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# WORKING OF TITANIUM

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This invention relates to the working of titanium, particularly to a method for working titanium to obtain articles of improved properties.

The increasing technological importance of titanium metal is well known. Because of its light weight, high strength, maintenance of its strength at high temperatures and other advantageous properties, titanium has shown itself to be unique among the metals for many purposes. Titanium has, however, not attained wide spread usage because of the difficulty of recovering it from its ores and, also, of working it after it has been recovered in metallic form. As presently produced, titanium metal is generally obtained from its ores in the form of a coarse mass or "sponge" which has a very large surface area in proportion to its weight. The actual reduction of titanium to the metallic state is often effected by the use of a metal more reactive than titanium, e. g. sodium, aluminum, magnesium and the like, so that the sponge is frequently contaminated with an appreciable proportion of the more reactive metal. This must be removed as completely as possible if the most advantageous properties of the titanium are to be realized. Certain other metals present in the original ore are also likely to be converted to the metallic state along with the titanium and to appear therein as an impurity.

Because titanium metal is reactive with both oxygen and nitrogen when heated at moderately low temperatures to form oxides and nitrides, respectively, and because the metal melts at about 1800 degrees C., it is extremely difficult to work the metal without including in the worked product a very high proportion of the oxide and the nitride. Oxide and nitride formation proceeds at an appreciable rate at temperatures as low as 100 degrees to 150 degrees C. Titanium sponge as produced commercially contains a considerable proportion of the oxide and nitride, as well as some silicon and other impurities, even before any attempt is made to work it. Because of the high melting point of both the oxide and the nitride and because of the fact that the sponge is generally worked up into shapes and articles at temperatures well below its melting point and well below those of the nitride and oxide, e. g. at temperatures as low as 300 degrees C., it is practically impossible to effect any substantial removal of the oxide and nitride during the working operation. Actually, the proportion of these substances in the metal increases rapidly during working up of the sponge in the atmosphere even at only moderately elevated temperatures. Any calcium, sodium, aluminum or magnesium in the sponge is very likely to be converted to its oxide during such working operation. The net result of attempting to work up the sponge in an atmosphere of air at any reasonably elevated temperature is the formation of an article having such a high proportion of the oxide and nitride, together with the other substances mentioned, that it is brittle and substantially worthless. It may even comprise a major proportion of the oxide and nitride and only a minor proportion of the free metal.

Attempts have been made to avoid these difficulties following conventional procedures frequently employed in the working of aluminum and magnesium. Such attempts include the carrying out of the working operation in an inert atmosphere of argon or helium to prevent the formation of additional oxide and nitride during the working operation. Such procedures are costly to carry out and, furthermore, fail to remove the oxide and nitride already present in the metal. Obviously, they do not serve as a fluxing agent to convert the oxide and nitride, or any of the other impurities which may be present, to a liquid slag which can be squeezed or worked out of the metal readily. No entirely satisfactory fluxing agent for the working of titanium has heretofore been developed. It is apparent that any procedure which can be employed in the working of titanium to give products superior to those now possible to obtain would be of extreme value.

It has now been found that most of the difficulties encountered in the working of titanium due to the retention of non-metallic substances and of highly reactive metals in the worked metal, and to the conversion of metal to oxide or nitride, can be overcome almost entirely by hot-working the metal while keeping its surface blanketed with an atmosphere comprising a phosphorus oxide, such as phosphorus trioxide or phosphorus pentoxide. When the working is carried out in this manner, substantially all of the titanium oxide and nitride, most of the silica, the reactive metals and their oxides and many other impurities often associated with the metal in small proportions, are converted smoothly and rapidly to phosphorus-containing slags which are liquid over substantially the entire desirable working range of the titanium. Because of the conversion of these impurities to liquid slags they can be removed readily from the metal by hammering, squeezing, rolling and other conventional metal working operations. The production of metal of a high degree of purity during the working to form desired shapes or articles is thus facilitated enormously and the highly advantageous properties of the purified metal can be realized without difficulty. In addition, because of the exclusion of nitrogen and oxygen by a film of the slag during the working process, the worked metal is obtained with a clean, bright surface. The slag, which is thought to include titanium oxyphosphorus compounds of various sorts, adheres tightly to the metal surface even when the latter is bent or when it is cold worked using conventional procedures and contributes valuable anti-corrosive properties to the metal surface.

