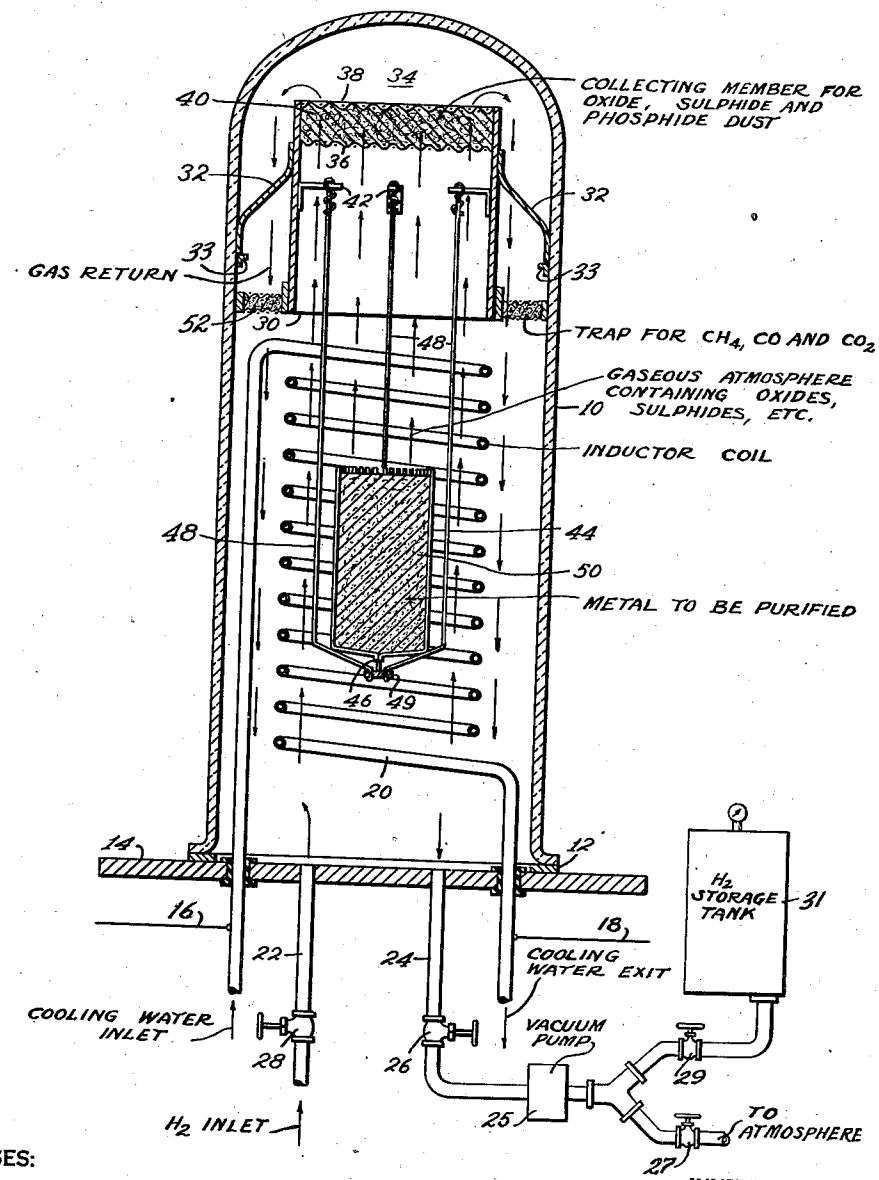
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METHOD OF PURIFYING METAL

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WITNESSES:

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METHOD OF PURIFYING METAL

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This invention relates to the purification of metals.

It has been recognized that the physical properties of metals in general may be considerably improved if the metals are freed of non-metallic contaminations. For example, it is known that the green oxide of chromium, Cr_2O_3 is very stable and, as such oxide is slightly soluble in chromium, it has an adverse effect on the ductility of chromium. Other metals are also adversely affected by similar oxides and other non-metallic impurities.

Heretofore attempts have been made to free the different metals of oxides present either as inclusions or in solution. It is known that hydrogen will reduce oxides but it has been impractical heretofore to reduce the lower oxides of some of the metals and alloys in that it has been impractical to produce hydrogen sufficiently free of oxygen-bearing gases in large enough volumes by conventional methods to enable the effective reduction of and removal of oxides from the metal.

