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PRODUCTION OF CARBIDE-SURFACED
WEAR-RESISTANT FERROUS BODIES
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FIG 1

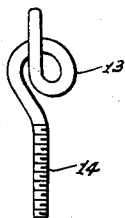
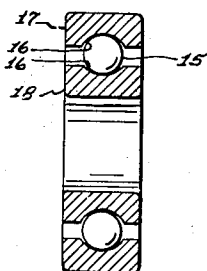


FIG 2



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PRODUCTION OF CARBIDE-SURFACED
WEAR-RESISTANT FERROUS BODIESSeymour J. Sindeband, Chappaqua, N. Y., as-
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3 Claims. (Cl. 148-6)

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This invention relates to wear-resistant bodies or articles of the type having a ferrous or steel base provided on its exterior with a hard wear-resistant continuous surface layer and to methods of producing such bodies.

Among the objects of the invention is a ferrous body or article provided with a wear-resistant continuous surface layer or casing consisting essentially of a carbide of at least one of the metals of the group consisting of titanium, columbium, tantalum, molybdenum and tungsten for use in applications requiring bodies or articles having exposed surfaces which are subject to wear.

A distinct object of the invention is a provision of a ferrous body or article provided with a wear-resistant surface layer or casing consisting essentially of a carbide of at least one of the elements of the group consisting of titanium, columbium, tantalum, molybdenum and tungsten having a Vickers hardness of about 1500 to 1600 or higher.

A particular object of the invention is a ferrous body or article provided with such wear-resistant carbide surface layer on only certain surface portions thereof, with other surface portions of the article being free from such carbide surface layers.

According to the invention, a ferrous body or article having at least in the surface layer thereof at least about 0.4 percent available carbon is provided with a wear-resistant continuous surface layer of a metal carbide having a Vickers hardness of at least about 1500 to 1600, by causing at least one of the metals of the above specified group to be deposited at an elevated temperature on the surface of the body—and cause the deposited metal to diffuse into the surface layer of the ferrous body and to combine with the carbon content thereof to produce a wear-resistant carbide surface layer of a thickness of at least about 8 microns having such high hardness.

As used herein in the specification and claims, "Vickers hardness" means hardness in numbers determined by Vickers diamond pyramid hardness tests, such as described for instance in the Metals Handbook, 1939 edition, published by the American Society for Metals.

The foregoing and other objects of the invention will be best understood from the following description of exemplifications thereof, reference being had to the accompanying drawings wherein:

Fig. 1 is an elevational view of a conventional thread guide having a wear-resistant carbide casing of the invention, and

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Fig. 2 is a cross-sectional view of a ball bearing having wear-resistant carbide surface regions of the invention.

For years past ferrous bodies or articles with hard wear-resistant surfaces have found many applications in the arts as for example the moving parts of machinery subject to wear and shock. Heretofore, it has been generally believed that the most satisfactory wear-resistant hard surface for a ferrous article is that provided by electrodeposition of a layer of chromium from an electrodeposition bath on the surface of the body. However, such chromium surface layer, even if formed under the most favorable conditions, exhibits at most about 800 Vickers hardness and has only a limited wear-resistance.

The present invention is based on the discovery that under certain critical conditions of a carbon content of the ferrous body and the thickness of its cross-sectional area it is possible to provide the entire or only a limited exposed surface region of such body with a wear-resistant titanium carbide layer forming an integral part of the body and exhibiting a Vickers hardness of 1500 to 1600 or even more, thus multiplying the life of such wear-resistant bodies or articles compared to the prior art chromium coated wear-resistant bodies.

In accordance with the invention a ferrous or steel body containing at least 0.4% carbon having a certain minimum thickness in relation to its carbon content will, when subjected at an elevated temperature to a surface alloying action in which titanium is deposited on the surface of the body, cause the deposited titanium to diffuse into the surface layer of the body and combine with carbon migrating from the interior to form a titanium carbide surface layer which permits continued deposition of titanium on the exterior surface of the body, the additional deposited titanium continuing to combine with the carbon in the surface layer until a titanium carbide surface layer of a thickness of at least about 8 to 16 microns having at least about 1500 Vickers hardness has been formed on the surface of the body as an integral part thereof.

