Feb. 25, 1958 V. L. HANSLEY ET AL 2,824,799

PROCESS FOR SINTERING AND RECOVERING SPONGE METAL

Filed Aug. 24, 1955 3 Sheets-Sheet 1

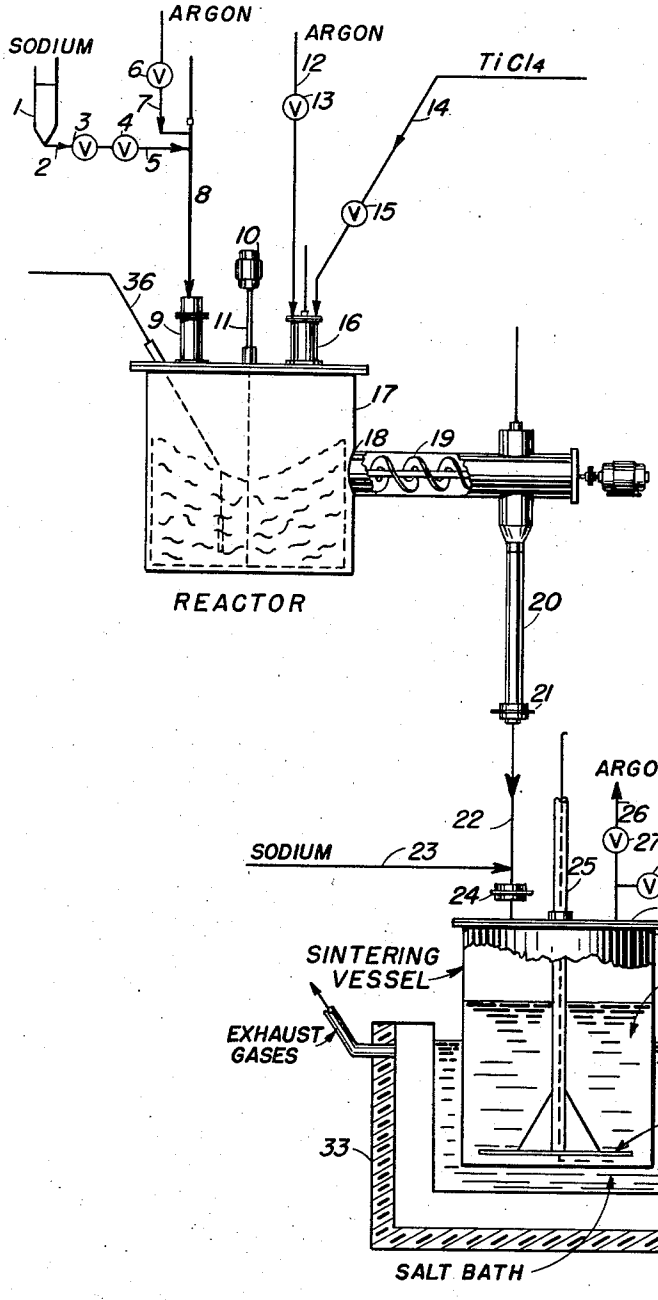


FIGURE I

VIRGIL L. HANSLEY
STUART SCHOTT
INVENTORS

BY E. J. Berry

Feb. 25, 1958 V. L. HANSLEY ET AL 2,824,799

PROCESS FOR SINTERING AND RECOVERING SPONGE METAL

Filed Aug. 24, 1955 3 Sheets-Sheet 2

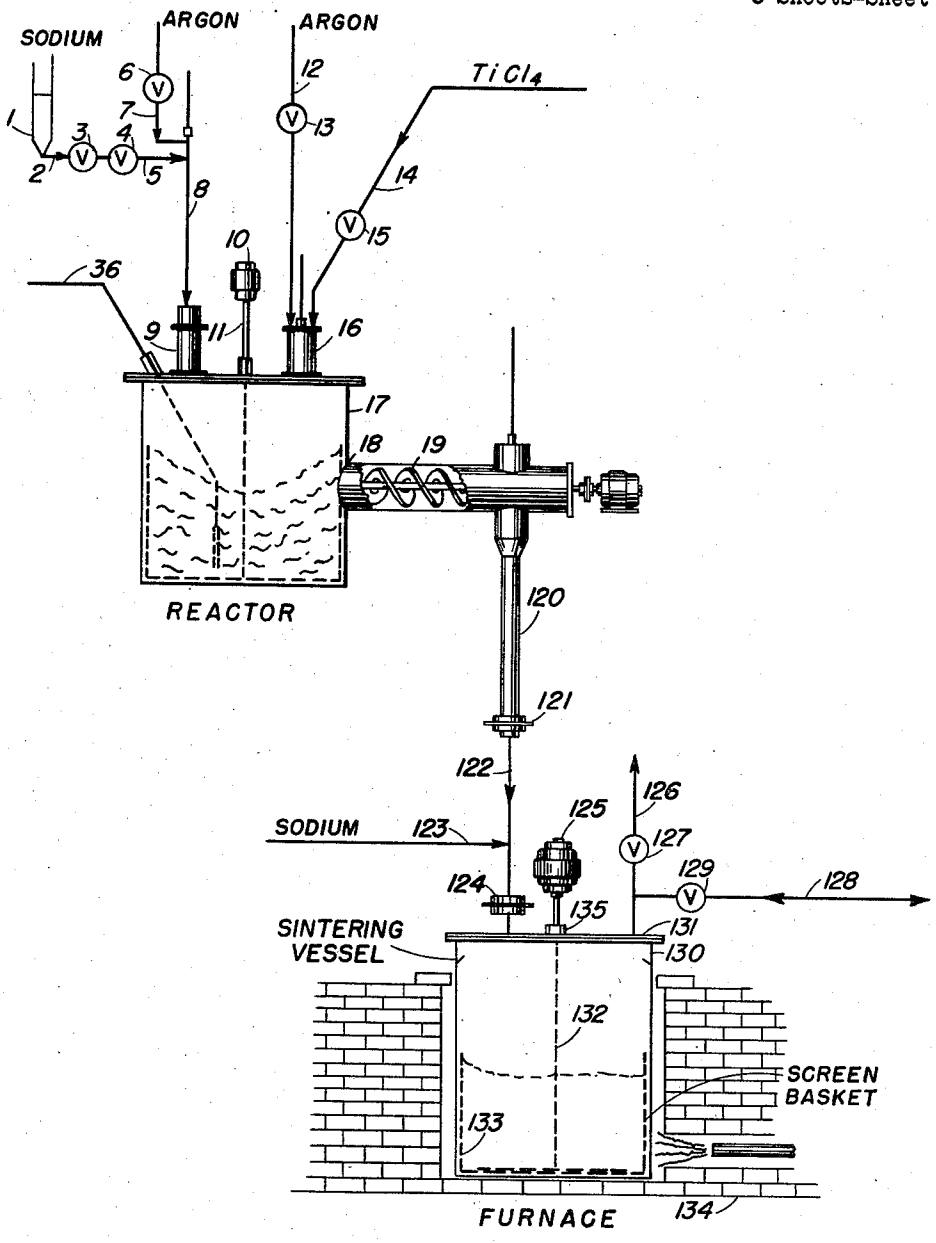


FIGURE II

VIRGIL L. HANSLEY
STUART SCHOTT
INVENTORS

BY E. J. Berry

Feb. 25, 1958 V. L. HANSLEY ET AL 2,824,799

PROCESS FOR SINTERING AND RECOVERING SPONGE METAL

Filed Aug. 24, 1955 3 Sheets-Sheet 3

