US 20040173288A1

(19) United States
(12) Patent Application Publication
Berglund
(10) Pub. No.: US 2004/0173288 A1
(43) Pub. Date: Sep. 9, 2004

(54) SURFACE MODIFIED PRECIPITATION HARDENED STAINLESS STEEL

(75) Inventor: **Goran Berglund**, Sandviken (SE)

Correspondence Address:
BURNS DOANE SWECKER & MATHIS L L P
POST OFFICE BOX 1404
ALEXANDRIA, VA 22313-1404 (US)

(73) Assignee: **Sandvik Aktiebolag**, Sandviken (SE)

(21) Appl. No.: **10/755,347**

(22) Filed: **Jan. 13, 2004**

(30) **Foreign Application Priority Data**

Jan. 13, 2003 (SE) 0300073-4

Publication Classification

(51) **Int. Cl.**[7] **C23C 8/38**
(52) **U.S. Cl.** **148/220**; 148/222; 148/326

(57) **ABSTRACT**

The present invention relates to a surface hardened and coated stainless steel said surface showing low static friction and with improved wear resistance. Moreover, it relates to a coating of the surface of said stainless steel, in which a surface hardening is accomplished simultaneously with said coating. The resulting coated steel showing a very high hardness simultaneously as it shows improved adherence. Said steel advantageously being used in applications with high requirements regarding a combination of high strength and/or toughness and wear resistance together with low friction, such as, e.g., shock absorbers and items for combustion engines and hydraulic systems, produced with a highly cost effective process.

The used precipitation hardened stainless steel substrate has the following composition (in weight-%):

Carbon	max about 0.1
Nitrogen	max about 0.1
Copper	from about 0.5 to about 4
Chromium	from about 10 to about 14
Molybdenum	from about 0.5 to about 6
Nickel	from about 7 to about 11
Cobalt	0 up to about 9
Tantalum	max about 0.1
Niobium	max about 0.1
Vanadium	max about 0.1
Tungsten	max about 0.1
Aluminum	from about 0.05 to about 0.6
Titanium	from about 0.4 to about 1.4
Silicon	max about 0.7
Manganese	max about 1.0
Iron	balance

and normally occurring usual steelmaking additions and impurities.

SURFACE MODIFIED PRECIPITATION HARDENED STAINLESS STEEL

FIELD OF THE INVENTION

[0001] The present invention relates to a surface hardened and coated precipitation hardened stainless steel said surface showing low static friction and improved wear resistance. Moreover, it relates to a coating of the surface of said stainless steel, in which a surface hardening is accomplished simultaneously with said coating. The resulting coated steel showing a very high hardness simultaneously as it shows improved adhesitivity. This steel can advantageously be used in applications with high requirements regarding a combination of high strength and/or toughness and wear resistance together with low friction, such as, e.g., shock absorbers and items for combustion engines and hydraulic systems, produced with a highly cost effective process.

BACKGROUND OF THE INVENTION

[0002] Normally, stainless steel alloys are softer than other steel materials. Therefore, they are frequently submitted to a hardening treatment, which basically may be a bulk treatment or a surface treatment. The bulk treatment is intended to harden the steel material homogeneously, such as a plate or a wire, throughout the entire cross-section of the material, while the surface treatment is intended to harden only the surface of the component, leaving the substrate substantially unaffected.

[0003] For instance, U.S. Pat. No. 5,632,826 (&WO-A-95/09930), which is hereby included in its entirety into the disclosure of the present application by this reference, discloses a precipitation hardened stainless steel in which the strengthening is based on the precipitation of particles throughout the material. The strengthening particles have a quasi-crystalline structure, said structure being essentially obtained at aging times up to about 1000 hours and tempering treatments up to about 650° C. This strengthening involves an increase in tensile strength of at least 200 MPa.

[0004] Other processes for precipitation hardening stainless steel and/or components made of said steel are disclosed in WO-A-93/07303, WO-A-01/36699 and WO-A-01/14601, which hereby are all incorporated into the disclosure of the present application by this reference. For example, according to WO-A-01/36699, the production of the material prior to aging/hardening shall be such that the item be subjected to cold forming to a degree of deformation sufficient for obtaining a martensite content of at least 50% preferably at least 70%.