Important factors affecting the nature of a titanium carbide casing formed on the surface of a ferrous article are the percentage of its carbon content, the thickness of the ferrous body in relation to its total carbon content, and the percentage of alloying elements having a greater affinity for carbon than titanium. The ferrous or steel article should have an available carbon content of at least 0.4% and should be of substantial thickness of at least about .020 inch so

that carbon of the interior can diffuse from relatively deep areas below the surface to combine with titanium deposited on the surface of the article at an elevated temperature from a gaseous or liquid titanium compound into a wear-resistant titanium carbide surface layer of substantial thickness. Highly satisfactory titanium carbide surface layers will form on ferrous articles containing 0.60 to 1.20% carbon.

A feature of the invention is the discovery that—for a ferrous body having a carbon content of at least 0.4% and a certain minimum thickness—the titanium carbide casing formed on its exterior by the treatment of the invention will increase in hardness as the thickness of the ferrous body increases until it reaches a maximum hardness which does not increase with a further increase in thickness of the ferrous body. The increase of the hardness of the titanium carbide casing caused by the increase in the thickness of the ferrous body shows that titanium of greater carbon content and greater hardness and formed on ferrous bodies having a certain minimum thickness than in ferrous bodies of lesser thickness. In other words, in order to form on a ferrous body containing at least 0.4% carbon a titanium carbide casing having a minimum of 1500 to 1600 Vickers hardness, the ferrous body must have a minimum thickness of at least about .020 inch so that the carbon from the interior may diffuse into the surface layer of the body on which the titanium is deposited to provide the additional carbon required for causing the deposited titanium to combine with the carbon of the body into a titanium carbide layer of a minimum of at least about 1500 to 1600 Vickers hardness.

There are indications that the hardness of titanium carbides increases with the increase of the carbon content of the carbide. Furthermore, there are indications that the hard carbide surface layer or casing of the invention of a thickness of at least about 8 microns and of at least 1500 Vickers contains or consists, at least to some extent, of a multiple carbide containing carbon combined with the deposited titanium and with iron of the base or article.

As used herein in the specification and claims the expression "metal carbide surface layer" and "metal carbide casing" are intended to mean a metal carbide surface layer or casing consisting essentially either of a carbide of the deposited metal or of a multiple carbide of the deposited metal and of iron from the article base or of a mixture or combination of carbides. This applies to carbide casings of the invention using as a carbide-forming coating metal, at least one of the metals of the group consisting of titanium, columbium, tantalum, molybdenum and tungsten.

When forming on the exterior of a ferrous body a titanium carbide casing of the invention, the interior of the ferrous body or its core is depleted of carbon or decarburized. If such ferrous body is thin and has been depleted of its carbon content by the formation of a titanium carbide casing on its exterior, the decarburized core of such body will lose its ability to be hardened through subsequent heat treatments of the type generally used for hardening steel bodies.

According to the invention, ferrous articles which are to be provided with a titanium carbide casing of the invention are chosen to contain sufficient carbon and be of sufficient thickness so that—after forming on the exterior of the body

the titanium carbide casing of a minimum thickness of at least 8 microns and at least 1500 to 1600 Vickers hardness—the ferrous core of the body will retain a carbon content of at least 0.2% so that it may be subjected to known heat treatments by which similar carbon-containing steel bodies are hardened. It is thus possible to provide ferrous bodies with a wear-resistant titanium carbide casing of the invention, which may be subjected to known heat treatment whereby the ferrous articles are given enhanced strength as well as other desired characteristics.

Among the various ferrous articles whose surfaces have been provided with a wear-resistant continuous surface layer of titanium carbide in accordance with this invention are thread guides, cylinders, pistons, dies, drills, cutters, ball and roller bearings with associated races, phonograph needles, etc. In general, the invention may be applied to any ferrous article having a surface which is subjected to wear.

Any of the known methods for depositing titanium from a gaseous or liquid titanium compound on the surface of a ferrous body heated to an elevated temperature below the melting temperature of the body may be employed for depositing titanium on and diffusing titanium into the surface layer of the ferrous body to combine with carbon and for forming a wear-resistant surface layer of titanium carbide.

These methods include chemical reduction or reaction of the titanium compound at the surface of the ferrous article as exemplified by hydrogen reduction of titanium halides and by displacement or reaction of the ferrous base metal with one of the constituents of the titanium compound. Another method that may be used for depositing titanium on and diffusing titanium into the surface layer of the ferrous body to combine with carbon and for forming a wear-resistant surface layer of titanium compound is thermal decomposition of a titanium compound at the surface of the ferrous article as exemplified by thermal decomposition of titanium halides at the surface of the ferrous article at high temperatures and by thermal decomposition of titanium carbonyl at the surface of the ferrous article at low temperatures.

