

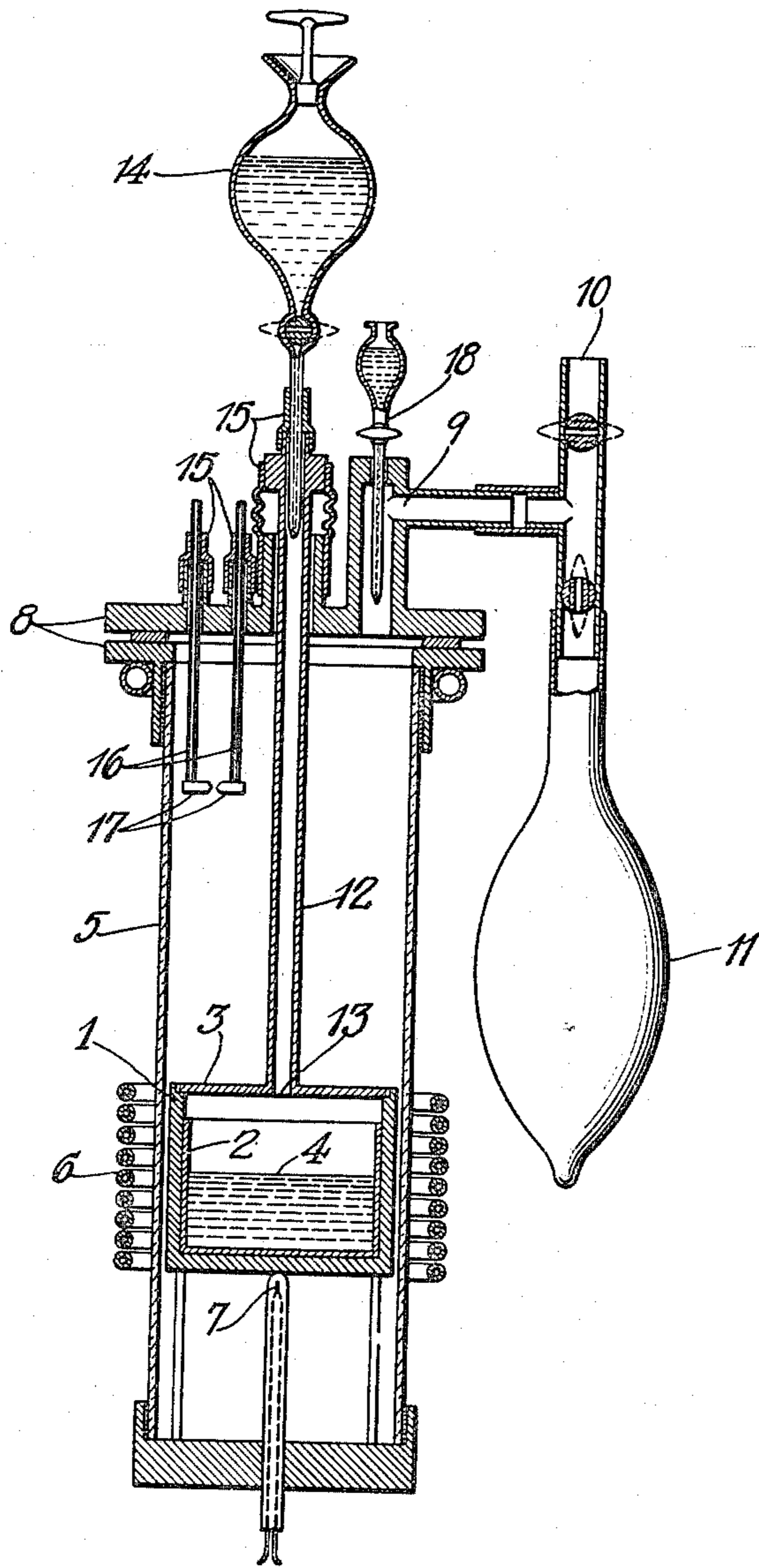
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METHOD FOR MANUFACTURING TITANIUM AND ALLOYS THEREOF

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METHOD FOR MANUFACTURING TITANIUM
AND ALLOYS THEREOF

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My invention relates to a method for producing titanium and alloys thereof.