[0005] Instead of a hardening treatment affecting the steel throughout and homogeneously, in many applications the stainless steel component is provided with a hardened surface, often referred to as casehardening. The concept of casehardening is to transform a relatively thin layer of material at the surface of the part by enrichment of carbon or other ingredients, in order to make the surface harder than the substrate, the substrate being the bulk of the steel that remains unaffected by the surface modification.

[0006] Stainless steels are often casehardened by carburization. This is a process where carbon atoms in solution diffuse into the surface of the substrate, i.e., the steel. Known casehardening processes are performed at high temperatures. Carburization processes are performed at temperatures of about 540° C. or higher (for stainless steel alloys). However, such high temperature processes can promote the formation of carbides in the surface of said stainless steel.

[0007] In many mechanical applications, not only the hardness but also the static friction, as indicated above, of the steel surface is a known problem. Even if lubrication is made, the static friction may cause considerable friction loss, especially in cases where a reciprocal movement will be performed. Examples of such applications are, e.g., shock absorbers for vehicles, hydraulic systems in the process industry and internal items of combustion engines, such as cam followers. At high-frequency changes of the type of movement or its direction, the static friction may cause a local temperature increase, which leads to deteriorated performance and/or service time and risks of leakage.

[0008] In order to decrease the static friction, exposed surfaces are usually coated with some form of layer with better properties than the under-lying steel substrate. Besides giving a lower friction, one desired property of said layer is to protect the substrate against mechanical wear. Therefore, the applied layer should be as hard as possible. In hydraulic steering control equipment in the process industry, a high static friction may cause a movement resistance, which deteriorates the precession of the hydraulic component. Said problems with static friction can occur, e.g., in combustion engines, in a cam follower for inlet and outlet valves. The surface on which the follower acts is exposed to a very high local load, which may result in serious wear problems.

[0009] A conventional way of lowering the static friction and to increase the hardness is to prepare a very smooth surface and then to apply hard chromium plating on this surface. Thereby a hardness level is achieved for low alloy wrought steel that amounts to about 1000 Hv. In order to support the layer, a surface hardening is often made before the hard chromium plating. The process is relatively complicated and involves several relocations of the work-piece due to the dimension alterations it undergoes during the hardening.

[0010] One possible solution of the problem of the difference in hardness of the substrate and the applied coating is to apply a system of layers. A treated work-piece comprises, e.g., of a base body or substrate of steel and a hard material layer system next to the substrate, supplemented by a metal layer and finally a sliding layer system, whereby the latter is preferably made of carbide, especially tungsten carbide or chromium carbide, and dispersed carbon. Although good hardness values and low static friction are achieved, the composite system of several layers is complicated, time-consuming and expensive to produce.

[0011] Another alternative is build a layer system, which comprises of an adhesive layer, which is placed on a substrate, a transition layer, which is placed on the adhesive layer and an outer layer, which is made of diamond-like carbon. The adhesive layer comprises at least one element from the group consisting, e.g., of the 4th, 5th and 6th subgroups and silicon. The transition layer consists of diamond-like carbon. The layer system has a hardness of at least 15 GPa, preferably at least 20 GPa, and an adhesive strength of at least 3 HF according to VDI 3824 ("Quality Assurance in the Case of PVD and CVD Hard Coatings"), sheet 4.

OBJECTS AND SUMMARY OF THE INVENTION

[0012] In view of the above, it is a primary object of the present invention to obtain a low static friction and wear resistant stainless steel surface.

[0013] Another object of the present invention is to obtain a low static friction on a very hard and wear resistant stainless steel surface in a simple and cost effective way, with as few procedural steps as possible.

[0014] Still another object of the present invention to produce components of sophisticated geometry of said stainless steel with a low static friction on a very hard and wear resistant surface.

[0015] In one aspect there is provided a coated, surface hardened precipitation hardened stainless steel with following composition (in weight-%):

Carbon	max about 0.1
Nitrogen	max about 0.1
Copper	from about 0.5 to about 4
Chromium	from about 10 to about 14
Molybdenum	from about 0.5 to about 6
Nickel	from about 7 to about 11
Cobalt	0 up to about 9
Tantalum	max about 0.1
Niobium	max about 0.1
Vanadium	max about 0.1
Tungsten	max about 0.1
Aluminum	from about 0.05 to about 0.6
Titanium	from about 0.4 to about 1.4
Silicon	max about 0.7
Manganese	max about 1.0
Iron	balance

[0016] and normally occurring usual steelmaking additions and impurities wherein said steel is coated and surface hardened in one and the same operation, having a combination of high strength and/or toughness and wear resistance together with low friction and improved adhesiveness.