According to the invention, it is also possible to provide ferrous bodies or articles which have a low carbon content with a wear-resistant titanium carbide layer by first forming on the surface thereof, by a known carburizing process, a carburized surface layer or casing of high carbon content, and thereafter subjecting the so carburized surface region to the titanium deposition and titanium-carbide-casing forming treatment.

When producing a titanium carbide casing on a smoothly ground polished or other mechanically worked surface of a ferrous article, surface imperfections arranged in a fashion suggesting scratches, tool marks, grinding marks, machining patterns, and/or welts will appear on the exterior surface of the titanium carbide layer. The formation of these protuberances and welts appears to occur to a lesser extent in low carbon steels. It seems that such protuberant swellings or growths appear at portions of the titanium carbide surface layer formed on worked or work-affected surface portions of the ferrous base. As used herein in the specifications and the claims, the expression "work-affected surface portions" means surface portions of a ferrous article the material of which was worked upon as by grind-

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ing, polishing, rolling, etc., thereby giving its surface structure a characteristic distinct from underlying portions with respect to the tendency to form the titanium carbide surface layer of the invention. It has been observed that the titanium carbide surface layer of the invention, when formed on work-affected surfaces of a ferrous article, exhibits such objectionable surface irregularities even when the article is subjected to a heating or annealing treatment in the initial stages of or prior to the titanium-carbide casing forming process.

According to another phase of the invention, the objectionable surface irregularities of the wear-resistant titanium carbide layer are eliminated, prevented or suppressed by removing the work-affected exterior surface stratum of the article before treating the article to form thereon the titanium carbide surface layer. Any known processes, such as etching, deplating and the like which are effective in removing a surface stratum from the exterior of a ferrous body without forming a new surface of the same kind, may be used for removing the work-affected surface layer of the article so as to suppress surface irregularities on the titanium carbide layer formed on the exterior of the ferrous article.

By way of example, the work-affected surface stratum of the ferrous article may be removed by treating the surface with a solution of HCl containing 50% by volume concentrated hydrochloric acid HCl, balance water, while heated at about 85° C. for 2 to 10 minutes. Other known etching compounds may be used for removing the work-affected surface layer from the surface portions of the article which are to be provided with the titanium carbide wear-resistant surface layer. Alternatively, the ferrous article which has a work-affected surface may be placed in an electrolyte bath of suitable concentration and connected as anode in an electrodeposition circuit for removing the work-affected surface layer by the electrodeposition process. Any known electrolytic deposition baths may be used for this purpose such as a bath formed of a HCl solution.

For most practical applications good results are obtained with wear-resistant ferrous or steel articles provided in accordance with the invention, with a wear-resistant surface layer of titanium carbide having a thickness of about 12 to 18 microns and up to about 25 microns or $\frac{1}{1000}$ of an inch, although in some applications it may be desirable to provide ferrous articles with wear-resistant titanium carbide surface layers of a thickness greater than about 25 microns.

It is possible, according to the invention, to provide only those surface portions of the ferrous article exposed to wear with the wear-resistant titanium carbide casing. Thus, in case of the thread guide shown in Fig. 1, the spirally shaped upper guide portion is provided with the titanium carbide surfaced layer and its threaded lower portion 14 is left untreated and without the carbide layer. Similarly, in case of the ball-bearing shown in Fig. 2, only the spherical surface of the balls 15 and the race surfaces 16 of the ball races 17 and 18 are provided with the titanium carbide layer of the invention.

Such partial titanium carbide casing may be formed by providing those surfaces on which formation of the carbide layer is to be prevented or suppressed with a stop coating or stop cover which prevents deposition of titanium on its surface while titanium is deposited on the wear-

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ing surfaces of the article to provide the desired titanium carbide casing or layer. Such stop coating may consist of a coating of metal such as copper which is lower in the electromotive series than titanium.

In a similar manner, exposed surfaces of a ferrous article of low carbon content—on which formation of a carburized layer is to be prevented or suppressed—are provided with a similar stop coating or stop cover which effectively prevents deposition of carbon on its surface with carbon is deposited by a carburizing action on the wearing surface of the article for producing thereon a surface layer of high carbon content.

By way of example, in case of the thread guide of Fig. 1, a copper stop coating is formed only on the threaded lower portion 14. In case of the bearing of Fig. 2, a copper stop coating is formed on all surfaces of the ball races 17, 18 except the two race surfaces 16.