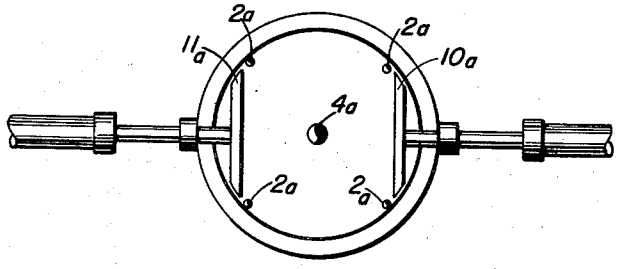


FIGURE V

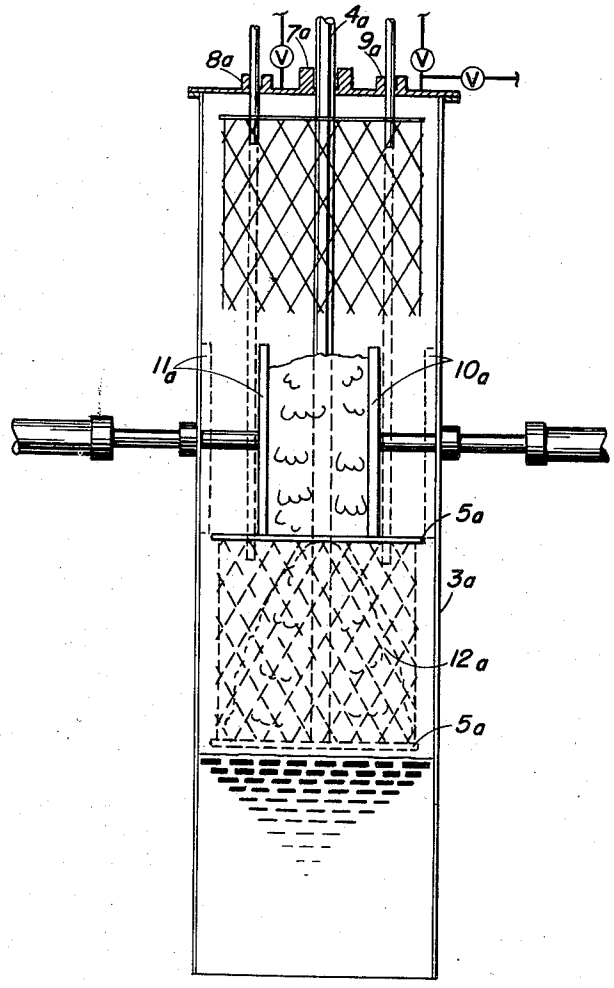


FIGURE IV

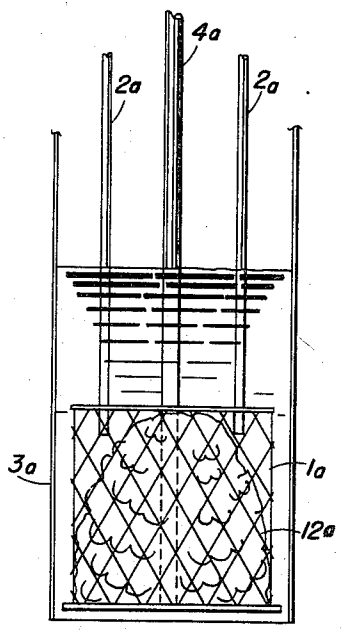


FIGURE III

VIRGIL L. HANSLEY
STUART SCHOTT
INVENTORS

BY E. J. Berry

United States Patent Office 2,824,799
Patented Feb. 25, 1958

2,824,799

PROCESS FOR SINTERING AND RECOVERING SPONGE METAL

Virgil L. Hansley and Stuart Schott, Cincinnati, Ohio, assignors to National Distillers and Chemical Corporation, New York, N. Y., a corporation of Virginia

Application August 24, 1955, Serial No. 530,276

2 Claims. (Cl. 75—223)

This invention relates to new and useful improvements in the sodium reduction of a titanium chloride such as titanium tetrachloride to produce titanium sponge in a substantially continuous manner and, more particularly, it relates to methods for production, recovery, and removal of titanium sponge from the salt by-product in which titanium sponge is formed from a finely divided titanium-salt powder previously produced in a separate step at a much lower temperature. More particularly, this invention relates to the mechanical removal of formed sponge from the fused salt zone in a manner which permits the major portion of salt to drain away or otherwise be separated from the sponge while said salt is in the liquid or molten state.