[0017] In another aspect there is provided a process for producing a stainless steel with a low static friction on a very hard and wear resistant surface, said process comprising using a PVD to apply a low static friction coating in the same operation as surface hardening, said stainless steel having the following composition (in weight-%):

Carbon	max about 0.1
Nitrogen	max about 0.1
Copper	from about 0.5 to about 4
Chromium	from about 10 to about 14
Molybdenum	from about 0.5 to about 6
Nickel	from about 7 to about 11
Cobalt	0 up to about 9
Tantalum	max about 0.1
Niobium	max about 0.1
Vanadium	max about 0.1
Tungsten	max about 0.1
Aluminum	from about 0.05 to about 0.6
Titanium	from about 0.4 to about 1.4
Silicon	max about 0.7
Manganese	max about 1.0
Iron	balance

-continued

[0018] and normally occurring usual steelmaking additions and impurities.

[0019] In a further aspect providing a process for producing a stainless steel with a low static friction on a very hard and wear resistant surface, said process comprising using PVD to apply a low static friction coating onto a plasma-nitrided surface of the stainless steel in the same operation, said stainless steel having the following composition (in weight-%):

Carbon	max about 0.1
Nitrogen	max about 0.1
Copper	from about 0.5 to about 4
Chromium	from about 10 to about 14
Molybdenum	from about 0.5 to about 6
Nickel	from about 7 to about 11
Cobalt	0 up to about 9
Tantalum	max about 0.1
Niobium	max about 0.1
Vanadium	max about 0.1
Tungsten	max about 0.1
Aluminum	from about 0.05 to about 0.6
Titanium	from about 0.4 to about 1.4
Silicon	max about 0.7
Manganese	max about 1.0
Iron	balance

[0020] and normally occurring usual steelmaking additions and impurities.

DETAILED DESCRIPTION OF THE INVENTION

[0021] Thus, the present invention relates to methods of application of a low static friction coating on a specific class of stainless steels. Moreover, this low static friction coating also results in a very hard and wear resistant surface. The coating is applied according to the well-known PVD ("Physical Vapor Deposition") technique, in accordance with the state of the art referred to above. The steel has turned out to possess the surprising property of having a considerable inner hardness increase when the coating is applied whereby the necessary hard and carrying surface layer is created to carry the hard and low-friction top coating. Since the PVD operation is performed at a relatively low temperature, the dimensions of the work-piece are maintained without any distortions. The utilization of the PVD technique on some special stainless steel alloys brings about a number of advantages for the produciton of, e.g., cylinder tubes and piston rods for shock absorbers, pistons for hydraulic guide means, and cam followers for combustion engines.

[0022] Before any surface modifications, a suitable group of stainless steels for the purposes of the present invention was selected. It has the following composition ranges (in weight %):

Carbon	max about 0.1
Nitrogen	max about 0.1
Copper	from about 0.5 to about 4
Chromium	from about 10 to about 14
Molybdenum	from about 0.5 to about 6
Nickel	from about 7 to about 11
Cobalt	0 up to about 9
Tantalum	max about 0.1
Niobium	max about 0.1
Vanadium	max about 0.1
Tungsten	max about 0.1
Aluminum	from about 0.05 to about 0.6
Titanium	from about 0.4 to about 1.4
Silicon	max about 0.7
Manganese	max about 0.1
Iron	balance

[0023] and normally occurring usual steelmaking additions and impurities.

[0024] This stainless steel contains quasi-crystalline particles in a martensitic microstructure as a result of a precipitation hardening, as described in the above mentioned prior art references U.S. Pat. No. 5,632,826, WO-A-93/07303, WO-A-01/14601 and WO-A-01/36699.