An object of this invention is to provide a method of purifying metals.

Another object of this invention is to provide for reducing the oxides of metals while at the same time producing hydrogen free of oxygen-bearing gases.

Other objects of this invention will become apparent from the following description when taken in conjunction with the accompanying drawing, the single figure of which is a view in section illustrating apparatus for practicing the method of this invention.

In general, it has been found that only those metals having a vaporization rate of not less than 4×10^{-3} grams per square centimeter per hour when heated at a temperature between 70% and 95% of the melting temperature of the metal can be successfully treated in accordance with the teachings of this invention to provide for the removal of the smaller residues of impurities such as oxygen, sulphur and phosphorus. Metal selected from the group consisting of titanium, zirconium, vanadium, chromium, manganese, copper, cobalt, nickel, iron, columbium, tungsten, molybdenum and hafnium and alloys thereof can be successfully treated as described hereinafter to purify the metal.

All of the metals referred to and the alloys of such metals, for example 18–8 stainless steel, molybdenum base alloys containing 10% to 20% tungsten with or without .05% to .5% chromium or other well known combinations of the alloying components, have melting points in excess of

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1000° C. and when heated sublimate or vaporize at rates depending upon the temperature at which they are heated. For example, tungsten, which has the lowest vaporization rate of the metals listed, has too low a vaporization rate when heated at a temperature of 2360° C. to be readily purified but when heated at a temperature of 3000° C. or approximately 90% of its melting temperature is found to have a vaporization rate of 4×10^{-3} grams per square centimeter per hour and to be readily purified by the method to be described.

Referring to the drawing, this invention is illustrated by reference to a representative apparatus utilized in effecting the purification of metals as contemplated by this invention. As illustrated, the apparatus comprises a bell jar 10 of suitable material, such as glass, inverted to seat on a sealing washer 12 disposed on a base member 14. The base member 14 is provided with suitable apertures for receiving in an insulated manner, the leads 16 and 18 of an inductor coil 20 and conduits 22 and 24. The inductor coil is of the usual type being formed of copper tubing through which a cooling medium, such as water (not shown) is disposed to be circulated, the leads 16 and 18 being connected to a suitable source of alternating-current power for producing an alternating magnetic field within the confines of the coil.

The conduit 24 has a valve 26 connected therein and is disposed to be connected to a vacuum pump 25 and from thence through a valve 27 to the atmosphere for evacuating the chamber formed by the bell jar 10 and the base 14, or through a valve 29 to a storage tank 31, as will be described hereinafter. Similarly, the conduit 22 is provided with a valve 28 and is disposed to be connected therethrough to a source (not shown) of hydrogen, the purpose of which will be explained more fully hereinafter.

Positioned adjacent the upper end of the inverted bell jar 10 is a cylindrical member 30 disposed substantially in alignment with the inductor coil 20 and maintained in its operative position by means of spring clips 32. The spring clips 32 are disposed in spaced relation about the outer wall of the cylindrical member 30 being secured thereto in any suitable manner, such as by welding, the outer edges of the spring clips 32 being spring biased into engagement with the inner walls of the bell jar 10 to maintain the cylindrical member 30 in its operative position relative to the inductor coil by a friction contact with the bell jar. If desired, suitable lugs 33 may

be provided on the inner side walls of the bell jar 10 for the free ends of the spring clips 32 to seat against when the cylindrical member 30 is in its relative operating position.

As illustrated, the cylindrical member 30 is provided with an obstruction 34 disposed adjacent to and across its upper end. The obstruction 34 in the embodiment illustrated comprises two spaced wire mesh members 36 and 38 between which is disposed a mass 40 of steel wool or the like, whereby the obstruction 34 comprises a labyrinthic collecting member being provided with a maze of passages therethrough, the purpose of which will be explained more fully hereinafter.

