

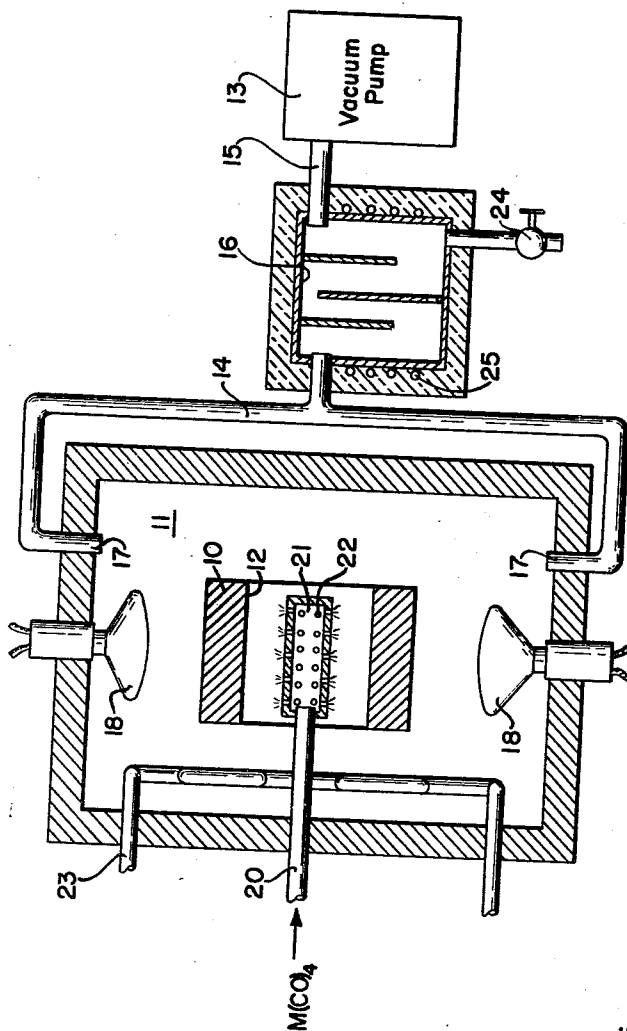
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H. A. TOULMIN, JR

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METHOD FOR HI-VAC ALLOYING AND COATED PRODUCT

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INVENTOR
HARRY A. TOULMIN JR.
BY
Toulmin & Toulmin
ATTORNEYS

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METHOD FOR HI-VAC ALLOYING AND
COATED PRODUCT

Harry A. Toulmin, Jr., Dayton, Ohio, assignor
to The Commonwealth Engineering Company
of Ohio, Dayton, Ohio, a corporation of Ohio

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This invention relates to a method of surface coating and impregnation of base metals with other elementary metals by the application of the elementary metals to the base metal in a solid state, and also relates to products obtained thereby.

It is an object of this invention to coat and impregnate base metals with other elementary metals in a manner that the elementary metal is deposited on the base metal in a solid state, and thereby eliminate any melting of either of the metals to obtain surface coating and surface impregnation of the base metal with the elementary metal.

It is another object of the invention to provide a method of depositing an elementary metal on a base metal in a manner that interstitial deposition of the elementary metal is obtained on the base metal.

It is still a further object of the invention to provide a method of obtaining deposition of an elementary metal on a base metal in which air is removed from the surface of the base metal and from the interstices at the surface of the metal to provide for a deposition and more secure bonding of an elementary metal to the surface of a base metal through interstitial deposition of the elementary metal in the base metal.

These and other objects of the invention are accomplished by depositing an elementary metal from a vaporous or gaseous or quasi-gaseous state onto the base metal under vacuum conditions whereby the deposited metal securely bonds to the base metal.

