

1

3,047,419

METHOD OF FORMING TITANIUM
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No Drawing. Filed Feb. 26, 1954, Ser. No. 412,960

4 Claims. (Cl. 117—46)

This invention relates to coating of massive titanium metal bodies, titanium alloy metal bodies which have a substantial titanium content, and other metal bodies which have been clad with titanium or titanium alloy metal as a surfacing material for enhanced properties available from such titanium metal bodies and its alloys, the coating of the titanium body consisting essentially of titanium silicides which impart to the titanium base metal resistance to gaseous attack in high temperature uses thereof, particularly resistance to oxidation in air at high temperatures. The invention more particularly relates to such titanium metal and titanium metal alloy products having a skin coating containing as the predominant component an alloy or intermetallic composition containing about 26% silicon and the balance titanium, namely Ti_5Si_3 , and to methods of forming these coated titanium metal and titanium metal alloy products.

The silicide coated titanium and titanium alloys containing a substantial quantity of titanium, at least about 5% titanium, have highly desirable properties in use at elevated temperatures. The desirable high temperature uses for silicide coated titanium metal and alloys thereof are as heating elements, nozzles for rockets, artillery pieces, burners, blades and buckets for turbines, and other uses wherein the metal is exposed at high temperatures to destructive gases, particularly oxygen in air, and wherein the inherent strength and light weight of the metal are desirably retained. In these several high temperature uses without the silicide coating of the present invention, it is usually necessary to exclude oxygen or other corrosive gases, and it is common for this purpose to supply a continuous flow of inert gas to the heated metal parts to avoid oxidation or other gaseous attack at the raised temperatures.

According to the present invention, the titanium or titanium alloy base has formed thereon an integral skin coating of silicon and titanium as an alloy or intermetallic composition, to impart optimum protection to the titanium base for use at raised temperatures, especially use in air at temperatures exceeding about 800° C., for long periods of time.

The alloy or intermetallic composition comprising the skin coating upon the titanium or alloy thereof consists essentially of a titanium silicide or a mixture of such silicides comprising the compound Ti_5Si_3 , which is a preferred component because it will resist fusion at temperatures up to about 2120° C., or a mixtures of Ti_5Si_3 and $TiSi_2$. The titanium silicide compound $TiSi_2$ has great utility when present in the skin coating upon the metal base because it will not melt at temperatures below about 1540° C. and because it enhances the resistance in air at high temperatures of the skin coating on the titanium base.

In general, in accordance with the present invention, the skin coating upon the titanium metal base is varied in proportions of silicon and titanium to produce titanium silicides in the skin coating variable in titanium-silicon ratios to encompass the compounds $TiSi_2$ and Ti_5Si_3 , but preferably are adjusted to predominate in the higher melting Ti_5Si_3 . Thus, the skin coating will generally vary in silicon content from about 20% to 65% by weight, preferably 26% to 54% by weight, of the skin coating,

2

the balance being essentially titanium available from titanium base into which the silicon is sintered or available from the alloys of the titanium with other metals when the alloy is used, but the titanium content of skin coating may be supplied at least in part extraneously with the silicon. Thus, the ratio of silicon to titanium in the skin coating will generally range from about 1 part of silicon to 1 part of titanium down to 3 parts of silicon to 5 parts of titanium by weight of the skin to produce a mixture variable between compositions of the formulae, preferably containing, as stated, Ti_5Si_3 as predominant component of the composition.

Although the optimum protection of the titanium metal in air at temperatures above about 1500° C. obtained with coatings or skins having a molecular ratio of about 3 parts of silicon to 5 parts of titanium, responding to a silicon content of about 26%, coat greater or less than that composition, such as compositions in the range of 20% to 65% silicon, the balance being titanium, also afford protection for the titanium core or base at these high temperatures, and at low temperatures may be more effective. For example, Ti_5Si_3 is more effective in resisting oxidation in air at temperatures below about 1500° C. than is Ti_5Si_3 .

Where it is indicated that the exterior skin comprises about 26% silicon and the balance titanium, this does not mean that the exterior layer consists entirely of intermetallic compound of silicon and titanium having the approximate percentage named, namely Ti_5Si_3 , but that the exterior layer consists largely of that pure intermetallic compound and may have associated with more or less of the intermetallic compound of silicon and titanium corresponding to 54% silicon, and the balance titanium ($TiSi_2$), preferably more, and/or silicon in amount somewhat less than or in excess of that required to form the preferred compound Ti_5Si_3 and vary in the range stated of about 20% to 65% silicon, balance being titanium.

