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PROCESS FOR CASE HARDENING METALS

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The present invention relates in general to a method for treating metals and more especially to a superior method for case hardening metals including metals of the fourth group of the periodic table.

The process of forming a hard adherent metal coating on ferrous metals by increasing the carbon content of the surface metal, and in some cases the nitrogen content as well, and thereafter heat treating the carburized surface has long been known in the art as "case hardening." By this process a composite structure is obtained comprising a relatively soft but strong and tough interior or core, and an extremely hard surface coating. Commercial carburizing of ferrous metals is carried out by any one of several methods, including pack carburizing, gas carburizing, carbonitriding and liquid carburizing. Of these methods, that of pack carburizing is one of the oldest and most extensively employed, the usual carburizing compound being a mixture of alkali or metal carbonates, charcoal and a binder.

Among the more recent developments in the field of refractory metals has been the commercial production of titanium and its alloys. This metal exhibits many properties which adapt it not only to specialty fields but to the more common construction uses. However, it has been observed that titanium has a marked tendency to gall and seize under certain conditions of use, which characteristics seriously limit its commercial applications. Moreover, while titanium metal has remarkably good wear and erosion resistance, it is advantageous to improve these properties as well as its resistance to certain types of corrosive attack at high temperatures.

An object, therefore, of the present invention is to provide a relatively inexpensive, simple and effective method for case hardening refractory metals of the fourth group of the periodic table.

Another object of the invention is to provide a superior method for case hardening refractory metals consisting largely of titanium to form a hard adherent coating thereon.

A further object of the invention is to provide a superior method for forming a hard surface coating on refractory metals so as to enhance the resistance of the metal to wear, erosion, corrosion at high temperatures and to overcome the tendency of titanium metal, in particular, to gall and seize.

As indicated above, in its more common usage, the term "case hardening" connotes carburizing, that is to say the diffusion of gaseous carbon monoxide at high temperatures into the surface of a ferrous metal being treated, followed by a heat treatment to form the hard case. As used herein, the term "case hardening" shall be understood to mean the solid state diffusion, into a refractory metal, of a solute species characterized as a metalloid atom or atoms of a metalloid compound of a metal

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from the fourth group of the periodic table, as for example the molecular carbides, borides, nitrides and silicides of titanium, zirconium and silicon respectively, which metalloid compounds of themselves produce a hard surface or case on the metal being case hardened, without the necessity for subsequent heat treatment.

While the mechanics of the action which takes place, by the method of the instant invention, may not be exactly understood, it is postulated that, in contradistinction to known processes of case hardening ferrous metal wherein gaseous carbon monoxide diffuses into the metal to form an iron carbide which is subsequently converted to a harder composition such as Martensite by subsequent heat treatment, the metalloid compound used in carrying out the method of the instant invention is itself an extremely hard material, and during the heating period, the metalloid atoms of this hard material diffuse into the lattice structure of the metal being treated, thereby going into solid solution therewith to form a hard adherent coating on the surface of the metal without need of subsequent heat treatment.

Although this may not be the exact explanation of the reaction which takes place, in any event it has been discovered that by embedding a refractory metal, such as titanium or zirconium, in a tightly packed metalloid compound powder of fine particle size, a hard case is formed on the refractory metal which penetrates deeply into the relatively soft core of the metal and adheres tenaciously thereto.

In its broadest aspects, therefore, this invention relates to a method for case hardening a refractory metal by embedding the refractory metal in a finely divided metalloid compound of a metal selected from the fourth group of the periodic table, packing the metalloid compound tightly around the refractory metal, and heating the embedded metal at a temperature and for a period of time sufficient to form a hard adherent coating thereon.