In some processes for making titanium sponge, wherein titanium tetrachloride is reduced in a batch operated process, making use of magnesium metal as the reducing agent, the reduction of titanium tetrachloride by magnesium and the sponge growth phases of the reaction are made to take place simultaneously in the same vessel, and at relatively elevated temperatures, that is, above 600° C., and up to and including sodium chloride fusion temperatures. This method of operation may result in the formation of hot spots in the reaction mixture where local temperatures are much higher than the 700–800° average temperature of the reaction mixture. In large scale practice, local temperatures may actually reach the melting point of titanium metal, because fused particles of titanium sponge are common and are found in the final product. Under such severe reaction conditions, by-product salts, and even incompletely reduced subhalides of titanium, become so completely surrounded or encased in dense massive titanium sponge that aqueous leaching operations are difficult or impractical. Volatilization of the residual by-product salt from the titanium sponge may be necessary. Drainage is used to remove the bulk of the salt by-product while still molten but, even after this, the drained sponge still contains substantial portions of residual salt which must be leached out or distilled away. Besides yielding a titanium sponge product which is difficult to purify, the simultaneous operation of the chemical reaction and sponge growing phases of the operation results in the formation of a type of sponge which adheres very tightly to the sides and bottoms of the reaction vessels making removal difficult. At times it may even be necessary to machine out the titanium sponge using a lathe.

In a more recently developed and improved sodium reduction process, these two steps of reduction and sponge formation are separated, thereby permitting each to be carried out in a more efficient manner and under more controlled conditions. The first or chemical reduction step is operated continuously and, preferably, at a relatively low temperature such as 150° to 600° C.

In operation, sodium and titanium tetrachloride are introduced more or less continuously or semi-continuously into a stirred reactor preferably containing at least a

quantity of the preformed mixture of finely divided solid products of the reaction as shown:

$$4Na+TiCl_4 \rightarrow Ti+4\,NaCl$$

As the above indicated product mixture forms, it is continuously or semi-continuously withdrawn from the vessel. This mixture consists of finely divided solids and substantially contains the theoretical percentage of titanium metal mixed with salt, that is, Ti:4NaCl (17 wt. percent Ti). The reduction process can be run at a temperature of from 150° to 600° C., or higher, as long as a finely divided solid reaction mixture is produced which can be easily handled by mechanical means and agitated with conventional type stirrers and mixers.

This reaction mixture may be cooled and stored or it may be immediately transported by means of a screw conveyor or other convenient transfer device to the sintering or soaking vessel which is the second or sponge formation zone. Thus, the heat of reaction during the reduction is liberated at a relatively low temperature level where control is relatively simple and thus materials of construction create no serious problems and, most important, the reduction process is operated substantially continuously and therefore is susceptible to more rigorous controls.

The sponge growing operation is a complex process and not strictly crystallization phenomena, although some crystals of titanium may form as a secondary and/or auxiliary phenomenon and in a relatively minor amount. Crystals which are formed appear to be the result of a secondary process associated with the presence of traces of unreduced titanium sub-chlorides. Such titanium crystal formation is usually associated with a deficiency of sodium in the sintering mixture in relation to the stoichiometrically equivalent amount. A slight excess of sodium and somewhat higher sintering temperatures, for instance, in the region of 900° to 1000° C., are consistent with minimum amounts or even the absence of titanium crystals. Sponge growth proceeds faster at the higher temperatures. The rate of sponge formation can be ascertained approximately by the density and tenacity of the sponge produced.

The sponge growing process commences almost immediately upon substantial melting of the by-product sodium chloride and proceeds well as long as the mass remains molten. The titanium metal collects and agglomerates in the form of fine particles which then become matted together as a sponge. The filaments are generally round in cross section and of smooth surface. They have the appearance as if the titantium had melted and solidified, although this sponge forming phenomenon takes place at 800–1150° C., almost 1000 centigrade degrees below the melting point of titanium. It is important to control the temperature during the sponge growing at a level substantially below the melting point of titanium since high temperatures may result in adverse chemical reactions.

The titanium metal as it forms tends to squeeze molten salt from the contracting titanium fiber network. The contraction of titanium sponge, away from the walls of the vessel, to form a column in the center is influenced by the conditions of the heating or sintering period and may also be influenced by other variables such as presence of sodium and sub-chlorides of titanium and by degree of agitation.