A still further object of the invention is to deposit elementary metal onto a base metal from a vaporous compound wherein the base metal is exposed to a vacuum atmosphere to remove air from the surface of the base metal and draw out air from the interstices at the surface of the metal while the base metal is heated to a temperature of decomposition of a compound of an elementary metal to be deposited so that the subjection of the so prepared base metal to a vaporous atmosphere of a compound of the elementary metal that is to be deposited will cause decomposition of the compound of the elementary metal with subsequent interstitial deposition of the elementary metal in the base metal and on the surface thereof, and thereby obtain a secure bonding of the elementary metal onto the base metal.

In accomplishing this object of the invention the compound of the elementary metal may be used in the vaporous phase as obtained either by spraying of a liquid into the vacuum atmosphere

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or by use of a gaseous state of the compound of the elementary metal.

The drawing figure illustrates an embodiment of the invention showing diagrammatically an apparatus for carrying out the method of this invention.

In the method of this invention, an object that is to be surface treated by the deposition of an elementary metal onto the surface is subjected to a vacuum atmosphere whereby air is removed from the surface of the object and any air retained within the interstices of the metal in any way connected with the surface of the metal is removed, thereby freeing all surfaces of the metal from the existence of air at the surface thereof to provide a clean metal surface free of the monomolecular film that is normally found on metals. Thus, the elementary metal can be deposited directly upon the base metal without interference of any gaseous medium.

While the object to be surface-treated is in the vacuum atmosphere, it is elevated to the temperature of decomposition of a compound of the elementary metal to be deposited so that subjection of the base metal to a vaporous atmosphere of a compound of the elementary metal will cause decomposition of the compound at the surface of the base metal with resultant deposition of the elementary metal on the base metal.

After the base metal has been so prepared, and while it is held under the vacuum conditions, it is subjected to a vaporous atmosphere of a compound of the elementary metal released under pressure into the vacuum in which the base metal is being held for a sufficient period of time to obtain deposition of the elementary metal to the desired depth.

Compounds that proved to be suitable for use in the process of my invention to produce the improved product of the invention are the metal carbonyls. Thus, nickel, cobalt, chromium, iron, tungsten and molybdenum in the form of their carbonyls may be contacted with base metals such as steel, cast iron and other metals or alloys for deposition of the elementary metal on the base metals. Some of the metal carbonyls such as nickel and iron can be used as liquids, whereas others such as chromium, cobalt, tungsten and molybdenum can be used in their gaseous phase upon heating of the crystal form of carbonyl to volatilize it into the gaseous phase.

Either the liquid or gaseous carbonyl compounds are introduced into the vacuum atmosphere around the object being surface-treated under pressure to obtain a high degree of dis-

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persion of the carbonyl in the vaporous condition. This results in uniform surface treatment of the object with rapid and complete permeation of the interstices in any way connected with the surface of the metal.

In the drawing figure illustrating an apparatus for accomplishing the method of this invention, an object 10 to be surface-treated is placed within a chamber 11. The object 10 is one adapted to have the surface 12 thereof treated, this being the bearing surface of a cylindrical bearing. The chamber 11 is connected to a vacuum pump 13 by means of the conduits 14 and 15 which have a refrigerated trap 16 therein. The conduit 14 is provided with a plurality of inlet connections 17 spaced around the chamber 11 to provide for a uniform withdrawal of the atmosphere from within the chamber 11. This is advantageous particularly during the period of continuous withdrawal of the atmosphere from the chamber 11 while the vaporous atmosphere of the metal carbonyl is being applied to the surface of the article being treated to avoid any directional flow of metal carbonyl which would cause non-uniform deposition on the surface of the article.

The object 10 may be supported in the chamber 11 in any suitable manner. To heat the object 10, a series of heat lamps 18 are provided around the object thereby heating the object by the radiant heat effect from the lamps. A vaporous metal carbonyl compound $M(CO)_4$, wherein the M may be nickel, for example when a liquid carbonyl is used, or chromium, where a crystalline metal carbonyl compound is used as converted to the gaseous phase, is supplied through the conduit 20 under pressure into a distributing head 21. The liquid or gaseous metal carbonyl is sprayed under pressure from the distributing head through a series of small jet openings 22 so that the metal carbonyl is directed toward the surface 12 of the object 10 in a vaporous condition through the series of jets 22. Release of a liquid metal carbonyl under pressure into the vacuum atmosphere obtains instant vaporization into the gas or vapor phase so that either this or the gaseous form of a metal carbonyl provides for an even distribution of the metal carbonyl at the surface that is undergoing treatment.