The cylindrical member 30 is also disposed to carry a plurality of spaced lugs 42 disposed about its inner surface and secured thereto in any suitable manner, such as by welding for supporting a receptacle 44 within the inductor coil 20. The receptacle 44 preferably is formed of molybdenum in the form of a wire bird cage so as to form a substantially open receptacle of vertical wires joined only at the base as at 46. The receptacle 44 is maintained in its operative position in the inductor coil 20 by being hung from the lugs 42 by means of fine strands 48 of molybdenum, the lower ends of which are looped over a ring 49 of ceramic material. The receptacle 44 seats within the confines of the strands 48. With a charge 50 of the metal to be purified within the receptacle 44, as illustrated, it is apparent that the metal 50 may be readily heated by supplying power to the inductor coil 20.

In practicing the method of this invention, a charge 50 of metal to be purified, is disposed in the receptacle 44 and the bell jar 10 is positioned on the base 14 with the receptacle 44 disposed centrally of the inductor coil 20. The charge 50 may be any of the metals referred to hereinbefore or their alloys but for purpose of illustrating the invention, the method will be described as applied to a charge 50 of chromium. The chromium may be in any suitable form such as a bar, plate or slab or may be a block formed of compacted granules. Power is then supplied to the inductor coil 20 to heat the metal 50 to a temperature in the neighborhood of 700° C. or somewhat higher and with the valves 28 and 27 closed, the valves 26 and 27 are opened to exhaust the bell jar. With the metal heated in this manner, it is found that the metal evolves sensible gases therefrom and where a vacuum of the order of 10^{-3} mm. of mercury is utilized, the chromium within the receptacle 44 is quickly denuded of sensible gases.

The valve 26 is then closed and the valve 28 opened to admit hydrogen to the bell jar 10, the hydrogen preferably being as pure as can be obtained by conventional purification methods whereby the hydrogen contains not over 2% of oxygen-bearing gases. Sufficient hydrogen is admitted to the bell jar 10 until a pressure of not less than one cm. on the mercury scale is obtained and at the same time the power supplied to the inductor coil 20 is increased, whereby the metal is heated inductively to a temperature between 70% and 95% of the melting point of the metal to effect vaporization of the metal 50 contained in the receptacle 44. In the case of chromium, it is found that a temperature of 1500° C. with a hydrogen pressure of approximately 10 cm. on the mercury scale is sufficient to effect the required vaporization of chromium.

As the chromium vaporizes, the evaporated metal atoms merge with the hydrogen containing

the oxygen-bearing gases as the gaseous atmosphere flows upwardly within the coil 20. It is, of course, appreciated that the gaseous atmosphere flows upwardly within the coil 20 by convection as the zone of vaporization within the coil is much hotter than the zone external of the coil 20, so that the gaseous atmosphere will tend to circulate within the bell jar 10 in the direction illustrated by the arrows.

As the evaporated metal atoms merge with and are somewhat cooled by the hydrogen containing the oxygen-bearing gases, they react in accordance with the formula

$$2Cr+3H_2O \rightarrow 3H_2+Cr_2O_3$$

to form the green oxide of chromium. The green oxide of chromium, Cr_2O_3, appears as a fume or fog in the hydrogen atmosphere and rises with the hydrogen by convection into the cylindrical member 30 where the hydrogen flows to and through the labyrinthic collecting member 40. As the hydrogen containing the reaction product flows through the member 40, the reaction products contact the collecting surfaces of the member 40, such surfaces being cool relative to the zone of vaporization referred to hereinbefore, and the reaction products are deposited on the surfaces of the collecting member 40 in the form of particles of green dust. The hydrogen emerging from the collecting member 40 is free of the reaction products and flows downwardly, as indicated by the arrows between the outer surface of the cylindrical member 30 and the inner surface of the bell jar 10 to be returned to the lower end of the inductor coil 20, where it again rises by convection to flow through the zone of vaporization described hereinbefore.

As the hydrogen freed of the reaction products flows upwardly within the coil 20, it envelopes the metal 50 in the receptacle 44 and by contact with the metal, removes oxides therefrom in accordance with the formula

$$Cr_2O_3+3H_2 \rightarrow 2Cr+3H_2O$$

The resultant oxygen bearing gases in the hydrogen thus formed, in turn, react with the evaporated metal atoms in the zone of vaporization to form the reaction products in the form of a fume or fog, as described hereinbefore, which by convection are carried to the collecting member 40 where the oxides are deposited on the collecting surfaces, thus completing the cycle.

