or the untreated addition compound, no metal will be separated under the same voltage conditions even if the temperature is raised beyond the melting point of the salt solution. After several hours of electrolysis, the current will drop. It will soon be restored to its original level by addition of further material. Electrolysis can in this manner be continued until the electrolyte is completely exhausted.

In the fusion electrolysis for the production of aluminium now commonly used, the solution consists of approximately 10% aluminium oxide Al_2O_3 and approximately 90% of an alkali aluminium fluoride, by way of example Na_3AlF_6. This fusion electrolysis is performed with a voltage between 5 and 6 volts and a temperature of approximately 950° C., and will yield a power efficiency of approximately 95%.

When the electrolyte additive obtained according to the method of this invention in the form of an ammonia addition compound of aluminium chloride or a stable product obtained from this intermediate product by means of heat treatment is added in a volume which is in the range of fractions of one percent and several percent, preferably 1% by weight in the case of the heat treated product, and at about three times this quantity, preferably approximately 3% by weight in the case of the intermediate product, a considerable increase in the conductivity of the electrolyte and a reduction of the melting temperature of the solution by about 150° C. to approximately 800° C. will be obtained. In order to maintain this solution temperature, the considerable increase in the conductivity of the electrolyte will necessitate a voltage of only about 1 volt. At this voltage, about the same current will flow as in the case where fusion electrolysis is performed without such additions at a voltage between 5 and 6 volts. In addition, the fusion electrolysis with the additives enables a power efficiency based on monovalent aluminium of about 95 to 97% to be achieved. The reduction in the voltage and the increase of the absolute current efficiency by means of the monovalence of the produced aluminium enable the electrical energy previously required for the production of 1 kilo aluminium in fusion electrolysis without additives to be lowered from 20 kwh. to 3 to 4 kwh. in the fusion electrolysis with additives. This improvement is quite considerable insofar as a large portion of the production costs of aluminium was accounted for by the electrical energy required for fusion electrolysis.

With the same advantage the method according to this invention may be applied to the fusion electrolysis recovery of almost all metals and relates particularly to the metals capable of forming addition compounds with ammonia or hydrazine in the form of halides, occasionally also nitrates, chlorates and perchlorates since for the performance of the process of the invention electrolyte additives in this form are required. These addition compounds, particularly ammonia addition compounds of metal halides, are largely unstable in air and humidity. Some of the halides are solid and stable in air. This is particularly true of halides of the Groups I and II as well as VI and VII in the Periodic Table of Elements. Apart from the group of the metalloids (Si, Ge, Sn) the center of the periodic table consists of the light metals and the so-called transition metals.

The method according to this invention is particularly suited to these groups. It therefore relates particularly to the metal compounds of titanium, zirconium, hafnium, thorium, niobium, vanadium, aluminium, beryllium, and boron. The method according to this invention may advantageously be applied also to compounds of other metals such as tin halides or halides of other metals which are hygroscopic, such as magnesium, beryllium and the halides of the other alkaline-earth metals, or to such metals whose halides are stable in air, such as the halides of cerium, lanthanum and the halides of other rare earths, molybdenum and the like.

Among the metals investigated in respect of the applicability of the method according to this invention, the following are singled out for mention which belong to the following six groups:

(I) Alkali metals: Li, Na, K, Cs, Rb.
(II) Alkaline-earth metals: Ca, Sr, Ba.
(III) Light metals: Be, Mg, Al, Ti.
(IV) Heavy metals:
  A. Nonferrous heavy metals: Cu, Pb, In, Hg, Cd, Sn, Sb, Bi, Ga^{III}, In^{III}, Tl, Cr, Th, U (Ni, Co) (Ni and Co only insofar as addition compounds are present which may be obtained under certain circumstances)
  B. Iron and steel improving agents: Fe, Mo, V, Mn, Nb, Ta. The W which belongs here yields no addition compounds, but nitrides.
(V) Semimetals: B, As, Te. Boron produces, besides the imides typical of semimetals, e.g. $(BH_2NH_2)_x$, also a boron trichloroborazol $(BClNH_3)_3$, which can be decomposed in glow discharges in the manner discussed.
(VI) Rare earths: Lanthanides, including scandium and yttrium.

Some addition compounds which may be formed with various metals selected from the number of metals in-

vestigated have already been listed in the specification. These addition compounds of metal salts are useful in this form or after heat treatment as electrolyte additives in the recovery of the same metal as the salt or for the recovery of different metals.

