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PRODUCTION OF ULTRAPURE TITANIUM NITRIDE REFRACTORY ARTICLES

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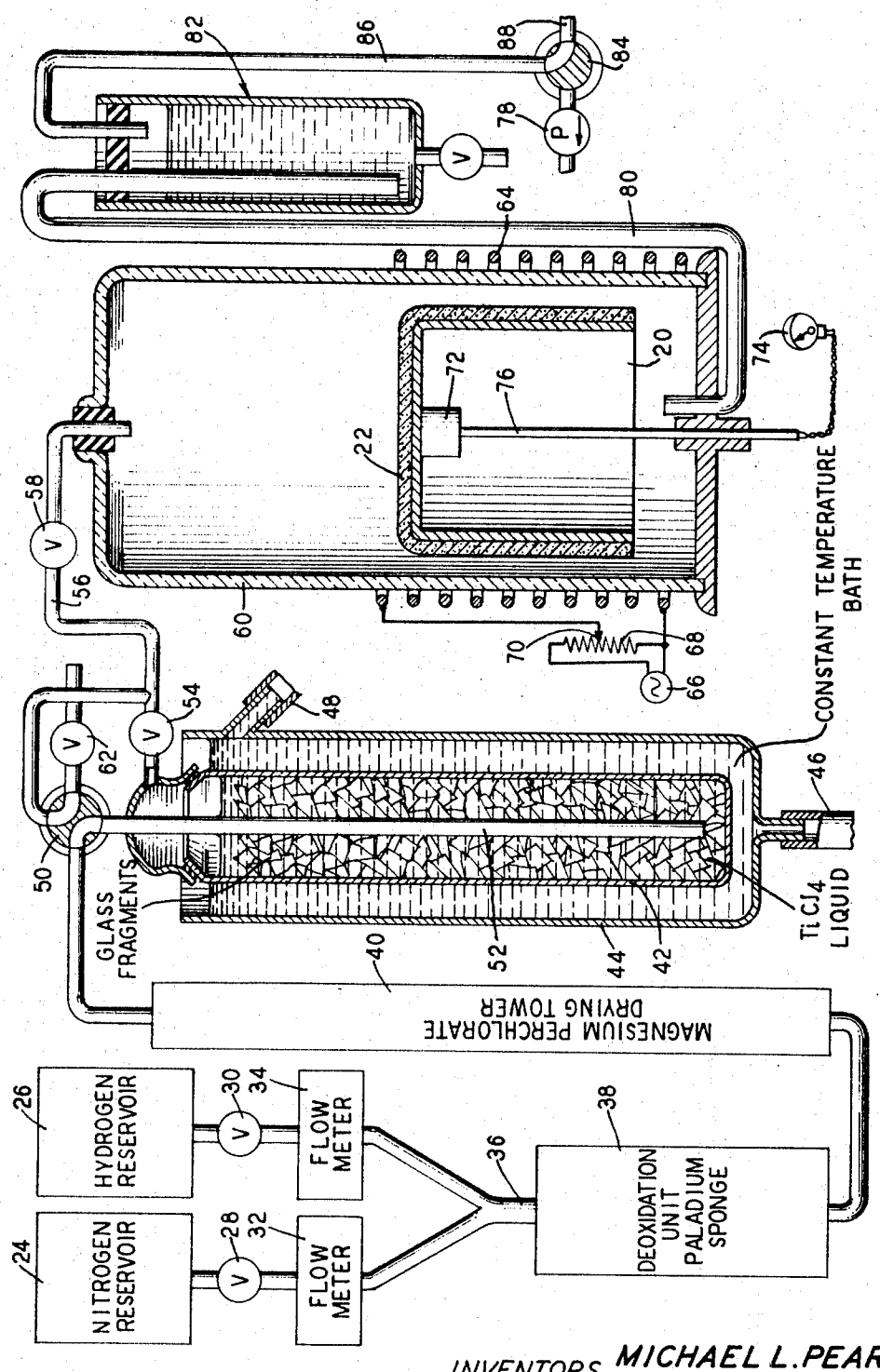