For the heat soaking stage, heat is introduced into the mass during a period of time when the by-product salt becomes molten. Temperatures above 1150° C. are to be avoided since they may cause reversal of the reduction reaction with consequent formation of sub-chlorides of titanium and alloying of the metal with such impurities as iron and nickel. The preferred temperature for

soaking is 850–1050° C. After the salt has melted substantially completely, mild agitation may be employed, if desired, to hasten the growth of the fine particles to form larger particles and thus agglomerate more rapidly.

It is necessary to provide a satisfactory means for holding the mass of titanium sponge which thus forms, said holding means being designed in such a manner that the mass of titanium sponge can be physically removed and separated from the fused salt phase and allowed to drain while the salt is still fluid and while maintaining an atmosphere or argon or other inert gas around the sponge while salt is draining or otherwise being removed therefrom.

This invention is concerned with the recovery of titanium and its separation from the molten salt in the sintering vessel. This can be accomplished in a number of related ways. It is also further highly desirable that the titanium sponge be recovered as free as possible from the molten by-product sodium chloride prior to leaching operations. In order to accomplish these objectives, the titanium is separated by physical removal of the titanium sponge from the molten sodium chloride with means for permitting as much drainage of sodium chloride as is possible. Various specific methods for accomplishing this are described hereinafter. It is also highly desirable to remove additional amounts of molten sodium chloride from the titanium sponge, for instance, by compressing and compacting the hot sponge while at a temperature above about 800° C., and while either in the molten sodium chloride or in the vapor space above. Specific embodiments are described hereinafter.

The titanium sponge so recovered and handled is a dense, compacted product consisting of from 55 up to 95 weight percent titanium and from 45 to 5% salt.

In one embodiment of the invention, during the sponge forming or heat soaking stage, a titanium rod or similar device, equivalent for the purpose, is immersed in the Ti:NaCl mixture. The titanium sponge forming during the heating operation collects and adheres around this titanium rod or similar device. This sponge generally adheres sufficiently so that the rod can be withdrawn upward and in the removal process pull the sponge mass into the vapor space above the molten salt. This sponge can then be removed through a suitable lock and the molten salt drained away. The soaking vessel can then be refilled with Ti:NaCl mixture without opening it or the reactor to the air and the cycle repeated. It is also of value to employ in conjunction with the rod and as another and further embodiment of the invention, a perforated bottom plate or support attached at or near the bottom of the rod which can be used to assist in removing the titanium from the sintering zone.

A study of the titanium so produced has disclosed that the titanium sponge at the sponge formation temperature and during that period exhibits a more or less marked plasticity. Although a column of sponge so formed in a small diameter sintering vessel can readily be lifted or otherwise removed from the molten salt by means of a rod or a rod and bottom plate and support, such a procedure is not so satisfactory for use in a larger sintering vessel because of the plasticity of the sponge. The inherent weight of the sponge causes it to spread out at the bottom when lifting is attempted and the plastic titanium touches and wedges against the sides of the vessel when only partly withdrawn from the salt bath in which it was formed.

It has been found, however, that a metal screen or "punch plate" basket of light gauge metal attached to the bottom lift plate, effectively prevents sponge wedging against the sides of the vessel while being raised from the molten salt. The metal basket or screen is preferably positioned with rather close clearances within the vessel. Because of dilution of titanium in the fused salt mixture, not enough titanium forms between the screen and the walls of the vessel to cause the lifting device to bind. Both the sides and bottom of the basket are perforated with sufficient holes to permit rapid drainage of the fused by-product salt.

In order to effect the removal of the sponge for drainage by lifting it from the molten salt in this manner, it is necessary to operate the sintering vessel with the level of the titanium molten salt mixture such that there is a free space of ⅖ to ⅓ of the height of the sintering vessel. While it is herein described that the sponge is lifted only just above the bath of by-product salt and there allowed to drain and cool, it is not intended to limit the invention thereto. It is intended to cover the withdrawal of the hot titanium sponge, while still above the melting point of salt, completely out of and away from the sintering zone.

