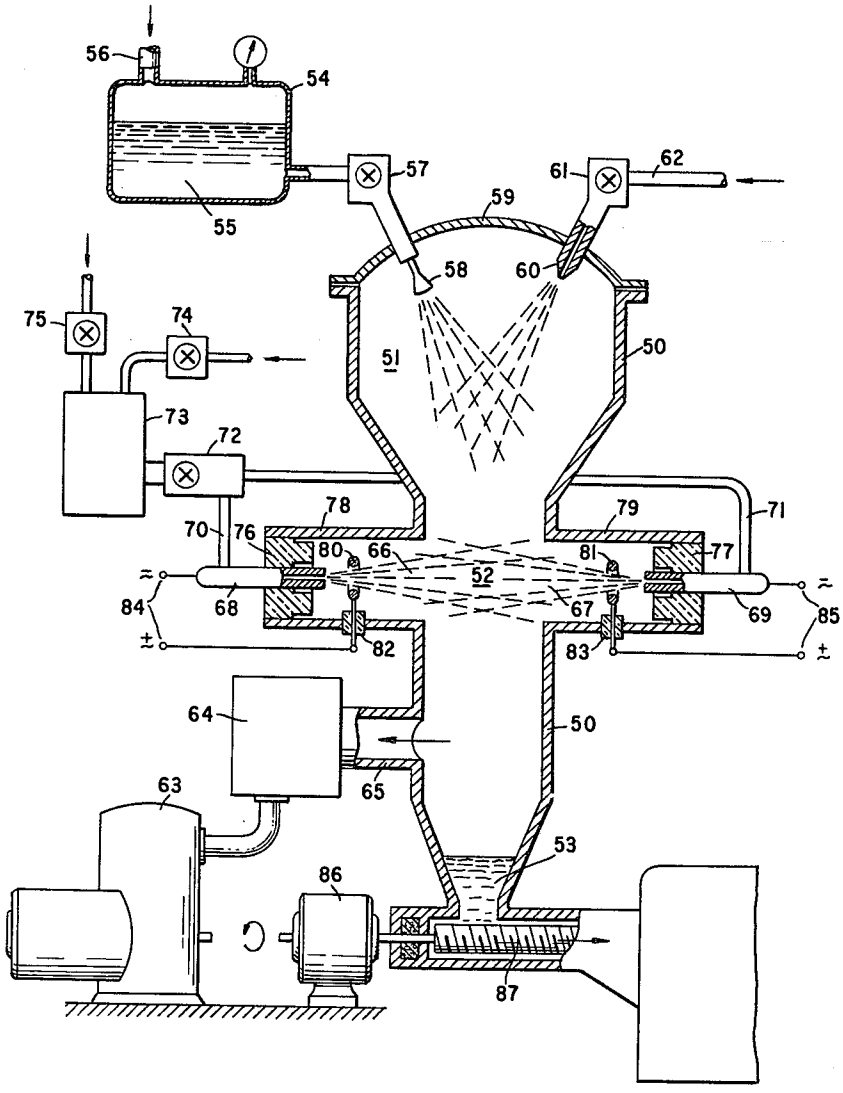
June 2, 1964 B. BERGHAUS ETAL 3,135,675

METHOD OF PRODUCING METALS

Filed July 14, 1959 2 Sheets-Sheet 2

FIG. 2



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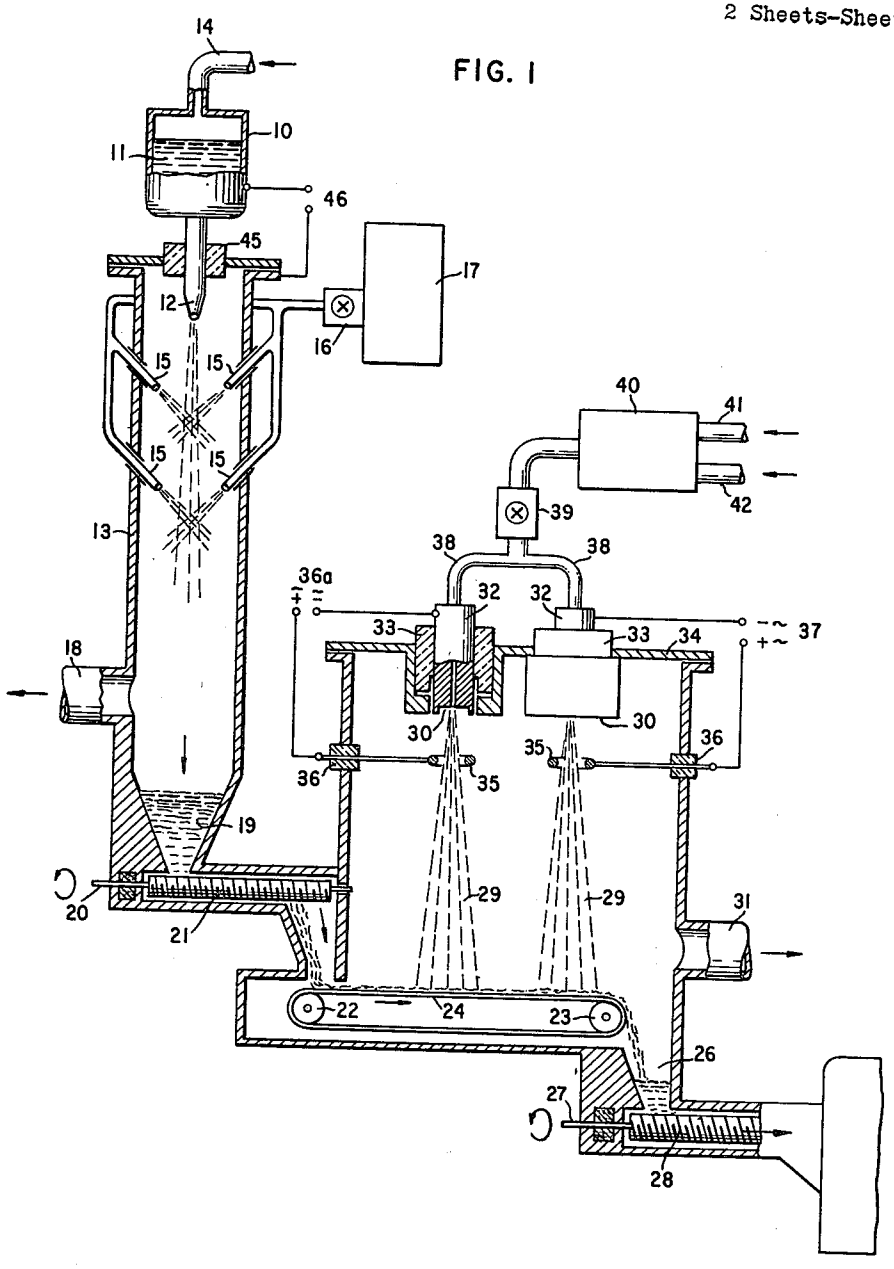
3,135,675

METHOD OF PRODUCING METALS

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2 Sheets-Sheet 1

FIG. 1



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METHOD OF PRODUCING METALS

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The present invention relates to the production of metals from initial substances containing at least one metal halide.

Among the large number of known methods for producing metals there are some in which the metal is obtained from its halide by chemical or electrolytic means. It has also been attempted to process liquid or gaseous metal halides by electrical action and to obtain the metal involved. By way of example, it has been proposed to obtain titanium from titanium tetrachloride by means of an electric arc or by silent electrical discharges.

The present invention is concerned with the production of metals from their halides by means of a process performed in at least two stages. In the first stage, at least one metal halide is converted into a reactive intermediate product by means of nitrogenous and hydrogenous reagents which include mixtures of nitrogen and hydrogen and gaseous combinations thereof such as ammonia. In the second stage, a product which contains at least portions of free metal is obtained from the intermediate product either under the action of an ionized gaseous atmosphere containing at least one of the components nitrogen and hydrogen, or by calcination followed immediately by electrolysis in a fused salt bath.

The method according to this invention is disclosed in greater detail in conjunction with FIGS. 1 and 2 of which each represents a basic diagram of a plant for the performance of the method according to the invention.

The details of the present method will first be described for the production of titanium from titanium tetrachloride, but the method is not limited thereto. It may, in a similar manner, be employed for the production of silicon from $SiCl_4$, of vanadium from VCl_4, of tin from $SnCl_4$ and of aluminum from $AlCl_3$. The metal compounds containing chlorine may also be replaced by suitable metal compounds containing bromine, iodine and fluorine. In all cases, the production process must be performed in at least two stages, the first stage being designed to produce the reactive intermediate product, to which end the metal halide to be processed is treated with nitrogenous or hydrogenous reagents or a mixture thereof.