FIG. 1

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FIG. 2

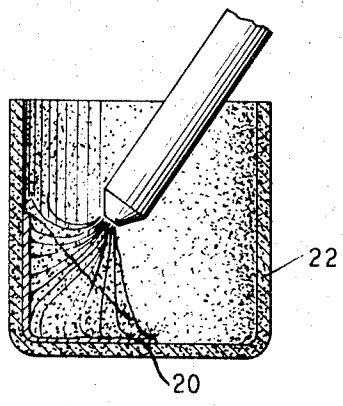
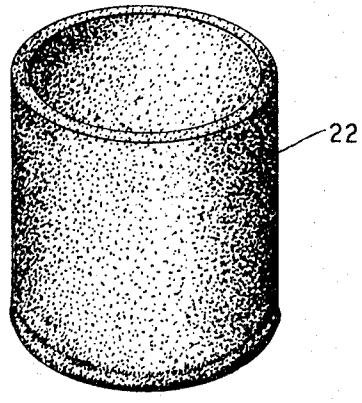


FIG. 3



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PRODUCTION OF ULTRAPURE TITANIUM NITRIDE REFRACTORY ARTICLES

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U.S. Cl. 23—191 3 Claims

ABSTRACT OF THE DISCLOSURE

Pure titanium nitride articles are formed by chemical vapor deposition of a coating upon a substrate that has the desired form of the article, by heating the substrate in a gas stream which consists of a mixture of hydrogen, titanium tetrachloride, and nitrogen for sufficient time to deposit the required amount of titanium nitride coating on the substrate, and subsequently destroying the substrate by chemical or physical means to leave the finished article in a free-standing state.

The invention relates to method and apparatus for producing free-standing, crack-free structures of refractory material, particularly titanium nitride.

Vapor deposition of titanium nitride upon a substrate is known, as is also the formation of free-standing articles of titanium nitride, without the use of a substrate, from compacted powder which is sintered into a monolithic structure. Another known method is to make an article of titanium which is nitrided after fabrication. It has been reported also that a tube of silicon carbide has been formed by vapor deposition of silicon carbide upon a silicon rod, followed by chemically dissolving the rod to leave the silicon carbide tube free-standing.

The invention resides in a novel product and a method of making the same by chemical vapor deposition of titanium nitride in a massive coating upon a substrate followed by subsequent removal of the substrate by physical or chemical means to leave a crack-free, free-standing article of high purity titanium nitride of substantially the theoretical density of 5.43 grams per cubic centimeter.

The invention solves several problems which have been of concern in the art, particularly with regard to the manufacture and use of refractory containers, including crucibles, boats, etc.

With respect to inertness and corrosion resistance, that is, chemical reactivity or solubility of the container with reference to the contents, the titanium nitride container made in accordance with the invention is superior to anything available for the purpose.

The finished article is found to suffer no detectable dilution in the form of material of the substrate during manufacture. When used as a crucible, the article is extremely inert to corrosive materials such as molten glass, molten iron, etc., even when these materials are heated to liquefying temperatures in the crucible. Accordingly, the glass or iron after being so melted is found to contain barely measurable amounts of contamination in the form of material of the crucible. After use and surface cleaning, the crucible retains substantially no detectable residue of the melted material, making re-use of the crucible feasible. The material of the crucible is not destroyed or appreciably attacked if cleaned with commonly employed strong acids which attack or destroy other kinds of crucibles.

Articles made by depositing titanium nitride upon a substrate and used without removing the substrate have the disadvantage that the limiting upper temperature for use

is determined by the melting point of the substrate material. In the case of a graphite substrate, which can withstand high temperature the difference in the coefficient of thermal expansion in the graphite and in the coating causes cracking of the coating when the article is subjected to heating and/or cooling. In the case of an alumina substrate, the product (substrate and coating) is not adequately resistant to thermal shock.

Free-standing articles of titanium nitride made by hot pressing in a mold are porous and impure. Because of impurities, the article is not nearly as inert as the articles made in accordance with the invention. The bulk titanium nitride from which the powder for molding is made has different properties from pyrolytic titanium nitride formed by vapor deposition. It has been found that the mold must be made of graphite and the material of the mold contaminates the molded material by formation of titanium carbide. The porosity of the molded article presents a greatly increased surface for reaction as compared with the vapor deposited material.

Free-standing articles made from a titanium body by nitriding have the disadvantage that complete nitriding is practically impossible. As a result, the article is in fact titanium coated with titanium nitride. The melting temperature of the titanium is lower than that of the nitride, so that the useful temperature is limited by the melting point of the titanium.