As will be appreciated, by continuously circulating the hydrogen within the bell jar 10 as described hereinbefore, the oxides of chromium are progressively reduced and the reaction products are collected in the labyrinthic collecting member 40, whereby an extremely pure hydrogen atmosphere is obtained in addition to effectively reducing the oxides of the chromium. As soon as the oxides of the metal 50 have been reduced in the manner described, the inductor coil 20 is disconnected from the power supply and the metal 50 is permitted to cool in the purified hydrogen atmosphere.

As a specific example, where bright annealed electrolytic chromium is treated in accordance with the method described, the oxide content of the electrolytic chromium is reduced from approximately 1%, which is standard for annealed electrolytic clean chromium, to .03%. This reduction has been obtained in a manner of 30 minutes or so with masses of chromium weighing approximately 1.5 kilograms. In another instance where a plate of electrolytic chromium

was subjected to the method of this invention it has been found that the metal of the plate is so purified in a matter of 30 minutes that the plate displays appreciable plasticity as compared to the extreme brittleness which in the past has characterized even annealed chromium plate. In all cases the surface of the metal so treated is so clean that it can readily be wetted by copper at temperatures only a few degrees higher than the melting point of copper. This is a striking demonstration of the absence of oxide films and, concomitantly, the high purity of the hydrogen attained by my method.

While reference has been made so far only as to the removal of the oxides of the metal it will of course be appreciated that other impurities such as sulphur and phosphorus when present in the metal will react with the vaporized metal atoms and be deposited as sulphide dust and phosphide dust in the labyrinthic collecting member.

As stated hereinbefore the vaporization temperature employed will depend on the metal or alloy which is to be purified. However, the vaporization or working temperature in all cases is between 70% and 95% of the melting temperature. If the vaporization temperature is more than 95% of the melting temperature, the metal being treated becomes so soft that it can not be successfully physically handled whereas if the temperature is below 70% of the melting temperature, the rate of vaporization is too slow to economically and efficiently effect the required purification of the hydrogen.

If the metal **50** being treated in accordance with this invention contains carbon, such impurity is also readily removed from the metal if a trap (not shown) containing charcoal, activated alumina or the like is positioned between the outer edge of the cylindrical member **30** and the inner surface of the bell jar **10**, so that as the hydrogen flows from the labyrinthic collecting member **40**, the reaction products of carbon and hydrogen, such as CH_4, CO and CO_2 will be trapped therein. The trap **52** may be carried by the cylindrical member **40**, being secured thereto in any suitable manner, such as by welding.

In all cases, it is found that the metals identified hereinbefore and their alloys are readily purified when treated in accordance with the method of this invention, and that the hydrogen obtained after such purification of the metal is of itself extremely pure. It will be appreciated that the method of this invention can be practiced by utilizing a very small quantity of commercially purified hydrogen as the hydrogen is recirculated as described. If it is desired, the purified hydrogen may be removed from the bell jar **10** after the metal **50** is cooled by closing valve **27** and opening the valves **26** and **29** and evacuating the bell jar to a suitable container **31** for storing the purified hydrogen.

I claim as my invention:

1. In the method of purifying metal having a melting point over 1000° C. and a rate of vaporization of not less than 4×10^{-3} grams per square centimeter per hour at a temperature between 70% and 95% of the melting temperature of the metal, the steps comprising, positioning the metal in a closed chamber, evacuating the chamber while subjecting the metal to sufficient heat to effect the evolution of sensible gases from the metal, admitting a hydrogen atmosphere containing oxygen-bearing gases to the evacuated chamber, heating the metal at a temperature between 70% and 95% of the melting temperature of the metal to effect the vaporization thereof at a rate of not less than 4×10^{-3} grams per square centimeter per hour, reacting the vaporized metal with the oxygen-bearing gases of the hydrogen atmosphere, passing the hydrogen atmosphere containing the reaction products to and through a labyrinthic collecting member to deposit the reaction products thereon, and returning the hydrogen atmosphere freed of the reaction products to the zone of vaporization of the metal to effect the deoxidization of the metal.