The performance of this first stage of the manufacturing process will first be disclosed in conjunction with the embodiment of a suitable plant represented in FIG. 1. The metal halide employed is, by way of example, titanium tetrachloride in liquid form, which is held in a tank **10** and designated as **11**. From this tank **10** and through a nozzle **12** the metallic compound **11** is injected as a fine liquid spray into container **13** by means of gas pressure. The necessary gas under suitable pressure is supplied to the tank **10** via line **14**. A gas, such as argon, must be selected which cannot react with the metallic compound **11** and which can act as a protective gas for the intermediate product obtained in the container **13**. In the container **13** the finely dispersed titanium tetrachloride is intimately mixed with a nitrogenous and hydrogenous atmosphere, e.g. with ammonia, which is blown upon the liquid jet via the inclined lines **15**. This gas is supplied to the lines **15** via a control member **16** from tank **17**. Ammonia may be replaced by another compound containing nitrogen and hydrogen, and for many metal halides a mixture of nitrogen gas and hydrogen gas may be employed for the production of the desired reactive intermediate product. The volume of gas supplied is advantageously so adjusted to the volume of the metal halide supplied that the solid intermediate product will absorb as large a portion of this gas as possible. The surplus gas is pumped from the container **13** through the connection **18**, a comparatively small pump power being sufficient if the volumes of reagents supplied are suitably adjusted.

If titanium tetrachloride is sprayed through nozzle **12** and ammonia through lines **15**, the resulting intermediate product will be a solid addition compound containing titanium, which will settle at the bottom of the container **13**. If the volumes of reagents supplied are properly adjusted, the intermediate product will consist mainly of

$$TiCl_4.6NH_3$$

i.e. it will constitute an addition compound formed of titanium tetrachloride and ammonia. This intermediate product is stable if located in a suitable protective gas atmosphere. If desired, such a protective gas, e.g. argon, may be added to the gaseous reagent in the container **17** and be supplied to the reaction container **13** with the same. The protective gas should be selected so that it does not participate in the reaction in the container **13**.

The solid intermediate product is removed from the lower portion of the container **13** by a suitable conveyor, by way of example the worm conveyor **21** driven by the shaft **20**, and supplied to the processing station of the second production stage.

In order to obtain the free metal from this intermediate product, the latter is treated in an ionized gas atmosphere containing at least one of the components nitrogen and hydrogen. According to the processing conditions in this stage, a greater or lesser amount of free metal can be obtained from the intermediate product.

In the embodiment according to FIG. 1, the intermediate product obtained in the first stage is passed through the container **25** on an endless conveyor belt **24** running on rolls **22** and **23**, collected in the funnel **26** and removed from the container **25** by means of a suitable conveyor installation, such as the worm conveyor **28** driven by shaft **27**. The product thereby obtained in the present case will contain at least portions of free titanium metal.

During its passage through the container **25** the intermediate product on the conveyor belt **24** is subjected to the action of the ionized gas jets **29** blown into the said container **25**, by way of example by a pump unit attached to the connection **31**. As the whole inside of the container **25** is supplied only by the gas jets **29** an ionized atmosphere is created which can act on the intermediate product.

The gas jets **29** enter the metallic inner portion **32** via a nozzle-type bore, the said section **32** being electrically insulated from the metallic cover **34** of the container **25** by means of the insulators **33**. Arranged in front of each nozzle **30** is an annular counterelectrode **35** electrically insulated with respect to the metal wall of the container **25** by means of insulators **36**. One metallic internal lead **32** and its associated counterelectrode **35** are connected to the pair of terminals **36***a*, the other metallic internal lead **32** and its associated counterelectrode **35** being connected to the pair of terminals **37**. Suitable arrangements for the obtention of ionized gas jets by means of such nozzles are described in Patent No. 2,837,654 and copending patent application Serial No. 813,760 filed May 18, 1959. The designs and arrangements therein disclosed in greater detail may be employed, mutatis mutandis, for the present method.

The gas held in the container **40** is supplied, under adequate pressure, to the bores of the metallic internal leads **32**, i.e. the nozzles **30**, by lines **38** and the control unit **39**.

