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[54] **SUPERHARD MARTENSITE AND METHOD OF MAKING THE SAME**

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[52] **U.S. Cl.** **148/143**; 148/1; 148/4; 148/31.5; 148/39; 204/164; 204/192; 219/121 P

[51] **Int. Cl.²** **C21D 1/00**; C23C 15/00

[58] **Field of Search** 75/123 R; 219/121 P; 148/31.5, 1, 36, 4, 39, 143, 144, 145; 204/164, 192

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[57] **ABSTRACT**

A superhard martensite and method of making the same wherein ions of an element which is insoluble in iron are implanted into or/and planted onto a steel substrate. The steel is then heat treated, resulting in very fine grained martensite.

14 Claims, No Drawings

SUPERHARD MARTENSITE AND METHOD OF MAKING THE SAME

CROSS-REFERENCE TO RELATED APPLICATION

This is a continuation-in-part of my copending application, Ser. No. 279,244, filed Aug. 9, 1972, entitled "Ion Plating Method and Product Therefrom".

BACKGROUND OF THE INVENTION

This invention relates to an ion implanted hardened steel and more particularly to a superhard martensite and method of making the same.

Various techniques have been employed to coat the surface of a substrate with a material, including ion deposition as disclosed in my above-identified copending application. An apparatus employed by me for such ion plating as hereinafter described is described in NASA Technical Note D-2707, "Deposition of Thin Films by Ion Plating on Surfaces Having Various Configurations", by T. Spalvins, et al., November, 1966.

A steel substrate has a cubic body centered lattice. When the substrate is heated, the configuration changes to a cubic face centered lattice (austenite) which, when quenched, forms a tetragonal body centered lattice. The tetragonal form is martensite.

By nucleating and/or inhibiting the growth of the martensite grain in the hardening process, a super-fine grain will be obtained. The finer the grain in the martensite, the harder will be the steel. Simultaneously insoluble embedded atoms act as barriers for the movement of dislocations contributing further to hardness and strength.

SUMMARY OF THE INVENTION

Briefly described, the growth of martensite grains is inhibited by ion implanting in the substrate (steel matrix) a sufficient amount of any element which is insoluble in iron. These elements include helium, neon, argon, krypton, xenon, radon, lithium, sodium, potassium, rubidium, cesium, francium, calcium, strontium, barium, radium, silver, cadmium, mercury, thallium, lead and bismuth. The following additional elements can be utilized in the present method as they all possess a marked low solubility in iron or have a solubility limit: beryllium, magnesium, yttrium, lanthanum, zirconium, hafnium, thorium, tantalum, copper, indium, selenium, tellurium, and polonium. This process produces an exceptionally hard martensite useful in producing excellent cutting tools with wear resistant surfaces - it also can be used in gear wheels, ball bearings, measuring tools, etc. The fine grained martensite also provides improved fatigue and impact strength useful in springs, hammers and the like.

DESCRIPTION OF THE INVENTION

It has been found that the present method works best on normalized or spheroidized (annealed) steel, i.e. steel of low hardness.

The preferred substrate for use in the present invention should be a steel with sufficient interstitial alloy atoms therein to be "hardenable", usually an alloy content ranging from 0.3 to 1.8% by weight with the optimum range being from 0.5 to 1.0% by weight. Such interstitial alloy atoms are from the second period of the periodic table and are selected from the group consisting of beryllium, boron, carbon and nitrogen. Substitutional alloying elements found within the steel substrate

are generally of no significance in the present invention.

It has been found that an element which is insoluble in iron, when implanted into a steel substrate, will retard the growth of or/and nucleate the grain during martensite formation, thereby producing a more uniform and finer grained martensite structure, resulting in a harder substrate.

To treat, according to the present invention, a hardenable steel substrate or object (0.6% carbon, for example) the steel should first be cleaned on its surface. This is accomplished by any conventional cleaning method. The substrate is then placed inside a vacuum chamber on a suitably supported and insulated metallic plate to form the cathode, to which one terminal of a high potential d.c. current source is connected. Larger objects may be placed on insulators and directly connected to the negative side of the d.c. source.

The other terminal of the d.c. source is connected to a suitable anode which may be the conducting metallic base of the chamber. More often the substrate is placed at the bottom of the chamber and the anode above it to make it easier to load and unload the chamber.

The chamber is next evacuated to a pressure of about 1×10^{-5} mm Hg. It is cyclically flushed with Argon or whatever inert gas is to be used or to be implanted in the substrate and evacuated, two or three times.

