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PROCESS FOR OBTAINING PURE CHROMIUM, TITANIUM, AND CERTAIN OTHER METALS AND ALLOYS THEREOF

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The present invention relates to the production of chromium, titanium and certain other metals in a solid, dense, malleable and ductile state; such metals being of the class, which at temperatures required to work them readily combine with atmospheric nitrogen, and which have melting points in excess of 1550 degrees centigrade.

In modifications thereof, the invention relates to the production of alloys of the aforesaid metals, as for example, an alloy of chromium and cobalt, whereby to enhance the toughness or other attributes of the metal, better to meet the requirements of any particular use thereof.

The metals, such as chromium and titanium, with which we are here concerned, have not heretofore been obtainable in pure form except as powders, crystalline lumps, or as bars or masses of such porous or brittle nature as to be useless as a material from which to form tools or machine parts. Furthermore, in the sintering and other steps which have heretofore been employed in attempts to make the material dense, ductile and workable, the material has been exposed at high temperatures to gases which are not inert, such for instance as atmosphere, hydrogen or nitrogen, with the result that the masses of material so treated have had surfacings of nitrides, oxides, hydrides, etc., formed thereon. Such surfacings have often been as hard as of the order of No. 9 on the Mohs' scale; and have been too hard for practical tooling, working, or shaping of the metal masses.

An object of the invention is the conversion of powder, or granular masses, of chromium, titanium and other metal, of any desired purity, into dense, solid, ductile and workable bars, billets or other configurations, of like purity, of the metal treated; without the formation at any step of the process of any objectionable nitrides, oxides, hydrides or other compounds of such metal, at the surfaces of the masses being treated.

As illustrative of the invention, I have, by a process hereinafter more particularly described, produced bars, billets, and other configurations of solid, dense, and ductile, pure chromium, of a hardness only of the order of from No. 4 to No. 5 on the Mohs' scale; and I have produced this pure chromium in cold state, unsurfaced by any compound of metal, and in solid bars and billets of from one to two inches thick; there being no limitations as to thickness in the product of the invention. Obviously, a metal of a hardness of only No. 4 to No. 5, Mohs, is readily machined or shaped to any desired form.

Important as may be, in certain arts, the production of chromium, titanium and other metals, either pure or as alloys, having attributes such as mentioned in the last paragraph hereof, nevertheless the production of a metal or alloy having such softness is not the ultimate aim of the invention. A metal or alloy of this softness would be of little utility as a tool or as an element of a machine. An important consideration in connection with the invention lies in the fact that the carbides, silicides, nitrides, and hydrides of chromium, titanium and other metals are among the hardest known substances. It has been mentioned above that the incidental and undesired formation of these compounds in the past art has resulted in a product that could not be machined or shaped to desired form in any commercially practical manner. These compounds are of a hardness of the order of No. 9 on the Mohs' scale: the diamond being No. 10.

It is an ultimate object of the invention to provide for the production of tools, ball and other bearings, cylinder blocks of gasoline engines, valves and valve seats, and other machine elements of such hardness as to be practically unwearable. As material of such hardness cannot be worked or shaped to the desired form, it is an object of the invention to produce the chromium, titanium or other metal in such state that it can be worked or shaped to the desired form, and thereafter be case- or skin-hardened or compounded to the desired hardness for the purpose intended.

This hardening may be effected by heating the pre-formed chromium, titanium or other articles to the proper temperature, for the proper time, and under the proper conditions, in the presence of carbonaceous or other gas, liquid, or powder, containing the element which it is desired to have combined with the chromium, titanium or other metal. Processes for effecting this hardening are hereinafter more fully specified.

A summary of the objects of the present invention may be stated to be: first, the obtaining of a malleable metal; second, the working of the malleable metal to desired shape; and third, the hardening of the shaped metal. The malleable metal can be obtained by compressing a powder of the metal, and heating the same to a sintering point; or, by melting powder, lumps, or other particles of the metal in a proper container. These sintering and melting operations must be performed in a vacuum, an inert gas, or in a gas tight envelope. The working of the malleable metal, thus obtained, may be effected slowly at

a temperature below 400° C., or by working at a high temperature after heating in a close fitting air-tight envelope. The metal thus worked is then ready for hardening, by heating in hydrocarbon gas, nitriding, cyaniding, or by other suitable and well-known methods for case hardening metals.