The container **40** is supplied with the gases required via lines **41** and **42**, the required gases being either nitrogen and hydrogen or compounds containing both nitrogen and hydrogen.

If an adequate pressure is maintained in container **25** by means of the connection **31** and the gas supplied through the lines **38** with a pressure ensuring that gas jets emerge from the bores of the internal leads **32**, a so-called electrical jet discharge will be set up by means of a voltage of e.g. 150 to 400 volts applied to the pairs of terminals **36** and **37**, the said discharge causing the gas jets **29** to be strongly ionized. The proper mode of operation for the obtention of such jet discharges has been described in the above-mentioned references. Different voltages may be applied to the pairs of terminals **36***a* and **37** in order to obtain jets of varying degrees of ionization.

Where titanium tetrachloride is employed as the initial material and ammonia as the reagent in the first stage, a solid yellowish intermediate product **19** is obtained which will change into a powdery product of a white or grayish color under the action of the ionized atmosphere in the container **25**. Analysis of this product has shown that it contains over 50% of the titanium ion originally present as free metallic titanium in powder form. The product obtained further contains hydrazine chloride, ammonium chloride and a small portion of titanium tetrachloride.

If other metal halides are employed, an intermediate product having the general formula

$$Me_m(Ha)_n.z(N_xH_y)$$

is obtained in the first production stage together with nitrogenous and/or hydrogenous reagents. Me is a metal, Ha a halogen, N nitrogen and H hydrogen, while the indices *m*, *n*, *x*, *y* and *z* express the integral numbers 1, 2, 3, 4 . . . Under the action of an ionized atmosphere consisting of nitrogen and/or hydrogen, this intermediate product will yield a material which contains at least portions of the free metal Me.

In the installation represented in FIG. 1, the two stages of the manufacturing process are each performed in separate reaction chambers, the first being performed in the container **13** and the second in container **25**. With the installation for the performance of the method suitably designed, the two stages of the manufacturing process may be performed during the passage of the materials involved through a common reaction chamber, the first stage being performed upstream of the second. FIG. 2 shows a diagrammatic view of such an installation having a common reaction chamber.

In the installation according to FIG. 2 a common container **50** is provided. The first stage of the manufacturing process during which the intermediary product is obtained is performed in its upper section **51**. The solid intermediate product drops into the lower portion of the container **50** and in so doing passes a zone **52** in which it is subjected to the action of an ionized atmosphere and in which the second stage of the manufacturing process is performed. At the lower end of the container **50**, the product **53** will collect and contain at least a portion of free metal provided that a metal halide has been supplied as the initial material.

Titanium tetrachloride is again taken as one of the initial materials. It is a liquid **55** held in the tank **54** and injected into the upper portion **51** of the container **50** via the control member **57** and a sprinkler-type multiple jet member **58** under the pressure of a protective gas supplied through line **56**. Arranged in the cover **59** of the container **51** besides this multiple jet member **58** is a gas supply nozzle **60** which is in turn supplied by the gas supply line **62** via the control member **61**. Nitrogen and hydrogen or a compound containing nitrogen and hydrogen such as ammonia gas is supplied through line **62**. If desired, a further gaseous component may be supplied to the container **50** as a protective gas, either through line **62** or together with the liquid initial substance **54**, or through a suitable separate gas supply line. A suitable exhausting unit comprising a pump **63** and the separator **64** maintain a prescribed gas pressure in the container **50** via the exhaust connection **65**, i.e. any excess of nitrogen and/or hydrogen or ammonia or protective gas is removed. Portions of the liquid titanium tetrachloride which may have evaporated are removed through the connection **65** and condensed in the separator in order to be returned to the tank **54**. Here, too, the volumes of titanium tetrachloride and gaseous reagents should preferably be so adjusted that the total volume of the substances supplied will form a solid addition compound. If this is the case, the pump power required is comparatively small.