This list furthermore shows that the number of the ammonia molecules which may be added to a metallic salt molecule apparently does not seem to have a definite upper limit. In addition, it may be seen that other metal salts may be substituted for the metal halides preferably employed for the production of addition compounds. However, the number of other metal salts in question is substantially smaller than the number of metal halides employable in the method according to this invention. In general, they are the anions NO_2, NO_3, ClO_3 and ClO_4. Further specific instances of metal salts which may also be considered for the method according to this invention are the following:

$Cu(ClO_3)_2$, $Cu(ClO_4)_2$, $Cu(NO_2)_2$, $Cu(NO_3)_2$, $Ca(NO_3)_2$, $Zn(NO_3)_2$, $Zn(ClO_3)_2$, $Cd(NO_3)_2$, $Cd(ClO_3)_2$, $Cd(ClO_4)_2$

A number of further examples of the production of electrolyte additives according to this invention are recited below: Production of titaniferous final product from ammonia gas and titanium tetrachloride.

Titanium tetrachloride is passed into the vessel **4** (FIG. 1), at room temperature, the yellow addition compound formed with ammonia collects in the boat **12** which is passed into the oven **16**. After heating to 680° C. and for approximately 1 hour, the boat held a black product intermingled with brown particles, which was largely stable in air. The analysis for titanium disclosed, in the largely brown particles, 73.5% Ti; in the largely black particles, 66.2% Ti, and 69.4 to 70.6% titanium in the average substance depending on the mixing ratio.

The sublimate in the tube **17** was grey-white to green-yellow consisting principally of NH_4Cl and between 0.4 and 2.9% Ti (0.4/0.5/0.6/0.8/0.9/1.1/2.5/2.9% Ti).

Produced in the same manner were:

An Al-containing electrolyte additive from an $AlCl_3$ addition compound,
A Be-containing electrolyte additive from a $BeCl_2$ addition compound,
An Hf-containing electrolyte additive from an $HfCl_4$ addition compound,
An Mg-containing electrolyte additive from an $MgCl_2$ addition compound,
A Th-containing electrolyte additive from a $ThCl_4$ addition compound,
A Zr-containing electrolyte additive from a $ZrCl_4$ addition compound,
A B-containing electrolyte additive from a BCl_3 addition compound,
A Ta-containing electrolyte additive from a $TaCl_5$ addition compound,
An Mo-containing electrolyte additive from an $MoCl_5$ addition compound,
A W-containing electrolyte additive from a WCl_5 addition compound,
A V-containing electrolyte additive from a VCl_4 addition compound.

In summary, the intermediate or final products obtained from a treatment in accordance with the present invention can be used with great advantage as electrolyte additives in obtaining metals by fusion electrolysis. Even a very small percentage of these products in the melt produces a substantial increase in the conductivity of the electrolyte and a not inconsiderable decrease in the temperature of the melt. Evaporation of the melt is also prevented. The increase in conductivity has the effect of enabling the cell voltage to be reduced, with consequent substantial saving in the electrical power that has to be used for each unit of quantity of the metal to be separated, and is to be regarded as the main advantage of the use of these end products as electrolyte additives. But the lowering of the temperature and the reduction in the evaporation of the melt are also substantial advantages; the lower temperature, in particular, considerably reduces the extent of the action of the melt on the cell material.

We claim:

1. A process for recovering a metal by fusion electrolysis comprising the steps of adding to an electrolyte containing said metal a substance selected from the group consisting of complexed addition compounds of the formula $M(Z)_n \cdot (C)_x$ where M is Al, Mg, Be, Ca, Ti, Zr, Hf, Th, V, Nb, Ta, Mo, U, or Ce, n represents the valence of M, Z is an anion of the group consisting of halide, nitrate, nitrite, chlorate or perchlorate, C. is a complexing moiety of the group consisting of ammonia, hydrazine, hydroxylamine or an organic amine or a product derived therefrom by heat treatment of said complexed addition compound in an oxygen free gas protective atmosphere to a temperature exceeding 200° C. until evolution of an ammonium salt of said anion ceases to form a product of increased stability containing metal, hydrogen, nitrogen and said anion and wherein the metal content is higher than that of the initial addition compound and the nitrogen content as determined by the Kjeldahl method is substantially less than the corresponding nitride and then separating the metal from the electrolyte.

2. A process according to claim **1** for the production of aluminum by fusion electrolysis of an electrolyte consisting essentially of alkali metal aluminum halide and up to 10% aluminum oxide, in which the electrolyte additive utilized is a product selected from the group consisting of an ammonia addition compound of an aluminum halide and a product derived therefrom by the heat treatment of said addition compound in an oxygen-free protective gas atmosphere under the conditions recited in claim **1**.