These coatings or skins on the titanium or the titanium alloy base furnish an exceedingly high resistance to oxidation as well as destruction by other gases at elevated temperatures. For example, it has been found that a sample of titanium according to this invention can resist oxidation for a period exceeding 2,000 hours when heated in air at 800° C., whereas, in contrast, uncoated titanium metal heated in air under similar conditions will usually be destroyed by oxidation in a period of less than hours.

These skin coatings, while they may be formed by sintering of mixtures of titanium and silicon powders on the surface of the base titanium metal or alloy thereof or by sintering to such surface of preformed titanium silicide powders, are generally formed by sintering or by heat application of elemental silicon alone to the surface of the base titanium metal or alloy thereof.

The thickness of such coating is most conveniently measured herein as a thickness increase of the metallic titanium body or alloy thereof, and accordingly does not truly indicate the actual thickness of the coating since the silicon, by sintering, has substantially penetrated the surface comprising the original dimensions measurement of the uncoated base. In general, the coating of titanium silicide measured as a thickness increase should be at least 1/2 mil in thickness and may be as thick as 15 mils, but such thicker coatings, while increasing progressively by increased thickness to give enhanced resistance of the base to oxidation in air, will often result in reduced physical characteristics, such as flexibility and other strength characteristics of the original titanium and the coatings per se may have increased tendency to crack or peel off. Accordingly, it is generally preferred to apply coatings up to about 10 mils in thickness,

ing preferably being at least about 1.0 mil in thick-

here are several methods which may be used for applying the coating. Thus, the coating may be applied by using the heated metal titanium base or alloy thereof, reducing atmosphere having therein vapors of reducible compounds of silicon, such as a silicon halide, in fusing gas, such as hydrogen. If desired, such vapors also include vapors of titanium compounds for even position simultaneously of both titanium and silicon, whereby the skin coating is more readily controlled to therein the compound Ti_5Si_3 .

Another procedure usefully followed for applying a skin coating is with a flame spray, using a typical spray gun applying elemental silicon powder as a spray heat either in a vacuum or inert gas as a carrier therefor.

Still another method is by cementation, which consists generally in embedding the titanium base metal in a fine powdered bed or bath of silicon powder, or a mixture of silicon and titanium powders, or a powdered pre-reduced titanium silicide, the powder bath with the titanium work piece embedded therein being heated for several hours, ranging from about 3 to 30 hours, to a sintering temperature, usually about 900 to 1400° C. Cytolytic activators for the adhesion of the coating upon metal base, such as halogen, chlorine, bromine or iodine, or an alkali metal salt thereof, are desirably included in the powder in quantity of from a trace up to about 5%. Alternatively, an activating gas, such as chlorine, may be continuously passed in minute quantity through the powdered bed to activate the same during cementation.

And still another method, preferred because of its most ready applicability, is the application of the skin by paint-powders of silicon, or both silicon and titanium as elemental mixtures of their powders, or powders of pre-reduced titanium silicides suspended as a slurry in a solvent of a solvent containing a temporary and heat decomposable binder therefor, first to adhere the powders to the surface film coating in proper proportion to the titanium or titanium alloy work piece, and then to decompose the binder substance and sinter the powder to the titanium base metal as an integral skin layer thereon.

All of these methods a sufficiently thick coating may be applied as a single coating application, but it is preferred, particularly in the painting procedure, to apply a thin coating and then repeat the procedure to apply additional coatings thereon until the desired coating thickness has been obtained.

The several coating procedures outlined above are varied in utility by the degree of resistance to oxidation obtainable, the even thickness of the coating obtainable, the tendency of the coating to crack or peel off by the particular procedure used, and finally by the ready facility with which the coating may be applied. From such considerations, the paint method is preferred not only because of the apparatus and manipulation to obtain the coating is simpler, but more even and reproducibly thick coating of constant physical and chemical characteristics are readily available. Where a rough and uneven coating is not objectionable, it is possible to apply a coating of silicon in somewhat indefinite proportions by a hot dip procedure wherein the metallic titanium or titanium alloy is merely dipped in a molten bath of elemental silicon.