Insofar as is known, any oxide of phosphorus, including phosphorus pentoxide, phosphorus trioxide, phosphorus tetroxide and mixtures thereof, can be used in the process. Generally speaking, however, the process is carried out using phosphorus pentoxide or a mixture of oxides high in pentoxide content, such as is obtained by burning elemental phosphorus in an excess of air. When phosphorus trioxide is used it is likely that a large proportion of it is converted to the pentoxide during the operation of the process. For these reasons the invention will be described with particular reference to phosphorus pentoxide, but without limitation thereto. When the phosphorus oxide is prepared as used by burning phosphorus, care should be exercised to prevent as far as possible the contacting of elemental phosphorus with the titanium metal surface to avoid undesirable reactions and pitting of the metal surface. Elemental phosphorus may also dissolve in the metal to some extent.

It appears that the fluxing action of the phosphorus oxide may be due to the reaction of the oxide with traces of moisture present either on the metal surface or in the surrounding atmosphere to form phosphorus acids of a limited degree of hydration, such as metaphosphoric acid, when then reacts with titanium and other metal oxides, as well as with highly reactive metals, such as sodium, calcium, magnesium and the like which may be present, to form the corresponding salt, e. g. metaphosphates, constituting the liquid slags. In the case of the metal oxides, water is reformed and is available to promote the fluxing action further. It is probable that the phosphorus oxide itself contains sufficient moisture in the form of a phosphorus acid to initiate and maintain the fluxing action unless extreme care is used in its preparation. The affinity of phosphorus pentoxide for water vapor is well known. It may even be that the fluid nature of the slag formed is accentuated by the presence in it of some unreacted phosphorus acid. It is, however, desirable to avoid the access of excessive moisture to the working region to prevent the formation of undue amounts of the more highly hydrated phosphorus-containing acid, e. g. orthophosphoric acid, which are prone to react with titanium metal.

The working of titanium employing phosphorus pentoxide as a fluxing and protective agent can be carried out in a number of ways depending upon the form of the metal started with, the final shape or form desired, and other factors. In the conversion of sponge titanium to desirable forms, such as rods, sheets, billets and the like, it is convenient to heat the sponge at a suitable hot working temperature, i. e. at from about 300 degrees to about 1800 degrees C., while keeping it blanketed with an atmosphere comprising phosphorus pentoxide vapor, and to then work the sponge into the desired shape by hammering, rolling, forging, drawing or other conventional procedures. This can be carried out in a closed chamber containing phosphorus pentoxide vapors. Alternatively, the working can be done in the atmosphere and small quantities of phosphorus pentoxide added continually to the heated surfaces during the time the working is being carried out. In one modification, the heating is effected with a torch into the flame of which phosphorus pentoxide powder, or even elemental phosphorus, is fed continuously so as to furnish a blanketing atmosphere containing phosphorus oxide vapors on the heated surface. It is also convenient in many instances to mix cold titanium sponge with powdered phosphorus pentoxide and then to heat and work the sponge. In certain instances the working is carried out in such a manner that it causes the sponge to be heated due to internal friction and stresses created in the sponge. In such instances external heating of the sponge is often unnecessary.

In the hot working of solid titanium shapes, such as sheets, rods and billets by conventional rolling, drawing, forging, hammering and other processes, it is convenient to maintain the atmosphere of phosphorus pentoxide around the working area so that as fresh surfaces of the metal are exposed during the working operation they will be protected, the oxide and nitride in the metal will be converted to slag as it comes to the surface and the formation of additional quantities of oxide and nitride substantially prevented.

It is apparent that, when the working operation is carried out in the open air, oxygen and nitrogen are not excluded entirely from the vicinity of the heated metal surface even though the concentration of phosphorus pentoxide in the vicinity is high. It appears, however, that the complete exclusion of oxygen and nitrogen is unnecessary and that the surface of the titanium is almost completely protected even from high concentrations of these gases by a thin film of phosphorus-containing slag which forms almost immediately when the pentoxide vapors are caused to contact the slag-forming constituents in the heated metal surface and that this film spreads rapidly over new metal surfaces as soon as they are exposed. It may, of course, be that when a new metal surface is exposed during the working, a surface film of oxide or nitride forms on it and that this film then reacts with phosphorus pentoxide vapor to form a protective film of slag.

Certain advantages of the invention are apparent from the following examples which are given by way of illustration only and are not to be construed as limiting.

*Example I*

A steel die was prepared by drilling a 3/16 inch hole through a one-inch block of steel and then splitting the block through the longitudinal axis of the hole. The two halves were secured together by bolts, the die being placed on a flat steel plate to close one end of the hole during the loading and working operations subsequently described.