An article made by depositing a coating of silicon carbide, or other refractory material except titanium nitride upon a substrate and thereafter removing the substrate, is not an anticipation of an article made in accordance with the invention, because it is not possible to predict from experience with the other coating materials what properties would in fact result from substituting titanium nitride for such other coating material. For example, experience with silicon carbide would not enable one to predict the extreme degree of chemical inertness which is in fact obtained with titanium nitride. Information previously published indicates that titanium nitride dissolves slowly in hydrofluoric acid, whereas crucibles made in accordance with the invention do not dissolve in hydrofluoric or other strong acids.

The finished article in accordance with the invention is at least 99.99 percent pure titanium nitride, so that there are substantially no impurities present to react with the container or its contents.

The finished article is extremely resistant to thermal shock, to a much higher degree than conventional high purity ceramics.

The electrical conductivity of the article is higher than that of typical graphites and lends itself to electrical induction heating in a gaseous atmosphere as well as in a vacuum.

The titanium nitride article has a higher useful temperature than any refractory material currently being used, except graphite. Titanium nitride has a melting point in excess of 3200° C. as compared with about 1900° C. for silica SiO_2, 2200° C. for alumina Al_2O_3, 2800° C. for magnesia MgO, and 2900° C. for zirconia ZrO_2.

Whereas graphite crucibles have comparable electrical and refractory properties to titanium nitride, they have been found invariably to lead to serious contamination of melted contents and are inferior with regard to oxidation resistance. While the oxidation resistance of titanium nitride is inferior to most ceramics, it is much better than graphite.

FIG. 1 is a combined schematic diagram and flow sheet for a process embodying the invention;

FIG. 2 is an elevational view, partly in section, illustrating the manner in which a substrate can be removed from a coating that has been deposited upon the substrate to leave a free-standing article; and

FIG. 3 is a perspective view of a finished article.

Referring to FIG. 1, there is shown a substrate **20** of graphite upon which there has been deposited a layer **22** of titanium nitride.

The chemical reaction by means of which the titanium nitride is formed is

$$TiCl_4+2H_2+\tfrac{1}{2}N_2\rightarrow TiN+4HCl$$

The nitrogen and hydrogen are supplied, as from reservoirs **24** and **26**, respectively, individually controlled by valves **28** and **30**, respectively. The flow of each of these gases is regulated by individual flow meters **32** and **34** respectively, although the ratio of these flows is not critical, and the gases are mixed in a conduit **36**. The mixed gas is passed through a deoxidation unit **38**, which may comprise a paladium sponge to remove oxygen as a contaminant. The gaseous mixture is passed then through a drying tower **40**, which may comprise magnesium perchlorate to remove water vapor.

The titanium tetrachloride is supplied in liquid state and maintained at a temperature in the range from about 85–95° C. in a reservoir **42** as by means of a constant temperature bath in a vessel **44** surrounding the reservoir **42** supplied with warming fluid, usually water, entering the vessel **44** through an inlet tube **46** and leaving through an outlet tube **48**.

A suitable mixture of titanium tetrachloride, nitrogen and hydrogen is formed by bubbling the mixture of nitrogen and hydrogen through the liquid titanium tetrachloride, which latter is highly volatile. The mixture of nitrogen and hydrogen from the drying tower **40** is passed through a two-way valve **50** and a tube **52** to the bottom portion of the mass of liquid in the reservoir **42**. The gaseous mixture from the top of the reservoir **42** may be conducted through a valve **54**, a conduit **56** and a valve **58** to the interior of a quartz furnace or bell-jar **60** containing the substrate **20**. At this stage, a valve **62** is kept closed.

Deposition of titanium nitride upon the substrate **20** takes place with the substrate heated to approximately 800° C. to 1300° C. in an atmosphere composed of the reaction mixture, the optimum range being 1200° to 1300°. The substrate is heated by electric induction by means of a coil **64** which may be wound upon the exterior of the quartz vessel **60** and may be energized by a high frequency alternating current generator **66** with power input control elements **68** and **70** for adjusting the temperature of the substrate. The latter temperature may be ascertained by means of a thermocouple embedded in a sheath **72** and electrically connected to a calibrated meter **74**. The electrical leads for the thermocouple are brought out through a tube **76** which also may support the sheath **72**. The sheath **72** may be used as a convenient support for the substrate **20** during the coating process.