The following methods, as outlined in greater detail in U.S. Pat. 2,800,050, 0.050" sheet pure titanium, or titanium alloys Ti-130-B)¹ 0.065" sheet and (Ti-150-A)² 0.050" sheet were used for all coating work. The specimens were cut into strips 6" long and 1/2" wide and machined tensile test specimens having a reduced section of 0.25". Prior to coating, the edges and sharp corners

C-130-B is an alloy of Ti 92%, Mn 4% and Al 4%. Ti-150-A is an alloy of Ti 96%, Cr 2.7% and Fe 1.3%.

ners of the strips were removed and the strips were then blasted with grit for purposes of cleaning and slight roughening for best adhesion of the coating. The strips were then finally cleaned in a mixture of nitric and hydrofluoric acids.

PAINTING AND SINTERING METHOD

This method consists of painting a suspension of coating substance such as powder suspended as a slurry in a solvent containing an organic binder substance capable of decomposition by heat. The painting may be done with a paint spray gun or by hand brushing. The painted specimens are allowed to dry and are then sintered. The coating in each case is repeated until a desired thickness of coating is obtained, such as a skin upon the titanium exceeding 0.5 mil in thickness, preferably about 1 to 3 mils.

The coating may exceed 10 mils in thickness, if desired, but such thicker coatings are not necessary and may even prove objectionable. While such coating may be applied by first coating and drying in a series of treatments and finally sintering, it is preferable to sinter with each coating before the next coating is applied. There is some variation in the life of the coating with respect to oxidation resistance in air at high temperatures depending upon the method of sintering, the fineness of the metal powders being applied as a slurry in the wet coating to the titanium base, and the characters of the binder resin and carrier liquid. Obviously, it is desirable that the coating be uniformly applied over the titanium to obtain a uniformly thick sintered coating.

(A) The Paint Resin

The resin of this paint is selected to be a thermoplastic resin because of its superior property to be volatilized and/or decomposed at high temperatures upon sintering to leave no substantial carbonaceous residue, and for imparting fluidity and even thickness to this paint. Any typical thermoplastic paint resin which leaves no substantial carbonaceous residue when heated to temperatures exceeding its decomposition temperature, such as above about 1300° C., may be used herein. Such resin will be understood to be a typical temporary bonding resin to firmly adhere the powdered elements silicon or silicon and titanium to the titanium base and maintain the adhesion until the resin is completely volatilized and/or decomposed. Alkyd resins are superior in this respect since they give good adhesion, good flow, hold the coating while heating, and leave no carbonaceous residue. Thermosetting resins, such as Bakelite, which leave a substantial deposit of carbon, are unsuitable. Typically useful resins are alkyd resins formed by reaction of polybasic organic acids such as phthalic acid, succinic acid, adipic acid, etc., with polyhydroxy aliphatic alcohols such as glycerin, ethylene glycol, etc., of which the reaction product of phthalic anhydride with glycerin, i.e. Glyptal resin, is preferred. The resin is applied in proportions of from 5% to 15%, usually about 10% by weight of the liquid carrier, and the quantity of resin related to powdered elements may range from about 1.5 to 3.5:1, usually about 2 to 3:1.

(B) The Solvent

Desirable solvents, particularly for alkyd resins, are ketones. We may use any volatile ketone such as acetone, methyl ethyl ketone, diethyl ketone, diacetone alcohol, and preferably for a Glyptal resin, a mixture of diacetone alcohol and acetone in a ratio of about 7:3 parts by volume, respectively, may be used.

(C) Silicon or Silicon and Titanium or Titanium Silicide Powders

The silicon is preferably fine commercial elemental silicon, about 97% pure, used in the form of a very finely powdered dust which will pass readily through a 325 mesh or even finer screen. A desirable form of silicon is obtained by further classifying 325 mesh silicon by stirring

5

a slurry thereof in water and pipetting off successive portions near the upper liquid surface to obtain an extremely fine elutriated silicon in this manner.

It is sometimes desirable to admix with the silicon, titanium or titanium hydride in proportions to approximate Ti_5Si_3 , or other proportions within the range given above for the desired silicon content, such as from 20% to 65% by weight silicon, the balance titanium. The powdered titanium metal per se when used with the silicon to coat the base also is substantially pure titanium metal, finely comminuted to a dust of about 325 mesh or less, the titanium and silicon powders being preferably uniformly sized and homogeneously admixed prior to suspending in the liquid paint carrier as a slurry, but they may be slurried into the liquid paint carrier in sequence, if desired. Alternatively, the titanium or a titanium hydride may be admixed with the silicon in proportions to form Ti_5Si_3 or other titanium silicide such as in the proportion range given above, and the dry powders homogeneously admixed are presintered in a vacuum furnace having an inert atmosphere, such as helium or hydrogen, at a temperature of 1300 to 1800° C., preferably about 1500° C., to preform the titanium silicide. The presintered composition is then broken to fine fragments and milled to a powder of about 325 mesh or less, and this presintered powder is then suspended in a liquid paint carrier, as described for other powders, for furthering sintering upon the titanium metal base.