The solid intermediate products obtained in the upper portion **51** of the container **50** sink, under their own weight and aided by the gas flow, in the direction of the exhaust connection **65** and reach a zone **52** of the reaction container in which an ionized gas atmosphere is created. This gas atmosphere is obtained, in the plant represented in FIG. 2, by gas jets **66** and **67** formed by the metallic nozzle bodies **68** and **69** respectively. These nozzle bodies are each provided with a bore which allows the gas supplied through lines **70** and **71** to emerge in the form of two gas jets. In the present embodiment, both nozzle bodies **68** and **69** are supplied with the same gas via a common control member **72**. This need not be so, for both nozzle bodies may be supplied separately. The control member **72** is connected to the mixing container **73** in which the gas or gas mixture required for the jets **66** and **67** is mixed. In the present case, the mixture contains two components supplied to the container **73** via control members **74** and **75** respectively. The gas jets **66** and **67** should be formed by either nitrogen or hydrogen, or by a mixture of nitrogen and hydrogen or by ammonia. The use of a gas mixture formed of ammonia NH_3 and nitrogen N_2 is particularly advantageous. The metallic nozzle bodies **68** and **69** are arranged in insulated relationship in lateral tubular extensions **78** and **79** of the container **50** by means of the insulating members **76** and **77**, respectively. Arranged closely in front of the mouth of the nozzle-type bore in the nozzle bodies **68** and **69** are counterelectrodes **80** and **81** respectively passed, in insulated relationship, through the metal wall of the tubular extensions **78** and **79** by means of insulating bodies **82** and **83**. The metallic nozzle body **68** and the counterelectrode **80** associated with it are connected to the pair of terminals **84**, while the metallic nozzle body **69** with its associated counterelectrode **81** are connected to the pair of terminals **85**. Set up across these pairs of terminals **84** and **85** is an electric field between the nozzle body **68** and **69** respectively, and the counterelectrode **80** and **81** respectively. This is preferably a D.-C. field in which the nozzle body **68** and **69** respectively operates as the cathode. The gas jets **66** and **67** emerging from the nozzle bores are strongly ionized provided that the voltage at the pairs of terminals **84** and **85** is high enough, as has already been described in the above-mentioned patents. The structural details of the designs disclosed in the said patents and the measures described for the obtention of ionized gas jets may here be applied mutatis mutandis.

The nozzle bores in the nozzle bodies **68** and **69** and the dimensions of the lateral tubular extensions **78** and **79** are such as to ensure that the entire cross-sectional area of the passage for the intermediate products produced and falling in the space **51** is uniformly and as intensively ionized as possible. If desired, more than two opposed tubular extension **78** and **79** each having a nozzle **68** and **69** may naturally be provided in order to ensure a sufficiently strong ionization in the zone **52**. By way of example, three gas jets radially converging may be provided, which is of particular advantage if they are supplied with the three phase voltages of a three-phase mains. It is also possible, and advantageous in many

cases, for the solid intermediate products dropping from the portion **51** to pass more than one zone **52**, to which end a corresponding number of lateral nozzles must be arranged one beneath the other along the lower portion of the container **50**. The two gas jets **66** and **67** may also be differently ionized if varying voltages are applied to the pairs of terminals **84** and **85**. This possibility constitutes an advantage if each nozzle body **68** and **69** is provided with a separate gas supply and if different gases are employed for the jets **66** and **67**, e.g. nitrogen for the one jet, and hydrogen for the other.

The powdery substances emerging from zone **52** and dropping will collect in the bottom portion of the container **50** and there form a powdery material **53** which is removed laterally from the container **50** by a worm conveyor **87** driven by the motor **86**. Instead of the worm conveyor **87** here provided, any other suitable removal unit for powdery solid materials may be employed.

The production of the intermediate product in the first stage of the production process may, if desired, be performed under simultaneous electrical action. By way of example, in the plant according to FIG. 1, the nozzle **12** forming the liquid jet may be incorporated in the cover of the container **13** by means of the insulating body **45**. It is then possible by means of an electrical direct or alternating voltage applied to the pair of terminals **46** to set up an electric field between the metallic nozzle **12** and the inner wall of the metallic container **13**, which may exercise an ionizing action and favorably affect the reaction between the reagents. A similar electrical action on the reaction performed in the first stage of the production process may also be obtained in a plant according to FIG. 2 if, by way of example, a cover **59** of the container **50** is formed of an insulating material and a sufficiently strong electric field similar to that in the plant according to FIG. 1 is created between the metallic lines to the sprinkler-type multiple jet member **58** and the metallic wall of the container **50** on the one hand, and the metallic gas nozzle **60** and the wall of container **50** on the other. With the plant according to FIG. 2 it is further possible, if desired, to ionize only the gas entering via nozzle **60** and to dispense with an electric field between the jet member **58** and the metal container **50**.