Titanium has hitherto been known as a hard and brittle metal not capable of being deformed in a warm or cold state. Above all, minute traces of oxygen render the titanium cold short, although the capability of the metal of being rolled in a warm state is only impaired to a slight extent. A cold short titanium cannot be employed for most purposes so that only such methods of manufacture appear suitable which produce from the beginning a titanium poor in or free of oxygen.

An object of my invention is to produce titanium which is ductile. Another object is to even render the titanium cold-malleable. An object similar to the foregoing but considered from another point of view is to produce titanium which is free of oxygen as compared with the aforementioned products. Other more detailed objects of the invention will become apparent from the following description.

According to the invention, a halide of titanium is caused to chemically react with an alkaline earth metal in the presence of a protective gas while maintaining normal pressure. Preferably the tetrachloride of titanium is employed as a halide. In order to prevent the absorption of oxygen the alkaline earth metals are heated in the presence of a protective gas to temperatures as high as possible and which are only limited by the crucible material or by the boiling point of the reducing metal. In this manner a highly sintered and in most cases even fused metal is produced which is hardly any more chemically attacked when being subsequently treated with acids and which does not tend to form colloids.

Since according to the invention the reduction is effected under normal pressure, the reaction need not take place in thick-walled flasks, which would limit the use of the method considerably. By "normal pressure" I understand a pressure in the neighborhood of atmospheric pressure, in particular a pressure which is not substantially higher than the atmospheric pressure. The reaction can also be effected below atmospheric pressure, for instance in vacuum or in a partial vacuum in which the pressure of argon is below atmospheric pressure; however if the pressure is too low the magnesium evaporates and difficulties arise owing to the evaporation of the tetrachloride. Both reagents may be brought into the apparatus at the same time and in the proper stoichiometric proportion, with a small ex-

cess of the reducing agent, if desired. Such excess has the advantage that from the beginning always the proper mixture is caused to react so that the efficiency is better than if the chloride is caused to drip onto the highly heated alkaline earth metal which at the beginning is present in great preponderance.

In accordance with the properties of the different substances to be used, the method according to the invention can be carried out in different ways.

As a rule, magnesium or calcium is preferable as reducing metal from an economical point of view, although lithium, strontium and barium may also be employed. Calcium possesses a much greater affinity to chlorine and permits to effect the reduction theoretically at about 1400° centigrade although in practice such a high temperature is not permissible owing to the use of steel apparatus. Consequently, the calcium presents the advantage that a much better thoroughly fused titanium can be produced. However, magnesium has a much lower boiling point (1070° centigrade) and a smaller but sufficient affinity to chlorine. The advantages resulting from the use of magnesium lie on the one hand in the low price, which is outstanding on account of the low specific gravity of magnesium. On the other hand the low specific gravity permits a better utilization of the space, and the durability when exposed to air is extremely more favorable than that of calcium. Both metals should be used in as pure a state as possible free of oxides. In this regard the magnesium again is more advantageous, since it is available commercially in a high degree of purity and it is very easy to purify at a low temperature by sublimation, whereas calcium must be freed of the impurities by distillation before being used. The reaction temperature in the case of magnesium is kept as close as possible to the boiling point in order to produce a compact metal free of colloids. Upon exceeding the boiling point the condensed magnesium clogs the supply tube. The temperature of some of the pieces of titanium increases up to the fusing point of the titanium, i. e. to about 1850° centigrade, although the average temperature of the bath is not higher than the evaporating point of magnesium. Local overheatings of the individual pieces of titanium therefore exceed the boiling point of magnesium to a considerable extent without a compensation of the temperature taking place.