The above, and other objects and features of the invention will now more fully and in detail be set forth.

A mass of the powder of chromium or other metal is first subjected to hydraulic pressure sufficient to create therefrom a bar, billet, or other configuration of the metal, having such adherence of the particles thereof as to permit handling of the same as a unit.

This compressed mass is then to be thoroughly sintered, in the absence of contact therewith of any gases or other substances which could effect undesirable chemical combination with the metal at sintering temperatures. To this end, the sintering may be effected in a vacuum, or in inert gases, as for instance, helium or argon. Or, it may be effected by first sealing the metal mass in a non-porous envelope, completely enclosing the metal, and of a material, such for instance, as certain cements, which can withstand sintering temperatures without injury to the envelope, and which will not enter into compound with the metal, and then subjecting the envelope and metal to sintering temperatures in any ordinary furnace. Of course, some amount of air will necessarily be included in the envelope with the metal, but the amount of air will be so small as to have no deleterious effects upon the metal.

The sintering temperature of the bar or billet may be as low as 1000° C., but will preferably be a temperature approximating 90% of the melting point of the metal: or a temperature as high as possible less than the fusing or melting point of the envelope used, if an envelope be used. Such temperature can be attained in a vacuum or inert gas, (*a*) by raising the temperature of the furnace sufficiently; (*b*) by passing electric current directly through the metal, sufficient to raise the temperature of the metal to the desired point: and (*c*) by inducing an electric current in the metal by either high or low frequency induction until the desired temperature of the metal is attained. The length of time of sintering will depend upon which of these methods is used, and upon the size and shape of the mass being sintered.

When sintering method (*a*) is used, care should be taken to hold the metal at the sintering temperature a time sufficiently long to effect thorough sintering. Where a gas tight envelope is used, care should be taken that the temperature does not reach the melting point of the material of which the envelope is composed. Steel may be used as the envelope: in which event the temperature should not exceed 1450 degrees centigrade. Sintering may be effected at this temperature, but a much greater length of time is required than at higher temperatures.

Whether the sintering was done in a vacuum, inert gas, or in an envelope which is to be removed, the sintered mass must be allowed to cool before it is removed from the furnace, or before the envelope is removed. Otherwise, it would be exposed at high temperatures to the atmosphere, with immediate resultant formation of nitrides and oxides thereon.

The sintered bars or billets are highly porous and the material thereof is therefore unsuitable for the making of tools, machine parts, and for other purposes. It must, therefore, be rolled, swaged, drawn or hammered, or otherwise treated, until of dense and ductile nature. These working operations cannot be carried on in commercially practical manner except in atmosphere: and the metal being worked is to best advantage at a temperature such that, were it exposed to the atmosphere, nitrides and oxides wuold be formed therewith which would thereupon preclude further proper working thereof.

Hence, the invention comprises the use of a gas tight envelope for the metal during the working of the latter, and the envelope must be of a nature to withstand, without cracking, not only the temperatures to which the metal must be subjected for working thereof, but also all movements, strains and stresses involved in the working of the metal. In other words, it must remain as a gas tight skin on the metal, whatever may be the rolling, swaging, hammering and drawing, and the bending and reshaping of the metal in the working of the same. A steel envelope, such as above mentioned, is suitable for this purpose.

It is possible to use the same steel envelope as may have been used in the sintering operation. Preferably, however, this is not done: because in the sintering operation, there is usually some shrinkage of the metal mass: which means that a steel envelope which originally fitted the metal mass, no longer fits it at the end of the sintering operation. The old envelope is ordinarily removed, and a new envelope applied for the metal working operations.

Assuming that the metal mass has cooled to the point where it no longer has undesirable chemical affinity for the nitrogen and oxygen of the air, it is removed from the furnace, or, as the case may be, the envelope is removed therefrom: and the metal is now ready for the application thereto of the envelope to be used in the working of the metal at renewed high temperature.