As explained above, the ferrous article must have at least about 0.4 to 0.6% available carbon content, and a certain minimum thickness of at least about .020 inch so that the carbon diffusing from relatively deep regions below the surface may combine with the titanium deposited at the surface for producing thereon a titanium carbide casing having a thickness of at least about 8 microns and at least about 1500 to 1600 Vickers hardness. The critical relationship between the carbon content of the ferrous body and its thickness to the character of the titanium carbide layer of the invention formed thereon can be shown by treating wedges of known carbon content to form on the exterior of the wedges a titanium carbide casing of the invention in the way analogous to that described in my copending application Ser. No. 206,380 filed January 17, 1951, in connection with Fig. 4 thereof. In the thin tip region of such edge, the deposited titanium will diffuse and become alloyed with the ferrous particles of the body, and it will have only negligible titanium carbide content. Such thin wedge tip remains relatively soft and has the characteristics of titanium alloyed iron.

The adjacent somewhat thicker region of such wedge will have on its exterior a thin stratum of titanium carbide overlying a relatively thick layer of titanium alloyed iron formed over an inner ferrous core which is substantially free of carbon, all the carbon having migrated to the surface to form with the deposited titanium the thin titanium carbide stratum. In the still thicker region of such wedge the titanium deposited on the surface will have combined with the carbon that migrated from its interior into a titanium carbide surface layer overlying the ferrous core which is substantially free from carbon. A still thicker region of the wedge will have on its exterior a titanium carbide surface layer overlying a core containing, in addition to a ferrous particle free from carbon, carbon containing pearlite formations. Such wedge will thus have a cross-sectional region of a thickness in which the first pearlite colonies appear, the core of the wedge becoming richer in pearlite content as its cross-section increases. Only the wedge portions rich in pearlite will retain the ability of becoming hardened by known steel-hardening heat treatments.

It can also be shown that the hardness of the carbide surface layer formed on such wedge increases until it reaches a maximum of about 1500 to 1800 Vickers hardness for certain thickness of the carbon containing ferrous wedge and the

hardness of the surface layer does not increase for a further increase of the thickness of the ferrous body. The desired great hardness of about 1500 to 1600 Vickers or more is reached only in the region where the carbide casing of great carbon content is formed, the hardness leveling off and approaching the maximum for greater thickness.

A suitable process for forming a surface layer of titanium carbide on a ferrous article involves the thermal decomposition of a titanium compound at the surface of the ferrous article. In this type of carbide surface forming treatment the titanium compound is decomposed and titanium deposited at surface regions of the ferrous article heated to an elevated temperature, and the deposited titanium diffuses into the surface layer of the article and combines with carbon migrating to the surface into a titanium carbide surface layer of substantial thickness. In such titanium carbide surface-forming treatment the titanium chloride gas may be passed through a retort of ceramic or like insulating refractory material containing the ferrous article. Selective induction heating of the exposed surfaces of the ferrous article—on which formation of the titanium carbide layer is desired—may be employed to cause decomposition of the titanium chloride gas, the deposition of titanium at said exposed surfaces, and the formation of a surface layer of titanium carbide on the exposed surfaces of the ferrous article.

Without hereby limiting the scope of the invention in order to enable those skilled in the art to readily practice the invention, there will now be described specific examples of satisfactory procedure for providing ferrous articles, such as thread guides in Fig. 1, with a titanium carbide layer on its looped guide part 13.

The ferrous articles to be treated are first dipped in an acid etching bath, for example, a bath containing 50%, by volume, of concentrated HCl, at about 80° C. for 2 to 10 minutes until the work-affected exterior surface stratum has been removed from the exposed surfaces on which the wear-resistant carbide layer is to be formed. After removal from the etching bath, the ferrous articles are packed within a packing mass which is effective in depositing titanium on the surface of the articles. The pack may consist, for instance, of 50% by volume ceramic lumps, such as porcelain pieces, and the balance a titanium alloy such as ferro-titanium. Good results are also obtained with such pack consisting of about 20% titanium oxide by volume, the balance consisting of ferro-titanium containing about 70% titanium.

The treating baskets containing the ferrous metal are then placed in a retort and heated to a temperature in the range of between 900° and 1200° C. and a stream of hydrogen and hydrogen chloride gas is passed through the retort for producing reactions causing titanium atoms to be deposited on the ferrous metal surface and to diffuse into the interior of the ferrous metal surface and combine with carbon present and/or diffusing toward the surface into a wear-resistant continuous titanium carbide surface layer or casing.