As to the protective gas, an inert gas, particularly argon, or hydrogen is employed as reducing

agent when using magnesium. In this case argon has the advantage that it excludes any danger of explosion. By the use of calcium only an inert gas is suitable, since hydrogen is absorbed by calcium under development of hydride. Although mixtures of hydrogen and inert gas may be employed, the hydrogen of such mixture is absorbed by calcium at the beginning of the reaction and is again liberated during the further reaction. Titanium also absorbs hydrogen to a high degree which, however, escapes above 1000° centigrade. Furthermore, titanium containing a considerable amount of hydrogen may be very difficult to be worked up during the subsequent high vacuum process owing to the continuous developing of gas. For this reason an inert gas is to be preferred also when using magnesium as a reducing agent.

The protective gases must be tested for percentage of oxygen. As a rule, commercial argon contains considerable amounts of oxygen and nitrogen. According to the invention care must be taken to use a protective gas as poor as possible in oxygen. This may be easily accomplished by atomizing alkaline earth metal in the argon-filled reaction chamber, for instance by evaporating magnesium, calcium or barium in a small molybdenum crucible heated by high frequency or by means of arcs or high-voltage sparks produced between electrodes consisting of the metal to be evaporated. The chamber thus "gettered" is prepared for effecting the reduction. The gettering has, furthermore, the advantage that humidity and above all the water film which has deposited on all objects are also eliminated. When opening the furnace after the test the air enters and the slight traces of evaporated alkaline earth metal chlorides retain the air humidity in a chemically combined form. However, under circumstances this humidity will not be retained by the alkaline earth metal fog. Therefore it may be advantageous to cause before or after the atomization of the alkaline earth metal an effective drying agent to act, $TiCl_4$ proving to be most suitable. Some drops of this compound are caused to enter the furnace. The chamber filled up with argon absorbs the chloride as gas which reacts with the residual humidity.

Of the titanium halides applicable, tetrachloride ($TiCl_4$) particularly is of practical value. The fluorides are all solid and therefore cannot be readily introduced into the reaction chamber. The alkaline earth fluorides resulting therefrom are insoluble in water and are therefore difficult to be eliminated according to the wet process. The same applies to the double fluorides in connection with the alkaline metals. Iodides and bromides which are also solid at room temperature are not so suitable owing to the relatively high price. Of the chlorides only the tetrachloride is liquid.

Dichloride is pyrophoric and also difficult to produce as is the trichloride. However, the tetrachloride can be purchased on the market with a sufficient degree of purity. Owing to its fluid property it may be introduced in the apparatus in the form of a uniform and regulatable current, for instance, with the aid of a dripping device. It either acts directly as liquid on the highly heated reducing metals when falling drop by drop thereon, or it evaporates previously as a gas and reacts in this state. Of course, the titanium tetrachloride may also be pre-gasified; however, this method does not present any particular advantages.

The above-described reaction would not be practical without the use of particular crucible materials at the high temperatures which are necessary to attain a compact metal. Iron reacts directly with the fusing titanium and a fusion of the whole mass will take place if care is not being taken to protect the steel wall against the very reactive titanium. The steel crucible is therefore lined according to the invention interiorly with sheets consisting of highly refractory metals. To this end, molybdenum has proved most suitable; however also tungsten, tantalum, niobium, vanadium, chromium, titanium, zirconium, hafnium and thorium may be employed. The surface of these sheets is somewhat oxidized so that the diffusion of the lining material into the steel wall is prevented. On the other hand a coat of titanium precipitates on these sheets so that finally only a titanium surface comes into contact with the titanium freshly produced. In the case of the mentioned metals the diffusion of titanium is so slight that they may be employed for a period of any duration. Massive crucibles consisting of these highly refractory metals may be used, but they are too expensive.