To avoid decomposition of the metal carbonyl within the chamber 11 except at the surface of the article 10 with subsequent deposition of the metal of the carbonyl directly on the surface of the article, the chamber 11 is preferably cooled by a cooling coil 23 which holds the internal temperature of the chamber to about 250° F. which is below a rapid decomposition temperature of the metal carbonyl. Since the object 10 is at or above a rapid decomposition temperature of the metal carbonyl, the metal of the carbonyl will deposit on the surface of the article and the carbon-monoxide of the compound will be released for withdrawal by the vacuum pump 13, which also retains the vacuum condition within the chamber 11 during the surface treatment of the article 10.

To prevent any excess metal carbonyl from reaching the vacuum pump 13, a refrigerated trap 16 is placed in the conduit 15 to condense out any metal carbonyl leaving the chamber 11, thus allowing only released carbon-monoxide to flow to the pump 13. A hand-operated valve 24 is provided on the trap 16 to periodically remove the liquid carbonyl condensed in the trap. A refrigeration coil 25 is provided around the trap 16 to reduce the temperature of the trap to the temperature of liquefaction of the metal carbonyl.

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In the event the metal carbonyl is that which crystallizes from the gaseous phase, then, of course, the trap may have a suitable opening to remove the crystals removed from the gas during passage through the trap.

According to the method of this invention, for example, tungsten carbonyl, which is of crystalline form at normal room temperature, is vaporized at a temperature of from 125° F. to 140° F. This is considerably below the decomposition temperature of the carbonyl of about 250° F. at which there is a slow decomposition of the carbonyl. The gaseous tungsten carbonyl is placed under pressure of from 10 to 15 pounds per square inch with any suitable pump or in a gas accumulator held at a temperature of 125° F. to maintain the carbonyl in the gaseous phase and is delivered to the surface of the object being treated in the vaporous condition upon release of the gaseous carbonyl through the small jet openings heretofore described.

The object being treated, such as the bearing 10 is subjected to the vacuum atmosphere in the chamber 11 of from 25" to 30" of water, this vacuum being continuously maintained by operation of the vacuum pump 13. The object 10 is heated to a temperature of from 350° F. to 400° F. at which temperature the gaseous tungsten carbonyl supplied to the surface of the base metal will rapidly decompose with resultant deposition of the metal tungsten upon the surface 12 of the object 10. The carbon-monoxide released by the decomposition of the tungsten carbonyl will be withdrawn from the chamber 11 through the pipe 17 by the vacuum pump 13. Any excess carbonyl will be crystallized in the refrigerated trap 16 in the manner heretofore described.

With the tungsten carbonyl being continuously supplied under pressure through the jets of the distributing head 21, and with the vacuum atmosphere maintained in the chamber 11, a surface application of tungsten of a thickness of .001" is obtained in approximately one minute, with the temperature of the article maintained at from 350° F. to 400° F.

When the metal carbonyl to be applied to the surface of the object is in the liquid form, such as nickel carbonyl, the liquid is sprayed through the jets 22 of the distributing head 21 under a pressure of from 10 to 15 pounds per square inch to obtain a vaporous condition of the liquid carbonyl which is applied to the surface of the object being treated.

To obtain an even more complete evacuation of the chamber 11, the vacuum treatment may be applied in what may be termed a "batch" treatment in which the atmosphere of the chamber 11 is reduced to a vacuum of from 18" to 23" of mercury.