(D) Paint Coating

The resin is first dissolved in a high boiling solvent as above identified, preferably Glyptal resin in a solvent comprising 7:3 volumetric mixture of diacetone alcohol and acetone respectively. The powder or powder mixture in the desired ratio is then stirred into the resin solution, for most purposes about 4 parts by weight of powder to 1 part by weight of resin, sufficient solvent being added to form a slurry that is readily applied by hand brushing as a smooth flowing slurry. For spraying in a spray gun, the slurry may be somewhat thinner, namely, contain more solvent. The wet coated titanium metal, whether coated by hand brushing or spraying, is then placed in an air drying oven and dried at moderate temperatures, such as about 100° C. or less, to evaporate the solvent and produce a substantially dry adherent coating of powder temporarily bonded to the titanium base by the substantially dry alkyl resin.

(E) Sintering

For sintering, the sample is placed in a furnace which may be either of two types:

(a) *Helium furnace*.—This furnace consists of an Inconel tube, heated in a Nichrome-wound furnace. The work is placed in the Inconel tube through which helium is passed. The helium is purified by passage through magnesium perchlorate and then through tantalum gauze heated to 1000° C.

(b) *Vacuum furnace*.—The vacuum furnace is of the induction type, consisting of a susceptor enclosed in a quartz tube. Power is supplied by an Ajax converter. An oil diffusion pump, backed by a mechanical pump, is used to evacuate the system.

In sintering the samples dried in the air drying oven after coating, the painted specimens are placed in grooves of a carrier block, such as an Alundum block or other inert carrier, and sintered either in the helium furnace or in the vacuum furnace maintained at a high vacuum, such as about 5 microns or less, preferably the latter. The coated samples are desirably first preheated to an intermediate temperature, such as 300° to 400° C., for a short period of time, say 2 to 30 minutes, sufficient to volatilize and destroy the alkyl resin binder, but substantially the same effect is obtained if the green samples are merely brought up to sintering temperature slowly. According to the sintering procedure, the sample is placed in the carrier within the tube of the furnace and slowly heated over a

6

period of ½ to 2 hours, usually about an hour, to the sintering in a temperature ranging from about 1 up to about 1,400° C., preferably 1,200° to 1,400° C.

EXAMPLE 1

Titanium alloy (RC-130-B) in the form of 0 thick sheets was cut into strips 6" long by ½" wide sharp edges broken off and smoothed, and grit blasted and cleaned by dipping in nitric and hydrofluoric acid. The dried samples were then painted with a slurry of fine elutriated silicon powder having an average mesh size of less than 325 (average particle size about 10 microns) mixed with a solvent comprising 7 parts of acetone alcohol to 3 parts of acetone by weight, in which was dissolved 1 part of Glyptal resin by weight ratio. The silicon powder, the quantity of solvent being such as to give a smooth flowing paint. The samples were painted and dried in an air oven for one hour. Thereafter the samples were placed in a helium furnace and heated at 350° C. for 15 to 30 minutes to volatilize and decompose the Glyptal resin binder. The coated samples were then placed in a furnace and sintered at temperatures from 1,000° to 1,400° C., generally about 1,300° C. for about an hour. By repeating the procedure, coatings of various thicknesses ranging from 1 to 10 mils may be obtained. The summary table below, tests of coatings obtained by this method are listed comparatively with tests upon coated product formed in other examples.