As a rule, the reaction is so initiated that the magnesium is raised to the suitable temperature of about 800° centigrade and then the chloride may drop onto the magnesium. Owing to the development of heat the reaction is automatically maintained and after the reaction has commenced the heating in the case of large furnaces may be adjusted from the outside. By a regulated rapid but controlled introduction of the tetrachloride, or by a controlled supply of a mixture of tetrachloride together with magnesium, the reaction may be maintained according to an initial ignition method. In all cases the temperature must be so controlled that a surpassing of the boiling point of the magnesium is avoided, which may be attained by adjusting the outer heating and by regulating the instilling speed.

The method according to the invention may also be used for the manufacture of metal alloys or compounds. For instance, iron-titanium may be manufactured by causing $TiCl_4$ to instil onto magnesium in an atmosphere containing argon and in the presence of carbonyl iron. The iron may be also introduced into the reaction chamber as gaseous iron trichloride. Finally, in some cases where it is possible to form an alloy, an alloy of the alkaline earth metals may be employed, such as, for instance, calcium aluminum, in which case aluminum titanium is produced. In a similar manner titanium boride and titanium carbide may be produced by the reaction of BCl_3 or $CCl_4 + TiCl_4$ on the one hand and of magnesium on the other hand. However, this method is, as a rule, not so suitable, since said alloys may be produced with a greater certainty by direct fusion or by sintering.

At the end of the reaction the crucible is filled with a mixture of fused alkaline earth metal chloride and compact titanium in large lumps. According to the invention the crucible content is bored, for instance on the lathe, with the aid of high-speed steel, which is easily possible owing to the slight hardness of titanium (about 280 Brinells). In this case the salts act as a support and the boring can be effected up to a slight distance from the molybdenum lining. The advantage of this method consists in that titanium chips are obtained which have become brittle by the cold boring and therefore may easily be pul-

5 verized. The mixture removed by boring is subsequently treated with water which removes $MgCl_2$, and then with diluted hydrochloric acid. In the meantime the pulverization is effected as far as possible in a wet state. The chips are ground according to the invention in a steel mortar or in a steel ball mill. Porcelain parts should not be employed when pulverizing in order to prevent the mixture from absorbing oxygen from ground-off porcelain particles. The pulverization is effected to such an extent as to permit the passage of the particles through a screen of about 150 meshes/cm.² and thereafter the particles are treated in a weak solution of hydrochloric acid by the application of heat. The mixture is rinsed in such a manner as to be free of chlorine and is subsequently etched with a slight amount of hydrofluoric acid. The purpose of this is to brightly etch the surface of the titanium and to convert alkaline earth metal as well as the salts thereof into fluorides free of oxygen. In this manner the metal grains containing magnesium or calcium are protected against the further action of humidity by the formation of a thick layer of fluoride. The washing is carried out with distilled water and alcohol and the subsequent drying at a temperature of 120° centigrade.

10 The dried titanium powder free of halogens, as a rule, still contains small quantities of gas. It may be preferable to remove this gas, particularly hydrogen, by an annealing treatment under high vacuum. The powder is heated under high vacuum to a temperature of 500 to 700° centigrade, in which case the greater portion of the hydrogen is forced out and the metal loses its cold hardness. Consequently, it is very soft and plastic after this treatment and may be pressed to compact briquets. The annealing temperature should preferably not exceed 700° centigrade, since otherwise an agglomeration of the powder takes place so as to entail a subsequent pulverization which is difficult owing to the ductility.

15 The pressed briquets are then sintered under high vacuum closely below the fusing point. In this case a small amount of occluded alkaline earth metal as well as the last traces of fluoride escape. When cooled down the sintered bodies may be given the desired shape.

20 However, it is preferable not to operate according to the sintering process but according to the fusing process, since when fusing, certain substances escape under formation of gas bubbles, which substances obviously exert a great influence on the capability of the titanium of being deformed. The hardness decreases when adopting the fusing process by about 50 Brinells.