Another embodiment of this invention involves a further removal of molten salt over and above that which is drained away during lifting of the mass of sponge into the vapor space above the molten salt. One method for accomplishing this desired result is the compression of the sponge while it is at a temperature above the melting point of the by-product sodium chloride and while it is located either in the molten salt or in the vapor space above. A means for accomplishing this compression of titanium sponge for further removal of by-product salt is described below in which the titanium sponge is compressed between surfaces to force out the molten salt. Operating thus, after sintering is complete at a temperature above the melting point of sodium chloride, the sponge is lifted by means of any suitable lifting device into the vapor space above the molten by-product sodium chloride. At this point the top of the sponge mass is positioned between the rolls. The rolls are pressed toward each other and then operated so as to pull the sponge mass upward through the rolls and in the process to squeeze a major portion of the remaining by-product sodium chloride out of the sponge and thus put it in a massive form which is suitable for direct arc melting.

Another method for achieving this result involves lifting the titanium sponge into the open space between the two plates of a press. When in place, the movable plate is actuated by a hydraulic system to squeeze the titanium sponge directly into a shape suitable for use as an electrode in a direct arc melting process.

In either case after the compression step has been finished, the sintering vessel and its contents are allowed to cool. The titanium mass is then removed and may be processed to an ingot in a consumable electrode furnace.

The compacted titanium mass as obtained in this process analyzes up to 95% titanium metal. This titanium sponge can be varied in properties from soft or low density material to high density material by varying the conditions of the sintering operation and the degree of agitation during the heat soaking step and the drainage and/or compression used during removal.

It is a further important feature of this invention to carry out the sintering operation in the presence of an excess of sodium, as about 0.01 to 5 weight percent over the stoichiometrically equivalent amount. It is desirable to operate the final stages of sintering, that is, after any subhalides present have been reduced, at a temperature where the excess sodium volatilizes out of the fused salt-titanium mixture. Thus, a shelf can be provided which catches and retains such excess sodium out of and above the fused salt mixture. As the temperature is raised during the sintering step, the excess sodium metal distills out into vapor space. An alternate procedure is to provide a side-arm to distill the sodium out of the sintering vessel into a separate receiver for recovery.

There are numerous advantages to this process. The density of the titanium sponge and its final salt content can be controlled. For instance, a titanium sponge can be produced which is both easy to leach free of remaining by-product salt with water and also has a structure

which permits its being readily crushed to a suitable size without involving undue labor or mechanical work. However, it is also possible to produce a dense sponge having only residual amounts of sodium chloride and which may be directly arc melted to ingot titanium.

Both the reduction and heat soaking reaction vessels are maintained free of gases with which titanium may react at elevated temperatures. Examples of such undesirable gases are oxygen, nitrogen, hydrogen, and the like. Preferably, the reactors should be blanketed at all times with an inert gas. It is preferred to use such inert gases as the rare gases and, of special importance for commercial use, are argon and helium. If desired, the sodium employed is stored and used under the same protective blanket.

Referring to the drawings:

Figure I is a sectional view of apparatus which may be employed in practicing this invention for the preparation and recovery of titanium sponge;

Figure II is also a sectional view of apparatus similar to that shown in Figure I with a different sponge recovery means;

Figure III is a sectional view of a modified sintering vessel useful in the apparatus shown in Figure I;

Figure IV is a sectional view of sintering apparatus wherein the raised sponge and hydraulic press plates **10***a* and **11***a* are specifically shown; and

Figure V is a cross sectional view taken on a horizontal plane of the section immediately above hydraulic press plates **10***a* and **11***a* of sintering vessel **3***a* in Figure IV.

The following examples will further serve to illustrate and describe the invention although it is not intended to limit the invention specifically thereto.

Example 1

The equipment and details of the process are further shown in Figure I, the operation of which is described below, as one embodiment of the invention. Referring to the drawing, reactor **17** is provided with agitator **11**, consisting of a power source **10** and suitable supports, shaft, and propeller and/or blades adapted to keep the reactor contents in a state of agitation. Provision is made for the continuous or at least semi-continuous introduction into reactor **17** of sodium from tank **1** through lines **2**, **5** and **8**, through which the flow is controlled by valves **3** and **4**, and thence into the reactor by inlet pipe **9**. Inert gas (argon) may be introduced into the reactor zone by line **7** controlled by valve **6**. Provision is also made for the introduction into reactor **17** of titanium tetrachloride via line **14**, controlled by valve **15**, and thence into the reactor by inlet pipe **16**. Inert gas (argon) may additionally or alternatively be introduced via line **12** controlled by valve **13**. The temperature is measured and controlled by means of thermocouple **36**. Suitable heating and/or cooling means are employed in conjunction with reactor **17**.