When this desired vacuum level has been reached, and the object 10 is raised in temperature to from 350° F. to 400° F., the metal carbonyl in vaporous condition is applied to the surface of the article being treated in the same manner as heretofore described. During this period, however, the vacuum pump is not operated because of the difficulty of maintaining the high level of vacuum in the chamber 11 when introducing any substantial volume of vaporous metal carbonyl into the chamber. When the vacuum level in the chamber falls to about 10" of mercury, the application of the metal carbonyl will be stopped temporarily and the vacuum level of the chamber again increased to from 18" to 23" of mercury, whereupon another metal carbonyl

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treatment is applied to the surface of the object. This "batch" process is repeated until the desired thickness of metal is built up on the surface of the object 10.

The latter method has advantage in that the carbon monoxide released as a result of the decomposition of the metal carbonyl is removed from the surface of the deposited metal and from the interstices of the base metal between each treatment of the surface under a very high vacuum removes all mono-molecular gaseous film from the surface of the base metal, and from the surface of any deposited metal so that the subsequent treatments with the vaporous metal carbonyl will obtain a firm bond of deposited metal to that previously deposited on the base metal.

By following the method of this invention, a more secure bond of the metal of the carbonyl to the base metal is obtained because of the removal of the mono-molecular film of gas from the surface of the base metal which allows the metal of the carbonyl to be deposited directly onto the base metal unaffected by any gas film which tends to restrict the movement of the metal of the carbonyl onto the surface of the base metal. Less scaling of the deposited metal, and more complete filling of the interstices of the metal that have any connection with the surface of the metal, is obtained.

The degree of impregnation of the surface of the base metal is, of course, dependent on the porosity of the base metal object. In extremely porous metals, somewhat deeper impregnation is obtained than in other metals.

The method of my invention is useful for treating metals and alloys to make them rustproof and subject to less corrosion and tarnishing by treating the metals with chrome or nickel carbonyls, for example. The method of my invention may also be used for the purpose of surface-hardening of metals, such as by the application of a tungsten metal to a base metal.

This application is a continuation-in-part application of my copending application, Serial Number 672,709, filed May 27, 1946 and now abandoned.

It will be understood that this invention is not restricted to the details given in the disclosure herein, but that it is susceptible to various modifications that fall within the spirit of the specification and the scope of the appended claims.

Having thus fully described my invention, what I claim as new and desire to secure by Letters Patent, is:

1. A method of coating and impregnating metal surfaces with another metal by gaseous deposition which comprises the steps of subjecting said metal surface to sub-atmospheric conditions and on the order of 18" to 23" of mercury, heating said metal to be coated while retained in said sub-atmospheric condition, introducing a heat-decomposable gaseous metal compound into said atmosphere and in contact with said heated metal, the temperature to which said metal is heated being high enough to cause decomposition of said heat decomposable gaseous metal compound whereby the same is decomposed and the metal constituent thereof deposited onto said metal surface and into the pores to form a coating of metal thereover which is firmly united to the metal surface.

2. The method of depositing elementary metals in the solid state upon other base metals and bonding the same thereto comprising, exposing the base metal to a vacuum atmosphere of between 18" and 23" of mercury and elevating the

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temperature of the base metal to the decomposition temperature of the carbonyl of the elementary metal to be deposited thereon, and subjecting the base metal while at elevated temperature and in said vacuum atmosphere to a vaporous atmosphere of the carbonyl of the elementary metal introduced under pressure into the vacuum atmosphere whereby to decompose the carbonyl and deposit elementary metal on the base metal.

3. The method of depositing elementary metals in the solid state upon other base metals and bonding the same thereto comprising, exposing the base metal to a vacuum atmosphere of between 18" and 23" of mercury and elevating the temperature of the base metal to the decomposition temperature of the carbonyl of the elementary metal to be deposited thereon, and immediately thereafter subjecting the base metal while at elevated temperature and in said vacuum atmosphere to a vaporous atmosphere of the carbonyl of the elementary metal introduced under pressure into the vacuum atmosphere in close proximity to the surface of the base metal on which the elementary metal is to be deposited whereby to decompose the carbonyl and deposit elementary metal on the base metal.