The cavity in the die just described was filled with a mixture of small pieces of sponge titanium and phosphorus pentoxide powder. A steel rod a little less than 3/16 inch in diameter was then forced into the cavity on top of the charge and hammered lightly until the charge filled only about 13/16 inch of the cavity. The entire die and contents were then heated at about 300 degrees C. and the 3/16 inch rod hammered into the die cavity until the slug remaining in the cavity was 1/2 inch long. The die was then cooled and the slug removed. It was noted that some of the slag which had formed had been forced out of the cavity between the two blocks of steel and also that some of it had been forced upward between the rod and the cavity wall. Some solid phosphorus pentoxide remained as small pockets in the compressed slug.



The die was closed again, the slug was inserted in the cavity and the die heated and held at about 550 degrees C. for about 4 minutes. The steel rod was then hammered into the cavity again and the slug compressed further until it was 5/16 inch long. The die was then chilled with water to about 150 degrees C., allowed to cool in the air and opened when cold. The titanium pellet thus produced appeared to be substantially free of voids or of cavities filled with slag or with phosphorus pentoxide and was removed from the die easily by gentle tapping without opening the die. The cavity wall was smooth and shiny and showed no sign of any adherent material.

The titanium pellet was quickly "neutralized" by immersing it in dilute aqueous ammonia for 15 minutes to remove all traces of phosphorus-containing acids and unreacted phosphorus pentoxide, and then air dried. The pellet thus obtained was in the form of a cylinder of uniform diameter free of pockets and voids with a shiny metallic surface. It could be filed easily without any sign of crumbling or shattering.

*Example II*

A short section of the 3/16 inch titanium pellet, produced according to the procedure of Example I, was hammered on a steel anvil into a thin flat sheet while heated at 400 to 550 degrees C. in the flame of a torch burning lead-free gasoline. A few milligrams of phosphorus pentoxide was sprinkled on the hot work piece and on the anvil after each few blows of the hammer. There was thus obtained a thin sheet estimated to be about 1/64 inch in thickness which was flexible and free from brittleness. The surface of the sheet contained a uniform tightly adherent coating which was not removed by vigorous washing of the sheet with water.

*Example III*

A second section of the 3/16 inch diameter titanium pellet, produced according to the procedure of Example I, was heated and hammered as before except that the hammering was on the circumference of the section, the section being rotated in such a way that the diameter of the section was decreased and its length increased to form a rod about 1/16 inch in diameter and of correspondingly increased length. During the heating and hammering operation a small amount of phosphorus pentoxide powder was dropped into the torch flame and carried by it to the surface of the work piece after each few blows of the hammer. The rod thus obtained was of uniform density, flexible, and contained insufficient occluded titanium oxide, titanium nitride and slag to detract seriously from its properties.

*Example IV*

The cavity of the die described in Example I was again loaded with small pieces of sponge titanium and phosphorus pentoxide powder and heated to 400 to 500 degrees C. and a 3/16 inch steel rod hammered into the cavity as before, the entire operation being carried out rapidly and without interruption. The 3/16 inch titanium pellet thus obtained was neutralized with dilute ammonia as before and appeared to be identical in substantially all respects to the pellet prepared as in Example I.

I claim:

1. The method for working titanium metal, which comprises working the metal and subjecting its surface during the working operation to the action of the vapor of a phosphorus oxide.

2. The method of claim 1 wherein the working operation is carried out at a temperature between about 300 degrees C. and about 1800 degrees C.

3. The method of claim 1 wherein the phosphorus oxide is principally phosphorus pentoxide.

4. The method for reducing the content of titanium oxide and titanium nitride in titanium metal which includes the steps of heating titanium metal containing titanium nitride and titanium oxide at a hot working temperature above about 300 degrees C., hot working the heated metal, and maintaining the surfaces of the metal in contact with the vapor of a phosphorus oxide during the working operation.

5. The method for converting sponge titanium to a

shaped form which comprises mixing sponge titanium with a phosphorus oxide, heating the mixture at a temperature above about 300 degrees C., and compacting the heated mixture to form a substantially uniform titanium article of desired configuration having a content of titanium oxide and titanium nitride in the metal lower than that in the titanium sponge.

6. The method for altering the form of a titanium



article which includes the steps of heating the article to a hot working temperature above about 300 degrees C., hot working the article to convert it to an article of desired configuration, and maintaining at the surface of the article during the working operation a substantial concentration of the vapor of a phosphorus oxide.

No references cited.