The gases in the reservoirs **24**, **26** are maintained at a moderate pressure, for example 2 to 3 centimeters of mercury, in order to propel the reactants through the system. In order to quickly remove air from the system, as at start-up, a pump **78** is provided. The used gases that are propelled out of the top of the furnace **60** pass through a conduit **80** into a trap **82**. Gases passing through the trap **82** leave via a conduit **86** and a two-way valve **84** to an exhaust pipe **88**, with the valve in the position shown. To connect the pump **78**, the valve **84** is turned a quarter turn counter-clockwise.

Initial purging of the furnace **60** and its contents may be accomplished by by-passing the nitrogen-hydrogen mixture around the titanium tetrachloride reservoir and directly into the conduit **56**. This may be done conveniently by rotating the valve **50** clockwise a quarter turn while maintaining valves **54** and **62** closed and valve **58** open, and while running the pump **78**.

With the substrate **20** up to the desired temperature, and the purging completed, the pump **78** is disconnected, the valve **50** is rotated a quarter turn counter-clockwise

and valve **54** is opened, admitting the full stream of the reactant gases to the furnace **60**.

With the substrate temperature about 1300° C., a layer of titanium nitride is deposited at a rate of from one-half millimeter to one millimeter per hour.

With the substrate in the form of a cup or crucible, the gases stream past the outer surface of the substrate and there is relatively negligible movement of gases inside the cup. Consequently, the deposition of the nitride is confined almost exclusively to the outside of the cup as desired.

To make a crucible of substantially pure titanium nitride, we have found that a suitable substrate is a thin-walled graphite crucible of the desired shape and size. As an illustrative example, we have used a graphite crucible of one-sixteenth inch wall thickness and up to about three inches in diameter. We obtain a coating of titanium nitride preferably at least as thick as the graphite or somewhat thicker. For example, on a graphite substrate one-sixteenth inch (1.59 millimeters) thick we obtain a coating two to three millimeters thick, requiring three to four hours with the substrate at about 1300° C.

By maintaining the titanium tetrachloride reservoir above room temperature we increase the partial pressure of the titanium tetrachloride in the mixture and by so doing incrrease the rate at which the reaction occurs and so increase the rate of deposition of the titanium nitride.

We find it is important to maintain a large excess of hydrogen over titanium tetrachloride for reasons separate and additional to the 8.1 ratio dictated by the stoichiometric proportions given by the equation of the reaction. This precaution seems necessary in order to obtain a pure and highly adherent coating of titanium nitride on the substrate. For this purpose, a gas composition characterized by flow rates of 1600, 400, and 5–20 milliliters per minute of hydrogen, nitrogen, and titanium tetrachloride, respectively, expressed in terms of normal temperature and pressure has been found acceptable from the point of view both of gas composition and rate of flow.

We find it is also important that the gas leaving the coating chamber contain substantial amounts of titanium tetrachloride. Approximately only about 50 percent of the titanium tetrachloride supplied to the coating chamber is transformed into nitride deposited on the substrate. While this may appear uneconomical, we find that deposition of a greater proportion of the titanium content of the tetrachloride results in impairment of the desired characteristics of the coating, primarily because the resultant coating is thicker near the gas inlet and thinner near the gas outlet. It will be evident, however, that the excess titanium tetrachloride can readily be reclaimed by known methods.

The initial purging of the coating chamber with the nitrogen-hydrogen mixture typically requires 10 to 15 minutes, providing the chamber is first evacuated using a pump. In the absence of a pump-down, longer times would be needed for safe practice in order to remove the air. When the ternary mixture is first introduced into the chamber after the initial purging, the temperature of the substrate is maintained at 600–800° C. Thereupon, the power input is increased and the substrate temperature is brought up to the desired level of 1200–1300° C. At the end of the coating period, the chamber is again purged with the binary gas mixture for approximately 30 minutes. Then the power input is removed and the workpiece is quenched in the binary gas stream. When cool, the chamber is flushed briefly with nitrogen alone, in order to remove the hydrogen. These procedures in terminating the coating operation have been found desirable in order to avoid a purple discoloration due to deposition of subchlorides at the lower temperatures as the workpiece cools.