25 The fusing process presupposes a suitable base or crucible for the titanium. Owing to the great reactivity of this element the selection of suitable highly refractory base or crucible materials is very limited. Alumina and zirconium oxide cannot be employed, since the formation of alloys takes place. It has been found that alkaline earth metal oxides, above all calcium oxide, may be employed after they have been overburned under high vacuum, provided that when fusing the fusing point of the titanium is not considerably exceeded. Also the titanates of these oxides may be employed under the same conditions. Somewhat above the fusing point of the titanium a sudden reaction takes place, in which case alkaline earth metal evaporates and the titanium is oxidized. Thorium oxide has proved to be

of particular advantage. This substance, after being overburned under high vacuum, ensures a good fusing base applicable within wide limits of temperature.

5 Furthermore, highly refractory metals, such as tungsten and molybdenum, as well as highly refractory compounds, such as titanium boride, titanium carbide, tungsten carbide or the like may be employed as fusing base or as crucible material. In the case of a slight overheating they are hardly dissolved in titanium; when proceeding with precaution a contamination of the titanium can be avoided by the use of these bases. For instance, crucibles are made of titanium carbide having titanium as binding agents, into which crucibles the titanium is fused, for instance, by means of high frequency. By suitable devices the crucible content may be cast under high vacuum into a mold placed thereunder.

10 When employing a metal base titanium-plated layers may be produced. If, for instance, titanium is fused on a thick tantalum, niobium, molybdenum or tungsten sheet this bimetal may be rolled as a whole in a subsequent rolling process. In a similar manner also wires may be produced which are titanium-plated, since the titanium when fused wets very rapidly the surfaces and creeps. Such titanium-plated highly refractory metals permit to attain new effects in the construction of electron tubes. Thus the getter effect of the titanium may be combined with the great resistance of molybdenum to heat, or without foregoing such getter effect considerable savings in tantalum or niobium may be effected by means of a titanium plating on tantalum or niobium. The different coefficient of expansion permits to produce in the same manner bimetallic springs of considerable thermal strength.

15 The above-described subsequent treatment of the reducing product may, however, be also effected in another way. When applying the wet process there still remains the danger of introducing of low oxides. The alkaline earth metal chloride may be eliminated from the crucible content by melting the content in a purified argon atmosphere or under vacuum after tilting the crucible over a mold which receives the molten and purified mass. After cooling down, the now loose pieces of titanium may be broken out and fused under high vacuum, thus permitting the residual chloride and alkaline earth metal to escape in a gaseous form.

20 The fused or sintered titanium is first to be deformed in a heated state in order to break up the crystalline structure or to close the pores. This is best accomplished in suitable salt baths in order to exclude gases. The titanium is heated in a salt bath which is preferably liquid and which must not chemically attack the titanium, and the titanium is rolled with the liquid salted hide. A mixture of carbonates of the alkali metals, preferably K_2CO_3 , Na_2CO_3 or Li_2CO_3 , has proved particularly suitable. In the case of a low temperature also nitrates may be employed. The deformation in a heated state is effected preferably at a temperature of about 700° centigrade. It can later on be continued up to about 400° centigrade. The stretching may be carried out at low temperatures below 500° centigrade by heating with the aid of a gas flame or an electric furnace, since at such temperatures a protective film impermeable to gas is produced. After a deformation to a great extent in a cold and heated state the metal can be rolled in a

cold state, i. e., by about 20%, intermediate annealings in salt baths or in high vacuum or under pure protective gas being applied. Short annealings in open air at temperatures below 500° centigrade are permissible for thick cross-sections.