[0025] In order to bring about a surface treatment according to the present invention, a specific precipitation hardened stainless steel was chosen having the following composition (in weight %):

C + N	max about 0.05
Cr	12.00
Mn	0.30
Ni	9.00
Mo	4.00
Ti	0.90
Al	0.30
Si	0.15
Cu	2.00
Fe	Balance

[0026] On this steel, a low static friction coating is applied, said coating consisting essentially of titanium nitride or diamond-like carbon (DLC), which is applied by PVD technique. This includes the metal piece being exposed to a temperature between about 450 and about 500° C. for a couple of hours. In the same temperature region, and after determined intervals, a hardening of the steel takes place, whereby hardness in the magnitude of 650 Hv is attained. In this way, an excellent support for the coating is obtained in the same operation. Thanks to the relatively low treatment temperature, the work-piece maintains its shape and dimensions with high accuracy, which results in a considerably simplified working process. At the same time, in spite of a thinner layer, the thickness of which is in the order of 6 μm, a superior wear resistance is obtained in comparison to conventional 25 μm thick hard chromium layers on a hardened surface. Thus, the great advantage of the present invention is that the application of the low static friction and wear resistant coating and the necessary surface hardening are brought about in one and the same operation.

[0027] Another significant advantage of the present invention is when the work-piece is of tubular shape for the manufacturing of tube-shaped items. Thanks to an excellent cold-workability of the stainless steel according to the invention, tubular products are readily produced. Costly long-hole drilling operations otherwise required for commonly available bar shaped products are thus eliminated.

[0028] It should be noted that when extremely hard and wear resistant surfaces are required, e.g., in some engine components, it would be a feasible modification of the present invention to include a plasma nitrided between the substrate and the PVD coating according to the present invention. Plasma nitriding is an alternative casehardening process, which is carried out in a glow discharge in a nitrogen gas-containing mixture at a pressure of about 100 to about 1000 Pa (about 1 to about 10 mbar). It is one of the methods used to treat stainless steel surfaces thereby resulting in a nitrogen diffusion layer having high hardness and excellent wear resistance. Nitriding hardening is induced by the precipitation of nitrides in the surface layer. The plasma nitriding is the most recently developed surface hardening procedure. This process replaces traditional nitriding methods, such as gas nitriding and nitrocarburation (short-term gas nitriding, bath nitriding and tenifer (a salt-bath nitriding process sometimes called the "Tuffride process") treatment), since identical thermo-chemical conditions can be established in this process. Plasma nitriding achieves higher hardness and wear resistance, while creating lower distortion. Furthermore, palsma nitriding is very cost effective. This is due to the fact that subsequent machining, finishing and residue removal processes are frequently not required. Similarly, supplementary protective measures, such as burnishing, phosphatizing, etc., are not necessary.

[0029] The plasma nitriding is performed in a vacuum furnace. Treatment temperatures in the range of about 400 to about 580° C. are employed, subject to the requirements of the process in question. Typical treatment temperatures are in the range of about 420 to about 500° C. Treatment times vary between about 10 minutes and about 70 hours, depending upon the component to be treated as well as the desired structure and thickness of the layer(s) formed. The most commonly used process gases are ammonia, nitrogen, methane and hydrogen. Oxygen and carbon dioxide are used in the corrosion-protective step of post-oxidation. Besides the type of process gas used, pressure, temperature and time are the main parameters of the treatment process. By varying these parameters in accordance with the knowledge of the skilled artisan, the plasma nitriding process can be fine-tuned to achieve the exact desired properties in any treated component.

[0030] Any iron-based material can be submitted to plasma nitriding. The process does not require the use of special types of nitriding steel. Moreover, the results attained by plasma nitriding can be reproduced with pinpoint accuracy. This is especially important in the manufacture of serial products. However, plasma nitriding does not significantly reduce the static friction. It would cause no problem to submit the stainless steel to temperatures in the range of about 450 to about 500° C. twice, since it will easily resist this temperature without showing softening tendencies.

[0031] Mechanical Properties of the stainless steel are:

Tensile strength, R_m	1700 MPa to 2000 MPa
Yield strength, $R_{p0.2}$	1500 MPa to 1800 MPa
Elongation	8% to 6%
Modulus of Elasticity	200 000 MPa
General hardness	450 to 650 Hv10, about 45 to 58 HRC
Surface hardness	about 3000 Hv10
Toughness	Impact strength (Charpy V) Min 27 J at −20° C.

[0032] The steel of the present invention maintains its mechanical properties even after long use at elevated temperatures up to about 400° C.