The cooled specimen is inspected for cracks or fissures in the titanium nitride coating.

The crack-free specimen is then subjected to oxidation in an atmosphere of air at a temperature of 550° to 600° C. for a period of 10–12 hours to weaken the graph-

ite by attacking the binder carbon. The specimen may now be cooled to room temperature and then the graphite is removed by means such as a blast from a sandblasting gun, as illustrated in FIG. 2, which gun may be of miniature size suited to the size of the specimen. The result is a free-standing crucible as illustrated in FIG. 3, composed of highly pure titanium nitride.

The removal of the graphite substrate in this manner is usually found to result in a dull appearance of the titanium nitride as compared with the bright appearance and golden color of freshly deposited titanium nitride. If desired, the luster and color can be easily restored by immersing the crucible for about 10 minutes in strong mineral acid.

To purge the quartz vessel and contents at the start of the process, a flow of argon or similar appropriate inert gas may be substituted for the binary mixture of hydrogen and nitrogen.

The titanium tetrachloride reservoir **42** is preferably partially filled with glass fragments, and the liquid always maintained at a depth sufficient to promote the attainment of essentially complete saturation of the binary gas stream with the vaporized titanium tetrachloride. The tube **56** by which the ternary mixture is transferred to the coating chamber should be heated or else sufficiently heat insulated to avoid condensation of titanium tetrachloride which may otherwise occur en route.

In addition to the need for de-oxygenation as a safety measure, the de-oxygenation and drying of the nitrogen and hydrogen is important to avoid the formation of titanium dioxide.

The flow meters **32** and **34** are preferably of the usual "floating ball" type.

Instead of a graphite substrate, a very thin, iron substrate may be used, in which case the subsequent removal of the substrate may be accomplished either by melting the iron, which melts at a considerably lower temperature than titanium nitride, and/or by acid leaching in strong hydrochlorid acid. Materials other than graphite and iron, for example numerous other metals, may be used as substrate, provided they are capable of withstanding the coating temperature and of being subsequently separated from the coating of titanium nitride.

Corrosion tests were made as follows on titanium nitride crucibles made in accordance with the invention, with results as stated below:

Molten iron at 1600° C. was retained for two hours in a crucible embodying the invention and the weight of titanium nitride in the crucible was measured before and after the retension of the iron. A corrosion rate of only 0.012 grams per square centimeter per hour was found. The iron was found to have accumulated titanium impurity to the extent of 0.3 percent.

A similar test was made retaining molten Pyrex glass at 1000° C. in the crucible for two hours, with an observed corrosion rate of 0.008 grams per square centimeter per hour. The glass was found to have accumulated only 30 parts per million by weight of titanium impurity as found by spectrographic analysis.

Tests were also made using a variety of acids retained in the crucible for 48 hours at a temperature of 25°. Corrosion rates were found to be 0.0007 grams of titanium nitride per square centimeter per hour using concentrated sulphuric acid H_2SO_4, 0.007 using hydrofluoric acid HF, and 0.083 using a mixture comprising 48 percent hydrofluoric acid mixed with concentrated nitric acid HNO_3.

Photomicrographs of the crucible-melt interfaces revealed no detectable deterioration of or attack upon the refractory material of the crucible.

X-ray diffraction measurements upon material made in accordance with the invention have shown that the unsupported material is highly pure crystalline titanium nitride having a density of 5.43 grams per cubic centimeter. The material is further characterized as substantially impervious and pore free.

While illustrative forms of apparatus and methods in accordance with the invention have been described and shown herein, it will be understood that numerous changes may be made without departing from the general principles and scope of the invention.

We claim:

1. An article of manufacture composed of highly pure crystalline titanium nitride, having a density of 5.43 grams per cubic centimeter determinable by X-ray diffraction measurements.

2. A pore free crucible of unsupported crystalline titanium nitride.

3. The method of producing a free-standing article of high purity titanium nitride, which method comprises the steps of heating a graphite substrate to an elevated temperature, forming a coating of titanium nitride by vapor deposition upon said heated substrate, said coating being at least as thick as said substrate, cooling said substrate, and removing said substrate from said coating by reheating the cooled coated substrate in air to a temperature of about 550 to 600° C. to attack the binder carbon in the graphite, followed by sand blasting the thus weakened graphite, thereby leaving the coating as a free-standing article.

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