By way of example, a mixture of gaseous HCl and H₂ is passed at about 1100° C., for 10 to 40 hours through the retort holding the ferrous articles packed in the titanium-chloride producing pack mass comprising a mixture of equal parts of porcelain and ferro-titanium lumps. The treatment is ended by turning off the heat and

permitting the retort with the contents to cool while continuing the flow of hydrogen through the retort until the temperature of its contents is brought down to room temperature. The titanium-carbide surfaced articles are then removed from the retort and subjected to an air blast for removing adhering packing material from the exterior surface of the treated articles.

By using procedure similar to those described above in connection with the formation of a titanium-carbide surface layer of substantial thickness on a surface region of a ferrous article, such ferrous articles may also be provided with a wear-resistant continuous surface layer of a carbide of columbium, tantalum, molybdenum or tungsten of a thickness of at least 8 microns having a Vickers hardness of about 1500 or even somewhat higher. In a generally similar manner, ferrous articles of a sufficient carbon content may be provided with the wear-resistant continuous surface layer of a mixture or solid solution of carbides of at least two elements of the group consisting of chromium, vanadium, titanium, columbium, tantalum, molybdenum and tungsten. To this end, the ferrous articles having carbon content of at least about 0.4% and are packed within a packing mass which is effective in depositing the desired mixture of at least two metals of the group consisting of chromium, vanadium, titanium, columbium, tantalum, molybdenum and tungsten on the surface of the articles.

The ferrous articles packed within such packing mass are then subjected to the surface alloying action described above—in which at least two metals of the group consisting of chromium, vanadium, titanium, columbium, tantalum, molybdenum, and tungsten are deposited on the surface of the articles—and the articles are heated to an elevated temperature in the range between about 500° and 1700° C., to cause the deposited metals to diffuse into the surface layer of the body and combine with the carbon of the ferrous article into a wear-resisting continuous metallic carbide surface casing of a thickness of at least 8 microns and composed of at least two metal carbides, or solid solution of the different carbides having a Vickers hardness of about 1500 or more.

As described previously, ferrous bodies or articles which have a low carbon content are provided with a wear-resistant titanium carbide layer by first forming on the surface thereof, by a known carburizing process, a carburized surface layer or casing of high carbon content, and thereafter subjecting the so carburized surface region to the carbide surface forming treatment described above.

By way of example, the low carbon ferrous article is first packed in a conventional carburizing pack mass and placed within a carburizing furnace and heated to a temperature of about 925° C., causing carbon to be deposited on the ferrous metal surface and to diffuse into the interior of the ferrous metal surface until a carburized layer of substantial thickness containing, for example, about 0.95% carbon is formed on the surface of the article. The pack may consist, for instance, of a mixture of approximately 20% BaCO₃, bound to a hardwood charcoal with oil, tar, or molasses. However, any of the known alternative carburizing procedures may be used instead.

The carburized ferrous articles are etched and treated as in the previous examples to form of

the carburized exterior the desired carbide casing.

As explained hereinbefore, after producing the carbide surfaced ferrous articles in which the core retains enough carbon to have a pearlite structure, they may be subjected to further heat treatment of the type applied to steel for imparting thereto high mechanical strength such as required by drills, cutters, and like articles. Such further heat treatment may be readily carried out without affecting the carbide surface casing previously formed on the article.

The principles of the invention described above in connection with specific exemplifications thereof, will suggest various other modifications and applications of the same. It is accordingly desired that the present invention shall not be limited to the specific exemplifications shown as described above.

I claim:

1. In the method of making articles having an exposed wear-resistant surface region consisting essentially of a metal carbide forming an integral part of said article and constituting only a small fraction of the mass of said article, the procedure comprising the steps of providing a ferrous body having a mechanically worked surface on a portion thereof that is at least 0.020 inch thick and containing adjacent the surface thereof at least 0.4% of available carbon, removing the stratum of work-affected ferrous surface particles from said surface region, depositing at an elevated temperature, on the exposed surface region of said body at least one metal selected from the group consisting of titanium, columbium, tan-

talum, molybdenum, and tungsten from a compound of said metal and causing the deposited metal to react with available carbon of said surface region to produce out of an integral surface layer of said surface region of said article a metal carbide layer consisting essentially of a carbide containing said deposited metal, and continuing said deposition of said metal and the carbide forming reaction of the so deposited metal with the available carbon of said surface region until an integral layer of said metal carbide at least about 8 microns thick having a surface hardness of at least about 1500 Vickers hardness is integrally formed on said surface region.

2. The method of claim 1 in which a portion of the exposed surface of the ferrous article is provided with a coating to prevent the formation of metal carbide thereon prior to the deposition of the carbide forming metal.

3. The method of claim 1 in which the metal deposited is titanium.

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