The method according to the invention will now be further elucidated by reference to the drawing which shows an example of a device for carrying out one of the possible ways in which the invention may be realized. A thick-walled steel crucible 1 which is lined inside with a sheet 2 of molybdenum 1 to 2 mm. in thickness and is closed by a thin iron sheet cover 3 serves to receive the reaction metal 4, in this case 345 g. (magnesium sublimed). The crucible 1 is lowered in the reaction furnace proper which consists of a quartz tube 5 provided exteriorly thereof with a high-frequency induction coil 6. At the bottom of this steel crucible 1 is arranged a measuring point for a thermoelement 7 which permits a control of the mean temperature. The head 8 of the quartz tube which is sealed up and water cooled carries a connecting branch 9 for the evacuation and the filling up with argon. Another inlet in the form of a tube 12 for the titanium tetrachloride is supported on the crucible cover and extends into the crucible through an opening. The upper end of the tube 12 is provided with a dripping device 14 which must be capable of being exactly regulated. The sealing against atmosphere is effected with the aid of flexible tubes 15. Two electrodes 16 are insulatedly arranged in the cover 8 and are provided with two calcium rods 17 which permit starting an arc in the gas chamber above the reaction crucible. Finally, a dripping device 18 is provided for introducing above the reaction crucible a small quantity of $TiCl_4$ through a bore of the cover. The crucible is heated by means of high frequency when being evacuated to about 200° centigrade, the small amount of about 1 ccm. $TiCl_4$ is caused to drop through the above-mentioned bore, then the furnace chamber is filled up with 99.6% argon supplied by a rubber balloon 11. An arc is started between the calcium electrodes 17, for which purpose 2 g. calcium are evaporated. The operating chamber is then prepared for the continuation of the method, since argon had completely been freed of oxygen and nitrogen by atomized calcium. The humidity had been previously neutralized by $TiCl_4$. The temperature of the crucible is then raised to an average temperature of 800° centigrade by heating by means of high frequency, at which temperature the magnesium 4 is already fused, and the main amount of $TiCl_4$ is now rapidly dropped into the crucible. At the beginning, the absorption takes place very rapidly and the temperature increases rapidly. Care should be taken to see that the temperature does not exceed the boiling point of the magnesium, and if a maximum temperature not higher than 950° centigrade measured at the bottom is chosen cloggings are prevented with certainty. The temperature is regulated either with the aid of the high-frequency part 6 or by decreasing the instilling speed. As soon as about 600 ccm. $TiCl_4$ has been instilled the greatest portion of magnesium is consumed and the reaction proceeds much slower. Further 50 ccm. are now caused to drop into the crucible while increasing the temperature above the boiling point of the magnesium, i. e., about 1150° centigrade, whereby occluded magnesium is evaporated out of the

fused mass and deposited on the crucible cover. A clogging is no longer to be feared owing to the small quantity of remaining Mg. The duration of the instilling process amounts to 1 to 1½ hours. The rubber balloon 11 is continuously observed. By its movements it can be seen whether the instilling is too slow or too rapid. In proper operation, the filling of the balloon 11 should not show any sudden rise and must be always rather uniform. With increasing temperature it inflates to a slight extent owing to the expansion of the argon. After shutting off the heating, the cooling down occurs at first in an atmosphere containing argon. Then the furnace is evacuated with an oil pump which is connected with conduit 10 and sealed with the aid of P_2O_5 against air humidity in order to remove the last traces of $TiCl_4$, which would be undesirable when removing the content from the crucible. After cooling down under vacuum or under air to room temperature the crucible can be removed. It is then bored on a lathe up to very close to the molybdenum lining. The chips are freed at first from the main quantity of $MgCl_2$ with the aid of water, subsequently treated for a short time with diluted hydrochloric acid and then, after neutralization of the solution if necessary, ground in a steel mortar to 150 meshes/cm.². The chips are then treated with a little amount of hydrochloric acid under application of heat until no gas development is observable, and are then washed out in absence of chlorine. A short subsequent treatment with a quantity of 2 ccm. concentrated hydrofluoric acid in a platinum bowl removes films of oxide and produces on occluded magnesium (if any) protective MgF_2 -coatings free of oxygen. After washing the chips with distilled water and alcohol they are dried at a temperature of 120° centigrade. The powder is freed from hydrogen to a great extent within three hours under a high vacuum at a temperature of about 600° centigrade, whereupon it is formed into briquets and fused on a ThO_2 -base under high vacuum. When heated in a bath consisting of 50% Li_2CO_3 and 50% Na_2CO_3 the whole is rolled with the fused salt cover at a temperature of about 700° C. As soon as the grain is broken the product can be cold stretched by 20% in a saltpeter bath by intermediate annealing treatments. The metal presents a hardness of less than 280 Brinells. A hardness of more than 320 Brinells indicates the presence of oxygen. The metal then may be still hot rolled but is very cold short.