3. A process according to claim **2** in which the electrolyte additive is selected from the group consisting of an ammonia addition compound of aluminum chloride and derivatives thereof prepared by heat treating said addition compound in an oxygen-free protective gas atmosphere under the conditions recited in claim **1**.

4. A process according to claim **1** in which the electrolyte additive is selected from the group consisting of a metal chloride-ammonia addition compound and a product derived therefrom by said heat treatment.

5. A process according to claim **1** in which the electrolyte additive contains a salt of the same metal to be recovered from the electrolyte.

6. A process according to claim **1** in which the electrolyte additive contains the smallest possible number of molecules of the addition material.

7. A process according to claim **1** in which the addition compound as electrolyte additive is added to the electrolyte in the presence of an oxygen-free protective gas atmosphere.

8. A process according to claim **1** for the production of titanium by fusion electrolysis of an electrolyte consisting essentially of alkali metal titanium fluoride in which the electrolyte additive is selected from the group consisting of an ammonia addition compound of a titanium halide and a product derived therefrom by heat treating said addition compound in an oxygen-free protective gas atmosphere under the conditions recited in claim **1**.

9. A process according to claim **1** in which the electrolyte additive utilized contains a salt of a metal other than the metal to be recovered from the electrolyte.

10. A process according to claim **1** in which a plurality of electrolyte additives are added to the electrolyte.

11. A process according to claim **1** in which in which the heat treatment of said addition compound is conducted at a temperature above 400° C.

12. A process according to claim **1** in which the heat treatment is continued until evolution of substances from the addition compound terminates.

13. A process according to claim **1** in which the electrolyte additive is a product derived from an addition

compound after heat treatment thereof in a flowing protective gas atmosphere.

14. A process according to claim **1** in which 0.2% to 5% by weight of the electrolyte additive is added to the electrolyte.

15. In a process for producing a free metal selected from the group consisting of titanium, aluminum, magnesium, beryllium, zirconium, thorium, uranium and boron by fusion electrolysis of a molten salt bath containing a halide of the metal to be produced, the improvement of adding to said salt bath an additive consisting of a temperature and humidity stable decomposition product of an ammonia addition compound of a halide of a metal selected from the group consisting of titanium, aluminum, magnesium, beryllium, zirconium, thorium, uranium and boron from which ammonium halide has been removed by heat treatment of the addition compound at 400° C. to 1300° C. in a protective atmosphere of ammonia to form a product consisting of said metal, halogen, nitrogen and hydrogen, the metal content of which is higher than that of the initial addition compound and the nitrogen content of which, as determined by the Kjeldahl method, is substantially less than that of the corresponding nitride and the halogen content, as determined by titration, is less than 10%, in an amount effective to decrease the melting point of said salt bath and lower the temperature at which said salt bath is conductive to an electric current, said free metal being derived primarily from said metal halide of said salt bath.

16. A process as claimed in claim **15** in which the additive is an ammonia addition compound of a halide of a metal selected from the group consisting of titanium, aluminum, magnesium, beryllium, zirconium, thorium, uranium and boron and said additive is added to the salt bath under a protective atmosphere of ammonia.

17. In a process for producing free titanium by electrolysis of a molten Na_2TiF_6 salt bath, the improvement of adding to said salt bath an additive consisting of a temperature and humidity stable decomposition product of an ammonia addition compound of $TiCl_4$ from which ammonium chloride has been removed by heat treatment of the addition compound at 400° C. to 1300° C. in a protective atmosphere of ammonia to form a product consisting of said metal, halogen, nitrogen and hydrogen, the metal content of which is higher than that of the initial addition compound and the nitrogen content of which, as determined by the Kjeldahl method, is substantially less than that of the corresponding nitride and the halogen content, as determined by titration, is less than 10%, in an amount effective to decrease the melting point of said salt bath and lower the temperature at which said salt bath is conductive to an electric current, said free metal being derived primarily from said metal fluoride of said salt bath.

18. A process as claimed in claim **17** in which the additive is an ammonia addition compound of $TiCl_4$ which is added to the bath under a protective atmosphere of ammonia.

References Cited by the Examiner

UNITED STATES PATENTS

2,022,404	11/1935	Claflin	204—71
2,952,599	9/1960	Suchet	204—164
2,974,092	3/1961	Sibert	204—64

OTHER REFERENCES

Fowles et al., J.C.S., 1953, pages 2588–89.

JOHN H. MACK, *Primary Examiner.*

WINSTON A. DOUGLAS, *Examiner.*

H. S. WILLIAMS, *Assistant Examiner.*