Argon or other gas is then slowly let into the chamber with simultaneous application of potential between the substrate or object and the anode. A pink plasma starts forming around 600-800 volts at a vacuum of about 2.0×10^{-5} mm Hg. The potential is then increased to any desired value, such as 4.5 K.V. The object is thus bombarded for a specific time (2 to 4 minutes) with this Argon or inert gas plasma. It is then cooled inside the chamber to prevent any oxidation.

When a solid is further ion plated for the formation of a wear resistant corrosion resistant or other purpose coat, the other terminal is connected to a tungsten wire anode which is then resistance heated to melt the coating material. An electron gun evaporator, a sputter evaporator or other vapor source may be used as the anode.

The object or substrate is subsequently heated up into the austenite temperature range and quenched to martensite in water, oil or air depending on the alloy content. The treated surface layer may also be heated into the austenite range by ion bombardment and quenched by the backing substrate material as a heat sink or by cooled contact holders. Helium, argon or other gases may also be let into the vacuum for quenching.

The voltage applied to the system can vary from 200 volts to 20,000 volts or more. Ion accelerators can also be employed which utilize up to 2,000,000 volts.

It has been found that a voltage of 4 K.V. applied for a few minutes will cause ion penetration of Argon into the substrate of approximately 20 microns. The implantation concentration fades out after 20 microns when 4 K.V. is applied.

The speed of the impinging ions will determine the depth of penetration. The higher the applied potential and the lower the gas pressure, the faster will the ions move when impinging on the substrate. The distribution of the unsoluble or insoluble implanted atoms are controlled by the hardness of the substrate and the history of potential and pressure applied during the implantation time.

In some instances the plasma can be better maintained and working conditions extended to pressures and/or potentials which could not otherwise be used, if a magnetic field, high frequency or radio frequency or radiation is applied to the plasma causing a further ionization of the gas beyond that caused by the static d.c. bias. Such methods are used often to increase ionization in plasmas.

Basically, any element which is insoluble in iron can be utilized in the present invention and include the inert gases: helium, neon, argon, krypton, xenon, radon; the alkaline metals: lithium, sodium, potassium, rubidium, cesium, francium; the alkaline earths: calcium, strontium, barium, radium; plus the insoluble metals: silver, cadmium, mercury, thallium, lead and bismuth. The following elements can also be effectively ion implanted into a steel substrate as they have either a marked low or limited solubility limit in iron: beryllium (0.1% by weight), magnesium (0.1% by weight), yttrium (low), lanthanum (0.1% by weight), zirconium (low), hafnium (low), thorium (low), tantalum (low), copper (low), indium (low), selenium (low), tellurium (low), and polonium (low).

Although all of the above identified elements can be employed in this implantation procedure, the preferred elements are those with an atomic size which is comparable to that of iron. This is best illustrated by examining the effectiveness of the inert gases in this process. In going down the list of these gases on the periodic table, it is found that helium is next to the lowest in effectiveness, neon is more effective, argon is the most effective, krypton is comparable to neon and xenon is the least effective. Argon is the most effective because its atomic size is about the same as iron; xenon and neon have atomic sizes which are too large and too small, respectively, as compared to iron.

The present method could also be performed by simultaneously or successively bombarding the substrate with one of the selected implantation elements and one of the selected interstitial alloy elements and then hardening. This procedure would produce the same result, namely, a superhard martensite. The present invention could also be performed by bombarding a mild steel with insoluble ions and carbonizing the steel by one of the conventional methods either before or after the ion bombardment, to obtain a core hardened product with superhard surface.

The following table I is illustrative of the process of the present invention. Steel substrates were ion implanted with various elements at various potentials for a selected time period and then hardened. The resultant product was measured for hardness. The Knoop hardness indentations were made with a 100 gram load and measured at 20 times magnification.

TABLE I

ELEMENT	VOLTAGE (kv)	TIME (minutes)	HARDNESS (Knoop)
Untreated Substrate			830
Argon	4.5	3	1,080
Argon	4.5	7	1,000-1,030
Argon	2.5	5	1,050-1,110
Xenon	4.5	5	910
Xenon	4.5	10	1,000
Helium	2.5	5	1,000
Helium	2.5	2	890-910
		(plus 3 mins. of silver ion plating)	
Silver	3.0	3	960

The following table illustrates the Knoop hardness obtained when elements (iron and titanium) which are soluble in iron are implanted into a steel substrate for a selected time period and then hardened:

TABLE II

ELEMENT	VOLTAGE (kv)	TIME (minutes)	HARDNESS (Knoop)
Iron	3.0	3	810
Titanium	3.0	3	840
Helium & Iron	He 2.5	2	790-810
	Fe 2.5	2	

In the examples of Table I, the steel substrates, employed, contained 0.95% carbon by weight, and the remainder iron. Each substrate was approximately 2 inches by $\frac{5}{8}$ inch by $\frac{1}{32}$ inch.