With the plant according to the embodiments shown in FIGS. 1 and 2, the ionized gas atmosphere required in the performance of the second stage of the production process is formed by a so-called jet discharge which is a variant of the known gas and glow discharges respectively. Other electrical means for the ionization of the atmosphere to be traversed by the intermediate product during the second stage of the process may be employed, by way of example electrical spray or brush discharges as known in high-tension engineering and occasionally termed corona discharges. Furthermore, it is possible to effect ionization of the atmosphere by means of high-frequency gas discharges. Ionization of the atmosphere by means of electric arc discharges is possible as well, but suitable measures must be taken (e.g. the magnetic enlargement of the arc) in order to obtain an area as uniformly ionized as possible without allowing the intermediate products to be detrimentally affected by excessive temperatures. Ionization of the atmosphere by impacting, e.g. by intensive irradiation or by accelerated corpuscules, such as electrons or alpha-rays, is possible as well.

In the performance of the present method it has proved to be of importance for the degree of ionization of the gas atmosphere in the second stage of the production process to be adjusted to the type and volume of the intermediate product to be processed. An excessively intense ionization is just as disadvantageous as one too weak. It has proved of advantage in a plant according to FIG. 1 for the gas jets impinging on the intermediate product to consist of a mixture of NH_3 and N_2 since it seems that the desired chemical reactions of the intermediate product are favorably influenced by the simultaneous recombination of dissociated nitrogen. It is possible that this favorable influence depends on whether exothermic and endothermic chemical processes take place simultaneously of which the thermal balance is relatively adjusted at least substantially.

These intermediate products of the general formula $Me_m(Hal)_n \cdot 2(N_xH_y)$, e.g. $TiCl_4 \cdot 6NH_3$ are all products stable only in the absence of air. In air, and particularly in humid air, they will spontaneously decompose into metal oxides and/or metal hydroxides and ammonium chloride. These decomposition products can be processed into free metal, if at all, only with the greatest difficulty.

It has now been found that calcining in an ammonia flow at higher temperatures, preferably at 900° to 1000° C. will produce a black substance from these intermediate products, which largely consists of TiNCl with the titanium compound and which is stable in air.

It has further been found that this TiNCl will dissolve in melted alkali titanium fluoride or, possibly, in other fused salt baths, e.g. in mixtures of anhydrous $MgCl_2$, $SrCl_2$, $CaCl_2$ etc. and that the metal can be obtained therefrom by fusion electrolysis. It is interesting to observe that titanium in a particularly pure form with at worst just traces of O_2 or H_2 is obtained and that it possesses a low Vickers hardness.

Another preparation for electrolysis consists in fuming off calcined products of TiNCl with small volumes of concentrated nitric acid. The substance will then change into a compound of the formula $TiN(NO_3)$, which is also stable in air and has a whitish color of a slightly greenish cast.

This compound, too, can be dissolved in melted salts and pure titanium be obtained by fusion electrolysis.

Example 1

In a plant similar to that described in conjunction with FIG. 1, 10 gms. titanium tetrachloride was processed. The liquid titanium tetrachloride was atomized by means of nitrogen gas and mixed with 10 liters NH_3 gas. A sulfur-yellow solid addition compound was spontaneously formed, which chemical analysis proved to be $TiCl_4 \cdot 6NH_3$. The two initial products supplied were converted into the yellow intermediate product to the extent of nearly 100%. This intermediate product can be kept indefinitely under protective gas, in the present case under nitrogen gas, but will rapidly disintegrate into a white compound consisting mainly of TiO_2 in air. A small portion of NH_4Cl can also be detected.

The yellow intermediate product was subjected to an ionized gas jet formed of nitrogen with the exclusion of air, i.e. under protective gas. The nozzle bore employed had an inner diameter of about 1 sq. mm. and the gas supply amounted to about 3–5 litres per minute. Between the counterelectrode **35** and the nozzle body **32** an electrical voltage of 150 to 190 volts was applied and a negative pressure of about 30 mm. Hg maintained in the container **25**. Under these circumstances, an electrical power of about 40 watts had to be supplied. The metallic nozzle body **52** formed the cathode of the glow discharge and, respectively, jet discharge set up. In view of the small quantity of intermediate product, it was piled only on one point of the conveyor belt **24** which was then placed underneath the ionized gas jet **29** and treated for four hours. The intermediate product changed its color from sulfur-yellow into white to grey.