A stoichiometric titanium and by-product salt mixture (Ti:4NaCl) from 2190 parts (4.8 wt. percent excess) of sodium and 4380 parts of titanium tetrachloride is prepared by charging the aforesaid reactants in a continuous manner into stirred reactor **17** maintained under an argon blanket. The reaction temperature is about 250–300° C. The titanium-salt powder is discharged via outlet **18** as formed after a heel of approximately 1500 parts of the finely divided mixture has been built up in reactor **17** into a sintering vessel.

The finely divided solid mixture of sodium chloride and titanium is discharged via outlet **18** from reactor **17** through pipe **19** which is suitably equipped with a screw device or other conveyor system for transferring finely divided solids. The solids in line **18** are discharged into line **20**, in which flow is controlled by slide valve **21**, and thence pass into line **22**. If additionally sodium is is required for optimum heat soaking conditions, such sodium is added via line **23**. The solid mixture is passed through valve **24** into sintering vessel **30**, which is constructed of a heat resistant metal, has a cover **31** and preferably at least carries a liner of mild steel. The contents of sintering vessel **30** are likewise maintained under a blanket of inert gas (argon) which is vented, if desired, via pipe **26** controlled by valve **27**. Additional inert gas may be introduced via line **28**, controlled by valve **29**. This sintering vessel may be provided with agitation means if desired. The sintering vessel is positioned within a molten salt bath **33** suitably equipped for heating and for inlet gas and air and outlet exhaust gases.

The sintering vessel is equipped with a "lift rod" **25** to which is attached a bottom plate **32** with suitable supports. Both plate and rod are made of a material resistant to the elevated temperatures and reactants. For example, they can be fabricated of titanium metal. The vessel is cleaned, purged with argon and then evacuated after heating to a dull red. It is then filled with argon and allowed to cool prior to charging the titanium-salt powder which consists of the approximate stoichiometric composition of 17% titanium and 83% sodium chloride.

The charged sintering vessel is heated at a temperature from 850° C. to 1150° C. for a period of about 8.5 hours. The sponge which forms as a sponge mass in the center of the fused salt is lifted free from the molten salt and molten salt allowed to drain. The lifting can be done mechanically or manually. The entire sintering vessel is then lifted from the furnace and allowed to cool. The cooled vessel is opened. The column of titanium sponge formed averaged between 2 and 2½" in diameter by 16" in height, and contained 50% titanium and 50% by-product sodium chloride. This compares with a mass of not more than 35% titanium content when the sponge is allowed to remain in the molten salt followed by cooling and chipping away the solid salt from the sponge. The contraction of the sponge unexpectedly takes place not only in relation to the sides of the vessel but also in a vertical condition. The recovered titanium metal is finally leached free of by-product salt with water and dried. The yield is 900 parts. This titanium has a Brinell hardness of 170 and a nitrogen value of 0.08%. The dried sponge is of porous consistency and fairly light weight or low density.

Example 2

A schematic diagram for carrying out another embodiment of the invention is shown in Figure II. This process is described in more detail below. A charge of 79,200 parts of finely divided titanium-sodium chloride powder (Ti:4NaCl) is prepared from sodium and titanium tetrachloride in a continuous manner under argon as described above in Example I. This mixture is transferred by line **120** controlled by valve **121** into sintering vessel **130**. This vessel is fitted with lifting bar **132** attached to a perforated bottom plate as described in Example I. This lifting bar operates through packing gland **135** in cover **131** of the vessel. The cover **131** is welded in place on the sintering vessel. The above amount of titanium-salt mixture is then transferred to the vessel, followed by a charge of 80 parts of additional sodium added via line **123**. This is to insure a slight excess during the sintering operation. All operations were performed under an atmosphere of argon which is vented, if desired, via pipe **126**, controlled by valve **127**. Additional inert gas may be introduced via line **128**, controlled by valve **129**. After charging, the sintering vessel is lowered into furnace **134** and the temperature brought up slowly to 850–870° C. at which temperature, sintering is allowed to proceed for a period of 12 hours. Then just before removing from the furnace the lifting device **125** is attached to the hoist and raised. To complete drainage of the salt from the sponge, the lifting device is raised only about four inches. During this raising, it jams or sticks and can not readily be lifted further,

The sintering vessel **130** is then removed from the furnace. Upon opening the vessel, it is found that the plastic titanium sponge which has formed has been forced outward against the sides of the sintering vessel by the upward pressure on the bottom of the sponge, during the sponge lifting operation.