The envelope may be applied as a sheath or sheet, wrapped and fitted around the metal mass, and closed at all joints to be absolutely air-tight. The envelope may be an electro deposit, as of nickel, on the metal. It may in some instances be applied by one or more dippings of the metal mass into molten envelope-material, provided the melting point of such material is sufficiently below the melting point of the material so dipped, and provided the envelope material when at its melting point has no tendency to combine with the metal being treated.

After the envelope has been set to the metal, the whole is brought to the desired working temperature in any suitable manner, and is then put through such rolling, swaging and other operations as may be necessary to attain the desired density and ductility of the metal.

On completion of the working, the envelope may be chemically dissolved from the metal within the same. The metal may then be further rolled, drawn or hammered, cold, to any desired shape: and be machined to the form of the article sought.

The working may be a cold working throughout, but since the sintered material is porous and has little strength, and is crystalline, in the nature of cast iron, an entirely cold working should be effected very slowly, with only a small reduction at a time. This, of course, is a tedious matter where the metal is to undergo any great change in shape. For instance, no envelope would be required for working at a temperature up to

about 400 degrees centigrade, but such working would have to be very slow until a fair density had been attained.

According to a modification of the invention, the sintering step, as a separate step, may be omitted. The metal powder may be placed in a container of any desired shape, and of material having a higher melting point than the powder, and be heated to a temperature, and for a time sufficient to melt the powder to a comparatively dense mass, of the configuration of the container. Thereafter, on removal of the container, the molded mass may be further worked, either cold, or at high temperatures in an envelope: or it may be in condition for immediate use, or for machining to desired form. The powder may be melted in a vacuum, or in an inert gas, or in an envelope such as hereinbefore described.

When shaped or machined to the form of the desired article, the metal may be case hardened, or hardened throughout, by heating in a cyanide bath, or heating in a hydrogen atmosphere, or by known methods of nitriding, or by heating in a carbonaceous gas. Ultimately, when thus treated, it may be of a hardness exceeding that of corundum, which is No. 9 on the Mohs' scale.

I am aware that by an electro-plating process, chromium and other metals of a very hard and condensed nature have heretofore been obtained. This, however, is only a plating, and is of limited thickness and durability. It can, and will, flake off, depending somewhat on the nature of the material plated, and on the thickness to which it is plated.

By mixing the powder of cobalt or other metal with the powder of chromium, titanium, or other primary metal, before the sintering operation, the toughness or other attribute of the final product may be enhanced or affected, according to the intended use of the alloy thus produced.

I claim:

1. A process of treating chromium, titanium and other metals of the class described, consisting in first compressing the powder of such metal to a coherent mass, then sintering said coherent mass in an air-tight envelope at a temperature and for a time sufficient to convert the mass into a soft, porous and ductile state, allowing the mass to cool, removing the envelope therefrom, enclosing sintered mass in another air-tight envelope, re-heating it to a working temperature, working the mass, with the envelope thereon, until it is dense and tough, removing the second envelope after cooling of the metal therein, and re-working the cooled metal to desired shape.

2. A process of treating chromium, titanium and other metals of the class described, consisting in first compressing the powder of such metal to a coherent mass, then sintering said coherent mass in an air-tight envelope at a temperature and for a time sufficient to convert the mass into a soft, porous and ductile state, allowing the mass to cool, removing the envelope therefrom, enclosing the sintered mass in another air-tight envelope, re-heating it to a working temperature, working the mass, with the envelope thereon, until it is dense and tough, removing the second envelope after cooling of the metal therein, reworking the cooled metal to desired shape, and then hardening the metal in any suitable manner.

3. A process of treating chromium, titanium and other metals of the class described, consisting in first compressing the powder of such metal to a coherent mass, then sintering said coherent mass in an air-tight envelope at a temperature and for a time sufficient to convert the mass into a soft, porous and ductile state, allowing the mass to cool, removing the envelope therefrom, enclosing sintered mass in another air-tight envelope, re-heating it to a working temperature, working the mass, with the envelope thereon, until it is dense and tough, removing the second envelope after cooling of the metal therein, reworking the cooled metal to desired shape, and then hardening the same by heating it to a proper temperature in hydrogen gas.