With reference to the type of metalloid compounds to be used as embedding materials, some degree of success has been achieved by the use of metalloid compounds currently available on the market. However, these metalloid compounds are usually prepared by grinding the product to the required particle size, usually by mechanical means, and hence the compounds are relatively impure and of non-uniform particle size. On the other hand, unusually consistent and superior results have been achieved by the use of metalloid compounds, the particles of which are of uniform size and purity having, for example, a particle size within the range of from 0.5 to 10 microns; and which are prepared by calcining an admixture of a hydrate of a refractory metal or silica and carbon, with or without addition agents, such as boric acid or nitrogen, depending upon the kind of metalloid desired, in accordance with the methods described in assignee's copending applications Serial No. 307,721, filed September 3, 1952; Serial No. 309,943, filed September 16, 1952; and Serial No. 397,470, filed December 10, 1953. Metalloid compounds of this type are of unusually uniform particle size, high purity and free of free carbon or other deleterious materials; and for purposes of identification are hereinafter referred to as hydrate-base metalloid compounds.

The case hardening process is carried out by embedding the refractory metal to be case hardened in one of the metalloid compound powders selected from the group consisting of the carbides, nitrides or borides of titanium, zirconium or silicon, or mixtures thereof, packing the metalloid powder tightly around the metal, and

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then heating the embedded metal for from about 1 to 18 hours at a temperature within the range of from 700° to 1200° C.

At the end of the heating period the refractory metal is removed from its metalloid compound bed and will be found to have acquired a uniformly hard well-adhered coating, the thickness of which will be within the range of from 1 to 5 mils, the hardness of the coating being of the order of 400-1200 Vickers.

While the method of practicing the invention, i. e. the technique employed in embedding the refractory metal in the metalloid compound powder and heating the embedded metal is important to the achievement of successful results, the type of metalloid compound used is of greater significance for it has been found that a superior case is formed when the metal is embedded in a metalloid compound of high purity and of relatively uniform and fine particle size as is characteristic of the hydrate-base metalloid compounds referred to above. Moreover, since it is essential that the metalloid compound be packed tightly around the metal being treated, the fine particle size of the hydrate-base metalloid compound is a distinct advantage. Conditions of temperature and length of heating period may be varied to some degree depending upon the nature of the case desired and the kind of refractory metal being treated as illustrated in the examples set forth below. In general, low temperatures produce a case substantially twice as hard as the core of the treated metal while high temperatures substantially quadruple the hardness of the core. Further, variations in the length of the heating period at the same temperature produce cases of varying thicknesses having the same order of hardness. It is also significant that it is not necessary to maintain a particular atmosphere over or around the metal being treated. Although an argon atmosphere was used in achieving the results set out in the tables below, it was found that similar results could be accomplished in any ordinary furnace atmosphere so long as the metalloid compound powder was packed tightly around the specimen being treated.

In order to more fully illustrate the invention, a series of experiments were made using metals of the fourth group of the periodic system and embedding these metals in the metalloid compounds identified above, or mixtures thereof. The results of these several experiments are tabulated below.

TABLE I
Case-hardening titanium¹

Metalloid Compound Packing	Time and Temperature	Thickness of Case, mils	Micro-hardness of Case, kg./mm. ² (Vickers)
TiC-----	18 hrs., 1,000° C-----	5	1,185
SiC-----	18 hrs., 1,000° C-----	4	836
TiB ₂ -----	18 hrs., 1,000° C-----	5	716
ZrB ₂ -----	18 hrs., 1,000° C-----	5	772
TiN-----	18 hrs., 1,000° C-----	5	770

¹ Commercial grade.

TABLE II
Case-hardening titanium¹

Metalloid Compound Packing	Time and Temperature	Thickness of Case, mils	Micro-hardness of Case, kg./mm. ² (Vickers)
TiC-----	6 hrs., 1,000° C-----	1-2	954
SiC-----	6 hrs., 1,000° C-----	1-2	946
TiB ₂ -----	6 hrs., 1,000° C-----	1-2	694
ZrB ₂ -----	6 hrs., 1,000° C-----	1-2	609
TiN-----	6 hrs., 1,000° C-----	1-2	752

¹ Commercial grade.