After this processing period the product obtained was removed from the container **25** and dissolved in water, a deposit of about 2 gms. being filtered off, which proved to be free metallic titanium. The titanium yield in the present example thus amounted to about 80%. Titration of the filtered solution by means of an iodine solution according to Stolle indicated a content of 5.7 gms. hydrazine chloride $(N_2H_5)Cl$. The balance of the solution consisted of ammonium chloride NH_4Cl and small quantity of unchanged titanium tetrachloride.

Example 2

20 gms. pure $TiCl_4$ was atomized into a container by means of N_2 gas, into which 20 liters of pure, dry NH_3 gas was introduced thorugh another bore. The intermediate product of $TiCl_4.6NH_3$ described in Example 1 formed spontaneously. It was passed into a tube under an ammonia flow and heated for one hour to 500° C. in a calcining furnace while NH_3 was passed through. The product was freed from excess NH_3 by passing through pure nitrogen and then charged into an electrolysis cell under N_2 protective gas. The said cell consisted of a graphite crucible which was kept at a temperature somewhat above the melting temperature of Na_2TiF_6 by means of an electric heating coil.

From 20 gms. $TiCl_4$ approx. 14 gms. calcined product of a brown-yellow color was obtained which was dissolved in 150 gms. of an electrolyte of Na_2TiF_6 kept at 850° C. After the calcined product had dissolved in the electrolyte, heating in the upper portion of the crucible was so reduced that a thin solid crust formed at the surface, and the N_2 flow discontinued. Electrolysis was performed at 4 volts and 3 amps. during 6 hours. Thereafter, a solid regulus of 3.6 gms. Ti had formed at the bottom of the cell, corresponding to 72% of the Ti employed.

We claim:

1. A process for producing metals of the class the halides of which form addition compounds with ammonia comprising forming an ammonia addition compound of a halide of a metal of said class and subjecting said ammonia addition compound to the action of an ionized atmosphere produced by an electrical discharge to thereby produce free metal, said process being conducted under a protective atmosphere to exclude oxygen.

2. A process as claimed in claim 1 wherein said free metal is a member selected from the group consisting of titanium, vanadium, tin, aluminum and silicon.

3. A process as claimed in claim 1 wherein said ionized atmosphere contains at least one component selected from the group consisting of hydrogen and nitrogen.

4. A process for producing metals of the class the halides of which form addition compounds with ammonia comprising reacting a halide of a metal of said class with a gaseous member selected from the group consisting of ammonia and a mixture of nitrogen and hydrogen to form an ammonia addition compound of said metal halide and subjecting said ammonia addition compound to the action of an ionized atmosphere produced by an electrical discharge to thereby produce free metal, said process being conducted under a protective atmosphere to exclude oxygen.

5. A process as claimed in claim 4 wherein said free metal is a member selected from the group consisting of titanium, vanadium, tin, aluminum and silicon.

6. A process as claimed in claim 4 wherein said ionized atmosphere contains at least one component selected from the group consisting of nitrogen and hydrogen.

7. A process as claimed in claim 4 wherein said gaseous member is ionized by an arc-free electric field.

8. A process for producing titanium comprising reacting titanium tetrachloride with ammonia in a first reaction zone to form an ammonia addition compound of said titanium tetrachloride, collecting said ammonia addition compound, transferring said ammonia addition compound to a second reaction zone, and subjecting said ammonia addition compound to ionized nitrogen produced by an electrical discharge in said second reaction zone whereby free titanium is produced, both of said reaction zones containing a protective atmosphere to prevent oxygen from contacting said ammonia addition compound.

9. A process for producing a metal selected from the group consisting of titanium, vanadium, tin, aluminium and silicon comprising reacting a halide of said metal in a first reaction zone with a gaseous member selected from the group consisting of ammonia and a mixture of nitrogen and hydrogen to form an ammonia addition compound of said metal halide, transferring said ammonia addition compound to a second reaction zone, and in said second reaction zone subjecting said ammonia addition compound to an ionized atmosphere containing at least one component selected from the group consisting of nitrogen and hydrogen to thereby produce free metal, said ionized atmosphere being produced by an electric discharge and both of said reaction zones containing a protective atmosphere to prevent oxygen from contacting said ammonia addition compound.

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