VAPOR PHASE DEPOSITION

According to this method, the heated titanium metal has passed thereover vapors of a silicon halide, such as silicon tetrachloride carried in a reducing gas such as hydrogen, to reduce the silicon compound upon the metal, forming therewith an integral skin coating of titanium silicide. For vapor phase deposition, the apparatus may consist of a Vycor tube wrapped in copper with heating supplied by an induction coil activated by a high frequency Ecco converter. The procedure is to pass purified hydrogen gas carrying therein controlled quantities of silicon tetrachloride or other volatile reduced silicon compound. The hydrogen carrier gas is purified first by contacting it with a hot copper gauze maintained at about 550° C., and then passing it through a magnesium perchlorate column. The purified hydrogen gas is then passed, as by bubbling, through a volatile, liquid silicon compound, such as silicon tetrachloride, at a rate to carry therewith a controlled quantity of silicon tetrachloride vapor, and the mixed gas and vapor then passed through the Vycor tube in which the sample of titanium to be coated is mounted. The titanium bodies to be coated are prepared in the same manner as described in Example 1 and supported within the Vycor tube in grooves of an Alundum block, a preferred type of support, although similar supports of molybdenum, silicon carbide or Ti_5Si_3 may be used. The titanium body within the tube is heated by induction heat to a temperature within the range of about 875° to 1400° C. for short periods of time, say 5 to 15 minutes. The evenness of the coating is desired maintained by reversing the sample occasionally to turn it over with respect to its support and present an open end with respect to the flow of gases thereover. By this method, coatings from about 0.5 to 3 mils in thickness may be obtained. As in the painting method described above, both silicon and titanium may be simultaneously deposited from their volatile halides, for example a mixture of silicon tetrachloride and titanium tetrachloride with simultaneous reduction and formation of a skin of titanium silicides in the desired ratio.

EXAMPLE 2

The titanium samples according to Example 1 are supported within the Vycor tube, heated in the preferred range at about 1000° to 1350° C. for two 5 minute periods, the first period being interrupted to reverse the sample in the tube and the second period thereafter ap

oxygen is first purified by passing it through hot copper maintained at 550° C. and then through dry magnesia perchlorate. It is then passed through liquid silicon tetrachloride maintained at a temperature of about 100° C. at a rate of about 800 cc. of hydrogen gas per minute and the vapor suspension then passed over the heated sample in the tube, the heating being terminated after each sample and the sample cooled in hydrogen gas alone. A coating of good appearance of about 1 mil thickness is obtained. Greater or lesser quantities of silicon tetrachloride may be supplied as a vapor in the hydrogen by varying the temperature of the liquid silicon tetrachloride, the higher the temperature the more vapors thereof being evolved in the hydrogen. In a similar manner, both silicon tetrachloride and titanium tetrachloride vapors may be carried in hydrogen gas, preferably by forming independent mixtures of the volatilized halides in hydrogen and then combining the separate hydrogen mixtures to a single flow just before passing into the Vycor tube. Several examples applied to the coated samples are summarized in the table below.

FLAME SPRAY METHOD

EXAMPLE 3

Flame spray coatings upon titanium and titanium alloys are readily obtained in thicknesses of from 3 to 10 mils. For this purpose, titanium samples as described in Example 1 are sprayed with silicon powder of less than 325 mesh particles size, using a Wall-Colmonoy powder gun. It is found that well-bonded coatings of any desired thickness in this range are obtainable in the hot spray of coated powder, the silicon being sintered by the heat of the gun at a temperature in a range of about 1000° to 1200° C. If desired, the porosity and the bonding strength of the coatings produced by this method may be further improved by further sintering, preferably in a vacuum furnace, or by further torch flaming. However, it is found that sufficiently good coatings are effected by the flame spray procedure so that subsequent steps of sintering, as in a vacuum furnace, are not essential. Comparative results of flame spraying with coatings by methods above are listed in the table below.

CEMENTATION METHOD

EXAMPLE 4

Samples of titanium base, prepared as described in Example 1, are placed in a bed by packing the work piece completely powdered —325 mesh silicon disposed in a tube-Inconel furnace, the tube being rotated while heated at a rate of about 1 revolution per minute. The bed is heated in the range of 900° to 1200° C. for a period of 30 hours to produce coatings ranging from 1 to 10 mils in thickness. During the heating period the silicon bed is mixed either with 2½% to 5% of iodine or cesium iodide, or a mixture of both in equal proportion, the mixture being preferred. Other volatilizable silicon compounds, such as alkali or alkaline earth metal silicides, or elementary halogen, may be used admixed with the silicon of the bed or the halogen may be continuously supplied thereto as the heating proceeds. Proceeding in accordance with the present example, a sample of titanium metal prepared as in Example 1 is embedded in silicon powder containing 2½% each of elemental iodine and potassium iodide, and the bed is heated by being rotated continuously and heat applied by raising the temperature over a period of 6 hours to 1000° C., and maintaining that temperature for a further period of about 26 hours. A continuous coating of about 10 mils is obtained. Lesser periods of heating at somewhat higher temperatures may be applied. This method is not as desirable as the others described herein.

COMPARATIVE TESTS

The following table lists comparative results of sample coatings obtained in Examples 1 to 3.