4. A process for converting a substantially pure powder of chromium, titanium, or other metal of the class described, intermixed with an alloying powder if an allow is desired, into a dense, tough mass of such metal, consisting in enclosing an agglomerate of such powder against access of air, hydrogen or other substances having an affinity for the metal at sintering temperatures thereto, and, while so isolated subjecting the same to heat at temperatures above the temperature at which hydrogen, nitrogen and other substances would normally combine therewith for a length of time sufficient to convert the powder into a self-sustaining malleable mass having the original metallic purity of the powder; then, while so isolated, cooling said malleable mass to a point below said affinity temperature and enclosing the same in an air-tight metallic envelope of a substance lacking affinity for the metal at the working temperatures of the latter and capable of being worked as a unit with the enclosed metal at desired working temperatures without melting, cracking or disintegration of the envelope; then heating the envelope and enclosed metal mass to such desired working temperatures above said affinity temperature, and under atmospheric conditions and at said working temperatures, working the enveloped metal mass until the same is dense, tough, and of desired configuration; and thereafter removing the envelope.

5. A process for converting a substantially pure powder of chromium, titanium, or other metal of the class described, intermixed with an alloying powder if an alloy is desired, into a dense, tough mass of such metal, consisting in enclosing an agglomerate of such powder against access of air, hydrogen or other substances having an affinity for the metal at sintering temperatures thereto, and, while so isolated, subjecting the same to heat at temperatures above the temperature at which hydrogen, nitrogen and other substances would normally combine therewith for a length of time sufficient to convert the powder into a self-sustaining malleable mass having the original metallic purity of the powder; then, while so isolated, cooling said malleable mass to a point below said affinity temperature and enclosing the same in an air-tight metallic envelope of a substance lacking affinity for the metal at the working temperatures of the latter and capable of being worked as a unit with the enclosed metal at desired working temperatures without melting, cracking or disintegration of the envelope; then heating the envelope and enclosed metal mass to such desired working temperatures above said affinity temperature, and under atmospheric conditions and at said working temperatures, working the enveloped metal mass until the same is dense, tough, and of desired configuration; cooling said enveloped mass below said affinity temperature; and thereafter removing the envelope.

6. A process for converting a substantially pure powder of chromium, titanium, or other metal

of the class described, intermixed with an alloying powder if an alloy is desired, into a dense, tough mass of such metal, consisting in enclosing an agglomerate of such powder against access of air thereto, and, while so isolated from the air, subjecting the same to heat at temperatures above the temperature at which nitrogen and other gaseous constituents of the air would normally combine therewith for a length of time sufficient to convert the powder into a self-sustaining malleable mass having the original metallic purity of the powder; then, without permitting access of air thereto, cooling said malleable mass to a point below said air-affinity temperature and enclosing the same in an air-tight envelope of a substance lacking affinity for the metal at the working temperatures of the latter and capable of being worked as a unit with the enclosed metal at desired working temperatures without melting, cracking or disintegration of the envelope; then heating the envelope and enclosed metal mass to such desired working temperatures above said air-affinity temperature, and, under atmospheric conditions and at said working temperatures, working the enveloped metal mass until the same is dense, tough, and of desired configuration; thereafter removing the envelope, and then hardening the exposed mass in any suitable well-known manner.

7. A process for converting a substantially pure powder of chromium, titanium, or other metal of the class described, intermixed with an alloying powder if an alloy is desired, into a dense, tough mass of such metal, consisting in enclosing an agglomerate of such powder against access of air thereto, and, while so isolated from the air, subjecting the same to heat at temperatures above the temperature at which nitrogen and other gaseous constituents of the air would normally combine therewith for a length of time sufficient to convert the powder into a self-sustaining malleable mass having the original metallic purity of the powder; then, without permitting access of air thereto, cooling said malleable mass to a point below said air-affinity temperature and enclosing the same in an air-tight envelope of a substance lacking affinity for the metal at the working temperatures of the latter and capable of being worked as a unit with the enclosed metal at desired working temperatures without melting, cracking or disintegration of the envelope; then heating the envelope and enclosed metal mass to such desired working temperatures above said air-affinity temperature, and, under atmospheric conditions and at said working temperatures, working the enveloped metal mass until the same is dense, tough, and of desired configuration; thereafter removing the envelope, then subjecting the mass to machining or other finishing operations under atmospheric conditions and while cool; and then hardening the mass in any suitable well-known manner.

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