After cooling completely to room temperature, the vessel is opened and 12,500 parts of titanium sponge recovered by aqueous leaching, spinning on the centrifuge and drying. This metal sponge shows hardness of 137 to 150 Brinell in different sections and an average nitrogen content of 0.038%. It is a more dense sponge, but still fibrous in nature, than that in Example I above. The sponge has a tenacity which permitted easy breakdown to useable size material. It is mass leached easily free of salt and gives a dried sponge with a chloride content of 0.03.

An exactly similar run is carried out as that described above except that a ¼" stainless steel screen **133** is employed as a basket which was welded to the bottom of the lifting plate at various spots around its periphery as shown more specifically in Figure II. With this variation, the plastic sponge titanium product is readily lifted above the molten salt in the vessel to permit more complete drainage of the molten salt therefrom. The titanium sponge is leached with water and dried as described above. Average hardness is found to be 148 Brinell.

Example 3

A run exactly similar to that described in Example I is prepared except that the sintering vessel is modified as illustrated in Figure III. The lifting device is similar to that shown in Figure II except that the stainless steel screen is not welded to the bottom of the lifting plate but is merely positioned loosely around the periphery thereof.

Example 4

The positions of the titanium sponge mass **12***a*, stainless steel screen **1***a* and lifting rods **2***a* and **4***a* are shown in Figure III prior to lifting.

The position of the lifting rods are shown in cross section in Figure V.

After sintering is complete, the titanium sponge is raised on lifting plate **5***a* to the upper position shown in Figure IV by operation of lifting rod **4***a* connected to plate **5***a*. Simultaneously the stainless steel screen **1***a* is raised by operation of lifting rods **2***a*. Lifting rods

2*a* and **4***a* extend upward through packing glands **7***a*, **8***a* and **9***a* in cover **6***a* of the sintering vessel. During the sponge lifting operation, the plates **10***a* and **11***a* of the hydraulic press are positioned as shown by the dotted lines.

The sponge mass is lifted until the top surface of lifting plate **5***a* is just below the bottom edges of the press plates **10***a* and **11***a*. The stainless steel basket is then lifted to the upper position shown following which the plates of the hydraulic press are operated to squeeze out the residual salt from the mass of titanium sponge, while the mass is still at a temperature above the melting point of sodium chloride following sintering.

The vessel and contents are allowed to cool, after which the compressed mass of titanium sponge is removed. It is in suitable condition for direct arc melting to ingot and analyzes over 95% metallic titanium.

What is claimed is:

1. In a process of production of a titanium sponge by heating at a temperature of about 850° to 1050° C. a mixture comprising finely divided titanium metal and sodium chloride wherein the sodium chloride is essentially in a molten state at the end of the heating period, the improvement which comprises carrying out said heating in a closed heating zone containing a perforated lifting zone containing a mixture of finely divided titanium metal and sodium chloride and, at the end of said heating period while the sodium chloride is molten, lifting the perforated lifting zone, containing titanium sponge formed during said heating, out of contact with the molten body of sodium chloride in the heating zone and permitting adhering molten sodium chloride to drain from the titanium sponge in said lifting zone while the lifting zone is out of contact with the body of molten sodium chloride and while the titanium sponge is not exposed to the atmosphere.

2. The process of claim 1 wherein said heat treatment is carried out in the presence of about 0.01 to 5 weight percent excess sodium.

References Cited in the file of this patent

UNITED STATES PATENTS

2,439,216	McLellan	Apr. 6, 1948
2,556,763	Maddex	June 12, 1951
2,676,882	Hatch	Apr. 27, 1954
2,707,679	Lilliendahl et al.	May 3, 1955