4. The method of depositing elementary metals in the solid state upon other base metals and bonding the same thereto comprising, exposing the base metal to a high vacuum atmosphere on the order of 18" to 23" of mercury and elevating the temperature of the base metal to the decomposition temperature of the carbonyl of the elementary metal to be deposited thereon, and immediately thereafter subjecting the base metal while at elevated temperature and in the vacuum atmosphere to a vaporous atmosphere of a metal carbonyl introduced under pressure into the vacuum atmosphere in close proximity to the surface of the base metal on which the elementary metal is to be deposited whereby to decompose the compound and deposit elementary metal on the base metal.

5. The method of depositing elementary metals in the solid state upon other base metals and bonding the same thereto which comprises, subjecting the base metal to a high vacuum atmosphere on the order of 18" to 23" of mercury to remove interstitially retained and pore-occluded gas from the base metal, heating the base metal to a temperature to cause the decomposition of the carbonyl compound of the elementary metal to be deposited thereon, and subjecting the base metal while thus heated and while retained in the vacuum atmosphere to a gaseous atmosphere containing the carbonyl of said elementary metal to be deposited and which is heat decomposed and depositing said elementary metal on the base metal.

6. The method of depositing elementary metals in the solid state upon other base metals from a heat-decomposable metal carbonyl compound and bonding the same thereto which comprises, subjecting the base metal to a vacuum atmosphere on the order of 18" to 23" of mercury and maintained at a temperature below the decomposition temperature of the carbonyl of the elementary metal to be deposited, elevating the temperature of the base metal to the decomposition temperature of the carbonyl of the elementary metal to be deposited thereon, and immediately thereafter subjecting the base metal while at elevated temperature and while retained in the vacuum atmosphere to a gaseous atmosphere

of the carbonyl of the elementary metal which is introduced under pressure into the vacuum atmosphere and said carbonyl heat-decomposed to deposit the elementary metal on the base metal.

7. The method of depositing elementary metals in the solid state upon other base metals from a heat-decomposable metal carbonyl compound and bonding the same thereto which comprises, subjecting the base metal to a vacuum atmosphere of between 18" and 23" of mercury, elevating the temperature of the base metal to between about 350° F. and 400° F., thereafter subjecting the base metal while at said elevated temperature and under said vacuum atmospheric conditions to gaseous metal carbonyl which is decomposable at the temperature of said base metal, said gaseous metal carbonyl being delivered under pressure of from 10 lbs. to 15 lbs. per square inch whereby said carbonyl is caused to decompose and deposit elementary metal on the base metal.

8. The method of depositing elementary metals in the solid state upon other base metals from a heat-decomposable metal carbonyl compound and bonding the same thereto comprising, subjecting the base metal to a high vacuum atmosphere of between about 18" and 23" of mercury, heating the base metal to the decomposition temperature of the carbonyl of the elementary metal to be deposited thereon, subjecting the base metal while at said decomposition temperature and while retained in the vacuum atmosphere to a gaseous atmosphere of the carbonyl of the elementary metal to be deposited whereby to cause decomposition of the carbonyl and deposition of the elementary metal on the base metal with resultant liberation of gas into the vacuum at-

mosphere, restoring the vacuum atmosphere to its initial condition while maintaining said base metal heated, and re-exposing the base metal to said gaseous atmosphere of said carbonyl of the elementary metal.

9. A method according to claim 7 in which the metal of the metal carbonyl is selected from the group consisting of nickel, cobalt, chromium, iron, tungsten and molybdenum.

10. A method according to claim 8 in which the metal of the metal carbonyl is selected from the group consisting of nickel, cobalt, chromium, iron, tungsten and molybdenum.

11. As a new article of manufacture, a metal product having a surface with minute irregularities, and a deposit of an elementary metal on the said surface obtained according to the method set forth in claim 7.

12. As a new article of manufacture, a metal product having a surface with minute irregularities, and a deposit of an elementary metal on the said surface obtained according to the method set forth in claim 8.

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