[0033] The coefficient of thermal expansion of the steel of the present invention is about 10% lower than that of carbon steel and more than 30% lower than that of a conventional stainless steel, such as ASTM type 304L. The steel of the invention is cold formable and bendable to tight radii. It is also suitable for common machining operations such as cutting, turning and grinding.

[0034] Further, the steel has good welding properties, when using TIG and MIG welding methods. Another advantage of the steel of the present invention is the improved corrosion resistance compared to, e.g., standard steel ASTM type 304L.

[0035] The principles, preferred embodiments and modes of operation of the present invention have been described in the foregoing specification. The invention which is intended to be protected herein, however, is not to be construed as limited to the particular forms disclosed, since these are to be regarded as illustrative rather than restrictive. Variations and changes may be made by those skilled in the art without departing from the spirit of the invention.

1. A coated, surface hardened precipitation hardened stainless steel with following composition (in weight-%):

Carbon	max about 0.1
Nitrogen	max about 0.1
Copper	from about 0.5 to about 4
Chromium	from about 10 to about 14
Molybdenum	from about 0.5 to about 6
Nickel	from about 7 to about 11
Cobalt	0 up to about 9
Tantalum	max about 0.1
Niobium	max about 0.1
Vanadium	max about 0.1
Tungsten	max about 0.1
Aluminum	from about 0.05 to about 0.6
Titanium	from about 0.4 to about 1.4
Silicon	max about 0.7
Manganese	max about 1.0
Iron	balance

and normally occurring usual steelmaking additions and impurities wherein said steel is coated and surface hardened in one and the same operation, having a combination of high strength and/or toughness and wear resistance together with low friction and improved adhesiveness.

2. The precipitation hardened stainless steel of claim 1 wherein said coating is applied on a nitrided surface of said steel.

3. The precipitation hardened stainless steel of claim 1 wherein said coating consists essentially of a single layer.

4. The precipitation hardened stainless steel according to claim 1 wherein said coating consists essentially of a single layer of diamond-like carbon (DLC).

5. The precipitation hardened stainless steel of claim 1 wherein said coating consists essentially of a single layer of diamond-like carbon (DLC) with addition of tungsten carbide.

6. The precipitation hardened stainless steel of claim 1 wherein said coating consists essentially of titanium nitride.

7. The precipitation hardened stainless steel of claim 1 wherein said precipitation hardened stainless steel has been strengthened by the precipitation of quasi crystalline structured particles.

8. A process for producing a stainless steel with a low static friction on a very hard and wear resistant surface, said process comprising using PVD to apply a low static friction coating in the same operation as surface hardening, said stainless steel having the following composition (in weight-%):

Carbon	max about 0.1
Nitrogen	max about 0.1
Copper	from about 0.5 to about 4
Chromium	from about 10 to about 14
Molybdenum	from about 0.5 to about 6
Nickel	from about 7 to about 11
Cobalt	0 up to about 9
Tantalum	max about 0.1
Niobium	max about 0.1
Vanadium	max about 0.1
Tungsten	max about 0.1
Aluminum	from about 0.05 to about 0.6
Titanium	from about 0.4 to about 1.4
Silicon	max about 0.7
Manganese	max about 1.0
Iron	balance

and normally occurring usual steelmaking additions and impurities.

9. The process of claim 7 wherein the low static friction coating comprises one or more of diamond-like carbon (DLC), diamond-like carbon with addition of titanium nitride.

10. A process for producing a stainless steel with a low static friction on a very hard and wear resistant surface, said process comprising using PVD to apply a low static friction coating onto a plasma-nitrided surface of the stainless steel in the same operation, said stainless steel having the following composition (in weight-%):

Carbon	max about 0.1
Nitrogen	max about 0.1
Copper	from about 0.5 to about 4
Chromium	from about 10 to about 14
Molybdenum	from about 0.5 to about 6
Nickel	from about 7 to about 11
Cobalt	0 up to about 9
Tantalum	max about 0.1
Niobium	max about 0.1
Vanadium	max about 0.1
Tungsten	max about 0.1
Aluminum	from about 0.05 to about 0.6
Titanium	from about 0.4 to about 1.4
Silicon	max about 0.7
Manganese	max about 1.0
Iron	balance

and normally occurring usual steelmaking additions and impurities.

11. The process of claim 9 wherein the low static friction coating comprises one or more of diamond-like carbon (DLC), diamond-like carbon with addition of titanium nitride.

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