Coating Procedure	Method of Sintering	Temp. (° C.)	Coating Thickness (Mils)	Test Temp. of Heating in Air (° C.)	Hours of Heating Before Failure
Uncoated				800	36
Example 1	Vacuum 1 hr.	1,200	2.0	800	240
Do	do	1,175	1.0	800	1,585
Do	do	1,175	1.0	800	1,420
Do	do	1,275	2.0	800	1,560
Do	Helium 1 hr.	1,200	1.0	800	1,275
Do	Vacuum 1 hr.	1,350	2.5	800	2,160
Example 2	Vapor Phase	1,995	1.0	800	489
Do	do	1,325	1.0	1,000	787
Example 3	Flame Spray		10.0	1,000	4,219

¹ Sintered only 5 minutes.

² Sintered for 10 minutes. All samples were of titanium alloy RC-130-B except underlined Example 1, which was Ti-150-A.

³ Heating in alternate 75-second cycles with intermittent cooling. Other samples not so designated were heated continuously.

⁴ Sample still in test without failure.

As shown by the above, very desirable physical properties are imparted to titanium base metal by coating the same with an integral skin layer comprising an alloy or intermetallic composition of the silicon with titanium in which the silicide Ti_5Si_3 is a predominant component. Of the many desirable properties of this coated product, the resistance to oxidation in air at high temperatures is outstanding. While the examples describe sheets in the several coating experiments, it will be apparent that various other shapes, such as bars, rods, tubes, plates, discs, pellets and the like, or irregular shapes, may be coated by the several procedures herein described.

Of the many procedures disclosed, certain give good coatings when the surface layer has a thickness in the lower range of ½ to 3 mils. Others, such as flame spraying, cementation, or hot dipping, give thicker coatings, such as from 2 to 15 mils, the thickness often being characteristic of the coating procedure, but any desired thickness may be effected, such as in the painting procedure, by repeating the coating process to obtain the same. A desirable guide for selection of proper thickness of coating and the procedure to obtain the same is the effectiveness and evenness with which the layer is bonded to impart satisfactory protection to the base metal at high temperatures without cracking, spalling, or blistering, etc. Certain of the coating procedures are outstanding because of the rapidity and economy of apparatus installations useful in effecting the coating. Others are preferred for their adaptability to coat large or irregular shapes without recourse to expensive apparatus. For relatively thin but highly effective coatings the painting method, as hereinabove stated, is preferred.

Many base metals, such as steel, nickel, molybdenum, etc., which are desirably modified to have some of the outstanding uses of titanium, may be first clad with titanium sheet or otherwise coated with titanium metal or alloy, and may thereafter have the titanium surface supplied with an exterior skin layer or coating of titanium silicides as herein described.

We claim:

1. The method of treating titanium metal bodies and alloys thereof to impart resistance thereto to the destructive action of gases at elevated temperatures comprising embedding the titanium metal base in finely powdered elemental silicon and heating the bed to a temperature in the range of about 900 to 1200° C. for a period sufficient to impart a coating thereto of at least ½ mil in thickness while supplying to said bed a catalyst comprising a halogen substance selected from the group consisting of alkali and alkaline earth metal halides and elemental halogen.

2. The method as defined in claim 1 wherein the catalyst substance is mixed with the elemental silicon as a component of the bed in quantity ranging from about 2½% to 5% thereof.

3. The method of treating titanium metal bodies and alloys thereof to impart resistance thereto to the destructive action of gases at elevated temperatures, comprising painting the titanium body with a liquid coating composition comprising a carrier liquid having dissolved therein a heat-decomposable, temporary, organic binder substance and having suspended therein a mixture of finely powdered elemental silicon and finely powdered elemental titanium, drying the coated body and heating the same in an inert atmosphere to decompose and volatilize the binder substance and sinter the silicon to convert the same to an integral exterior layer on the titanium comprising an alloy or intermetallic composition of silicon and titanium.

4. The method of treating titanium metal bodies and alloys thereof to impart resistance thereto to the destructive action of gases at elevated temperatures, comprising painting the titanium body with a liquid coating composition comprising a carrier liquid having dissolved therein a heat-decomposable, temporary, organic binder substance and having suspended therein a pre-sintered mixture of titanium and silicon containing substantial quantities of Ti_3Si_2 , drying the coated body and heating the same in an inert atmosphere to decompose and volatilize the binder substance and sinter the silicon to convert the

same to an integral exterior layer on the titanium comprising an alloy or intermetallic composition of silicon and titanium.

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