In the above-described example 269 g. titanium were produced, which corresponds to an efficiency of 92.2%. The consumption of magnesium amounted to 1.29 kg. per kg. of titanium produced. In the case of considerable charges an efficiency of approximately 100% was attained, in which case the consumption of magnesium dropped to 1.1 kg. per kg. of titanium produced.

The light titanium which can be produced by the wet process in the finest distribution may be employed to advantage as flash light powder. The titanium possesses in the range of the highest sensitiveness of photographic emulsions and in that of the best optical transparency of lenses a much higher spectral emission than any other metal, for instance, as zirconium hitherto employed for that purpose. The continuous radiation of a titanium flash light is also much more intense. As compared to zirconium, titanium has the advantage of being less expensive

while the atomic and specific weight is much smaller. It may be employed in a pulverized form mixed with oxidizing agents or in the form of thin foils in oxygen ampoules which contain electric ignition devices.

What is claimed is:

1. The method of producing cold-malleable titanium consisting in causing a halide of titanium to chemically react with an alkaline earth metal at an elevated temperature below the boiling temperature of said metal and in the presence of a protective gas while maintaining normal pressure.

2. The method of producing cold-malleable titanium, consisting in causing titanium tetrachloride to chemically react with magnesium at an elevated temperature below the boiling temperature of magnesium in the presence of hydrogen while maintaining normal pressure.

3. The method of producing cold-malleable titanium, comprising the steps of providing a reaction chamber with a protective gas, liberating said gas in said chamber from oxygen, causing a halide of titanium to chemically react at elevated temperature with an alkaline earth metal in said reaction chamber while bringing said halide and said metal gradually into contact with each other so as to avoid sudden increases of the pressure in the reaction chamber, and maintaining said pressure at a value in the neighborhood of atmospheric pressure.

4. The method of producing cold-malleable titanium, consisting in causing a halide of titanium to chemically react with an alkaline earth metal in the presence of a protective gas, maintaining said reacting substances at a temperature between the fusing point and the boiling point of the alkaline earth metal, and maintaining the reaction at normal pressure.

5. The method of producing cold-malleable titanium by causing a halide of titanium to react in a protective atmosphere within a closed reaction chamber with alkaline earth metal, consisting in heating said metal up to a temperature above the fusing point and near the boiling point of said metal, gradually supplying said halide to said metal so as to prevent sudden increases in temperature and pressure, and maintaining the pressure within said reaction chamber during said reaction at a value not substantially higher than atmospheric pressure.

6. The method of producing cold-malleable titanium by causing a halide of titanium to react with alkaline earth metal in a protective atmosphere within a reaction chamber having heating means, said method comprising gradually contacting said halide with said metal, heating said reaction products by said heating means to a temperature between the fusing point and the boiling point of said metal until the reaction is initiated, cutting off the operation of said heating means, controlling the speed of said contacting so as to maintain said temperature during the further progress of the reaction, and maintaining the pressure in said reaction chamber during said reaction at a value not substantially higher than atmospheric pressure.

7. The method of producing ductile titanium, consisting in placing alkaline earth metal on a highly refractory base consisting of a non-alloying substance with respect to titanium, heating said metal and causing a halide of titanium to chemically react on said metal in the presence of a protective gas at an elevated temperature,

and maintaining said reaction under normal pressure.