2. In the method of purifying metal having a melting point over 1000° C. and a rate of vaporization of not less than 4×10^{-3} grams per square centimeter per hour at a temperature between 70% and 95% of the melting temperature of the metal, the steps comprising, positioning the metal in a closed chamber, evacuating the chamber while subjecting the metal to sufficient heat to effect the evolution of sensible gases from the metal, admitting a hydrogen atmosphere containing oxygen-bearing gases to the evacuated chamber until a gaseous pressure of at least one centimeter of mercury is obtained, heating the metal at a temperature between 70% and 95% of the melting temperature of the metal to effect the vaporization thereof at a rate of not less than 4×10^{-3} grams per square centimeter per hour, reacting the vaporized metal with the oxygen-bearing gases of the hydrogen atmosphere, passing the hydrogen atmosphere containing the reaction products to and through a labyrinthic collecting member to deposit the reaction products thereon, and returning the hydrogen atmosphere freed of the reaction products to the zone of vaporization of the metal to effect the deoxidization of the metal.

3. In the method of purifying metal having a melting point over 1000° C. and a rate of vaporization of not less than 4×10^{-3} grams per square centimeter per hour at a temperature between 70% and 95% of the melting temperature of the metal, the steps comprising, positioning the metal in a closed chamber, evacuating the chamber while subjecting the metal to sufficient heat to effect the evolution of sensible gases from the metal, admitting a hydrogen atmosphere containing not over 2% of oxygen-bearing gases to the evacuated chamber, heating the metal at a temperature between 70% and 95% of the melting temperature of the metal to effect the vaporization thereof at a rate of not less than 4×10^{-3} grams per square centimeter per hour, reacting the vaporized metal with the oxygen-bearing gases of the hydrogen atmosphere, passing the hydrogen atmosphere containing the reaction products to and through a labyrinthic collecting member to deposit the reaction products thereon, and returning the hydrogen atmosphere freed of the reaction products to the zone of vaporization of the metal to effect the deoxidization of the metal.

4. In the method of purifying metal having a melting point over 1000° C. and a rate of vaporization of not less than 4×10^{-3} grams per square centimeter per hour at a temperature between 70% and 95% of the melting temperature of the metal, the steps comprising, positioning the metal in a closed chamber, evacuating the chamber while subjecting the metal to sufficient heat to effect the evolution of sensible gases from the metal, admitting a hydrogen atmosphere containing oxygen-bearing gases to the evacuated

chamber, heating the metal at a temperature between 70% and 95% of the melting temperature of the metal to effect the vaporization thereof at a rate of not less than 4×10^{-3} grams per square centimeter per hour, reacting the vaporized metal with the oxygen-bearing gases of the hydrogen atmosphere, passing the hydrogen atmosphere containing the reaction products to and through a labyrinthic collecting member to deposit the reaction products thereon, recirculating the hydrogen atmosphere freed of the reaction products through the zone of vaporization where the purified hydrogen combines with oxides to effect the deoxidization of the metal and the resulting oxygen-bearing hydrogen atmosphere reacts with the vaporized metal, continuing the circulation of the hydrogen atmosphere through the labyrinthic member and the zone of vaporization until the metal is purified, and then cooling the purified metal in the purified hydrogen atmosphere.

5. In the method of purifying metal having a melting point over 1000° C. and a rate of vaporization of not less than 4×10^{-3} grams per square centimeter per hour at a temperature between 70% and 95% of the melting temperature of the metal, the steps comprising, positioning the metal in a closed chamber, evacuating the chamber

while subjecting the metal to sufficient heat to effect the evolution of sensible gases from the metal, admitting a hydrogen atmosphere containing not over 2% of oxygen-bearing gases to the evacuated chamber until a gaseous pressure of at least one centimeter of mercury is obtained, heating the metal at a temperature between 70% and 95% of the melting temperature of the metal to effect the vaporization thereof at a rate of not less than 4×10^{-3} grams per square centimeter per hour, reacting the vaporized metal with the oxygen-bearing gases of the hydrogen atmosphere, passing the hydrogen atmosphere containing the reaction products to and through a labyrinthic collecting member to deposit the reaction products thereon, recirculating the hydrogen atmosphere freed of the reaction products through the zone of vaporization where the purified hydrogen combines with oxides to effect the deoxidization of the metal and the resulting oxygen-bearing hydrogen atmosphere reacts with the vaporized metal, continuing the circulation of the hydrogen atmosphere through the labyrinthic member and the zone of vaporization until the metal is purified, and then cooling the purified metal in the purified hydrogen atmosphere.

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