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TABLE III

Case-hardening zirconium¹

Metalloid Compound Packing	Time and Temperature	Thickness of Case, mils	Micro-hardness of Case, kg./mm. ² (Vickers)
TiC-----	18 hrs., 1,000° C-----	1-2	627
TiB ₂ -----	18 hrs., 1,000° C-----	1-2	554
ZrB ₂ -----	18 hrs., 1,000° C-----	5	1,254

¹ Commercial grade.

TABLE IV

Case-hardening titanium¹

Metalloid Compound Packing	Time and Temperature	Thickness of Case, mils	Micro-hardness of Case, kg./mm. ² (Vickers)
TiC-----	18 hrs., 750° C-----	3	536
ZrB ₂ -----	18 hrs., 750° C-----	3	416
TiC-----	1 hr., 1,200° C-----	1-2	870
ZrB ₂ -----	1 hr., 1,200° C-----	1	810

¹ Commercial grade.

As pointed out above, the invention is applicable to the refractory metals of the fourth group, as for example titanium and zirconium and their alloys. In this connection it may be anticipated that the temperatures used when treating alloys of titanium or zirconium may be somewhat different than those required for treating a substantially pure or commercial grade metal. Moreover, it is not necessary to limit the packing material to any one metalloid compound since mixed metalloids made up of any two or more of the above mentioned metalloid compounds are also suitable.

By the improved process of this invention, it is possible to form hard, highly tenacious, relatively thick coatings on refractory metals by the comparatively simple expedient of embedding the metal in a tightly packed, relatively pure metalloid compound of uniform and relatively fine particle size, and heating the embedded metal for a predetermined length of time and at a predetermined temperature, thereby to form a case on the refractory metal by solid state diffusion of the metalloid atoms therein.

The invention may be carried out in other specific ways than those herein set forth without departing from the spirit and essential characteristics of the invention, and the present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive, and all modifications coming within the meaning and equivalency range of the appended claims are intended to be embraced therein.

I claim:

1. A method for forming a hard adherent surface on a refractory metal, selected from the group consisting of titanium and zirconium comprising: embedding the refractory metal in a finely divided metalloid compound selected from the group consisting of the carbides, nitrides and borides of a metal of the fourth group of the periodic table, packing the metalloid compound tightly around the refractory metal, and heating the refractory metal therein for a period of time and at a temperature sufficient to effect solid state diffusion of a solute species of said metalloid compound into said refractory metal.

2. In a method for forming a hard, tough and adherent surface on a metal consisting at least mainly of titanium, the improvement which comprises: embedding the metal in a hydrate-base metalloid compound selected from the group consisting of the carbides, nitrides and borides of a metal selected from the group consisting of titanium, zirconium, and silicon and mixtures thereof, the particle size of the metalloid compound being in the range of

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from 0.5 to 10 microns, packing the said metalloid compound tightly around the metal, and heating the embedded metal therein for a period of time and at a temperature sufficient to effect solid state diffusion of a solute species of the said metalloid compound into said refractory metal.

3. In a method for forming a hard, tough and adherent surface on a metal consisting at least mainly of zirconium, the improvement which comprises: embedding the metal in a hydrate-base metalloid compound selected from the group consisting of the carbides, nitrides and borides of a refractory metal selected from the group consisting of titanium, zirconium, and silicon and mixtures thereof, the particle size of the said metalloid compound being in the range of from 0.5 to 10 microns, packing the said metalloid compound tightly around the metal, and heating the embedded metal therein for a period of time and at a temperature sufficient to effect solid state diffusion of a solute species of the said metalloid compound into said refractory metal.

4. In a process for case hardening refractory metals selected from the group consisting of titanium and zir-

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conium, the improvement comprising: embedding a refractory metal in a hydrate-base metalloid compound selected from the group consisting of the carbide, boride and nitride of a refractory metal selected from the group consisting of titanium, zirconium, silicon and mixtures thereof, the particle size of the metalloid being in the range of from 0.5 to 10 microns, packing the said metalloid compound tightly around said refractory metal, and heating the refractory metal therein for from 1 to 18 hours at a temperature in the range of from 700 to 1200° C. to effect solid state diffusion of a solute species of the said metalloid compound into said refractory metal.

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