8. The method of producing ductile titanium by means of a sealed furnace and of a crucible lined with highly refractory metal comprising the steps of placing alkaline earth metal into said crucible, placing said crucible into said furnace, filling the furnace with inert gas, heating said crucible to a temperature above the fusing point and not substantially higher than the boiling point of said selected metal, gradually introducing a titanium halide into said crucible so as to react with said selected metal, maintaining the pressure in said furnace during said reaction at a value not substantially higher than atmospheric pressure, removing said crucible, boring the reaction product out of said crucible so as to obtain cold deformed and therefore brittle chips, pulverizing said chips, degasifying the powder, briquetting the powder, and fusing the briquettes in vacuum.

9. The method of producing ductile titanium which comprises the steps of causing a fluid halide of titanium to gradually react in the presence of a protective gas with heated alkaline earth metal, maintaining during the reaction the temperature between the fusing point and the boiling point of said metal and maintaining the pressure at a value not substantially higher than atmospheric pressure, reducing the reaction product to small particles, liberating the product from its halogen component and annealing the remaining titanium component in vacuum, pressing the resulting material to briquettes, and solidifying the briquettes by heating them under vacuum on a highly refractory base of a non-alloying substance with respect to titanium at the heating temperature employed.

10. The method of producing ductile titanium which comprises the steps of causing a fluid halide of titanium to gradually react in the presence of a protective gas with heated alkaline earth metal, maintaining during the reaction the temperature between the fusing point and the boiling point of said metal and maintaining the pressure at a value not substantially higher than atmospheric pressure, removing and pulverizing the reaction product, liberating the powder from its undesired components so as to retain comminuted titanium, pressing the titanium to a shaped body, placing said body on a base consisting of a non-alloying substance selected from the group consisting of highly refractory metals, their highly refractory compounds, and highly fired oxides of alkaline earth metals and compounds of said oxides.

11. The method of producing ductile titanium which comprises the steps of causing a fluid halide of titanium to gradually react in the presence of a protective gas with heated alkaline earth metal, maintaining during the reaction the temperature between the fusing point and the boiling point of said metal and maintaining the pressure at a value not substantially higher than atmospheric pressure, removing and pulverizing the reaction product, liberating the powder from its undesired components so as to retain comminuted titanium, pressing the titanium to a shaped body, placing said body on a base consisting of a non-alloying substance selected from the group consisting of thorium dioxide and highly refractory mixtures containing thorium dioxide.

12. The method of producing ductile titanium comprising the steps of causing a fluid halide of titanium to gradually react in the presence of

a protective gas with heated alkaline earth metal, maintaining said metal during the reaction at a temperature between the fusing and the boiling point, maintaining a pressure not substantially higher than atmospheric pressure, heating the reaction product under high vacuum so as to fuse out the halide component, and solidifying the remaining titanium component by fusing.

13. The method of producing ductile titanium comprising the steps of causing a fluid halide of titanium to react at normal pressure and in the presence of a protective gas with heated alkaline earth metal, maintaining said metal during the reaction at a temperature between the fusing and the boiling point, reducing the reaction product so as to retain only the titanium component, solidifying the titanium component by heating it up to at least its sintering temperature, heating the solidified product in a salt bath, and rolling the product under a fused salt layer at a temperature above 500° C.

14. The method of producing ductile titanium by means of a heatable reaction chamber closed against the atmosphere, comprising the steps of

placing alkaline earth metal into said chamber, filling said chamber with an inert gas, heating said metal to a temperature between the fusing point and the boiling point, gradually instilling a titanium halide into said metal while maintaining an instilling speed which prevents a sudden increase in temperature, and maintaining the pressure in said chamber at a value not substantially higher than atmospheric pressure.

15. The method of producing ductile titanium by means of a heatable reaction chamber closed against the atmosphere, comprising the steps of placing alkaline earth metal, filling said chamber with argon, heating said metal to a temperature between the fusing point and the boiling point, gradually instilling titanium tetrachloride into said chamber so as to react with said heated metal, maintaining the instilling speed at a rate which prevents the temperature from increasing substantially above said boiling point, and maintaining the pressure in said chamber at a value not substantially higher than atmospheric pressure.

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