A chamber, similar to that described in the aforesaid NASA technical note D-2707, was employed, being first flushed several times with the gas to be employed and then evacuated to a vacuum at which the plasma could be sustained, namely in the neighborhood of 5×10^{-5} ($2-50 \times 10^{-5}$) millimeters of mercury.

When silver was ion implanted into the steel, a tungsten wire was used as the anode, and silver wire was wrapped around the tungsten wire. The tungsten wire was then resistance heated in the evacuated chamber to melt the silver, permitting it to vaporate onto the substrate. This procedure was also followed for the Table II metals, substituting them for the silver wire.

In the hardening step, each substrate, after being implanted or bombarded with ions in the chamber, was heated to from 850° to about 1050°C, preferably to about 1000°C so as to be in the gamma austenite range and then quenched in water, at about room temperature to produce martensite.

Thereafter, each sample substrate was etched on its surface using a 2% solution of Nital (nitric acid and ethanol). Instead of the usual accicular structure of martensite, which in the untreated sample had crystals the major length of which was about 40 mm at 6700 times magnification, the treated substrates exhibit a very fine grained martensite with grains no longer than 6 mm. Since the volume and weight of the grains are the third power of this length or diameter the treated structure has $40^3/6^3 = 305$ times as many grains and 50 times as much grain boundary area.

What is claimed:

1. Process of producing a fine grain iron substrate comprising the steps of:

a. subjecting steel having interstitial alloy atoms ranging from about 0.3 to about 1.8% by weight selected from the group consisting of beryllium, boron, carbon and nitrogen to an ion bombardment

- by an insoluble element selected from the group consisting of helium, neon, argon, krypton, xenon, radon, lithium, sodium, potassium, rubidium, cesium, francium, calcium, strontium, barium, radium, silver, cadmium, mercury, thallium, lead, beryllium, magnesium, yttrium, lanthanum, zirconium, hafnium, thorium, tantalum, copper, indium, selenium, tellurium and polonium sufficient to implant ions of the element into the surface of said substrate in sufficient quantity to retard the growth of crystals during the subsequent heat treatment of the substrate;
- b. heating the substrate containing the implanted element to an austenite temperature range; and
- c. quenching the heated substrate at a sufficient rate to produce crystals along the surface of said substrate which are substantially smaller than crystals which normally would have been formed on the surface of the substrate had the ions of the element not been implanted into the surface of the substrate.
2. A method as claimed in claim 1 wherein said insoluble element selected from said group is an inert gas and wherein the ion implanting step includes placing said substrate in a vacuum, admitting said inert gas into said vacuum, producing an electrical plasma discharge through said inert gas with said substrate as the cathode and maintaining the potential and the vacuum in the range which will support the plasma.
3. The process defined in claim 1 wherein said bombardment is carried on in a vacuum chamber by the application of an electrical potential of from about 200 to about 2,000,000 volts and said substrate forms the cathode therein.
4. The process defined in claim 3 wherein the element is heated by an electron gun.
5. The process defined in claim 3 wherein said implantation is to a depth of approximately 20 microns.

6. A method as claimed in claim 1 wherein the preferred amount of interstitial alloy in said steel substrate ranges from 0.5 to 1.0% by weight.
7. A method as claimed in claim 1 wherein said implanted element has an atomic size substantially like iron.
8. A method as claimed in claim 7 wherein said element is argon.
9. A method as claimed in claim 7 wherein said element is silver.
10. A method as claimed in claim 1 where the plasma is ionized in a magnetic field, high frequency or radio frequency, by radiation beyond the ionization caused by the static d.c. bias.
11. A superhard martensite comprising a steel substrate having interstitial alloys atoms ranging from about 0.3 to about 1.8% by weight selected from the group consisting of beryllium, boron, carbon and nitrogen in which the surface thereof contains an element insoluble in the iron of said substrate and embedded in said iron, said insoluble element being selected from the group consisting of helium, neon, argon, krypton, xenon, radon, lithium, sodium, potassium, rubidium, cesium, francium, calcium, strontium, barium, radium, silver, cadmium, mercury, thallium, lead, beryllium, magnesium, yttrium, lanthanum, zirconium, hafnium, thorium, tantalum, copper, indium, selenium, tellurium and polonium, said surface having martensitic structure with a grain structure substantially smaller than the structure which otherwise would have been produced by heat treatment.
12. The superhard martensite defined in claim 11 wherein said surface has a Knoop hardness above 1000.
13. A superhard martensite of claim 11 comprising a martensitic steel substrate in which said surface exhibits a grain size smaller than 0.001 mm as the longest dimension after normal quenching.
14. A substrate treated in accordance with claim 1 to produce a superhard martensite.
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