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(54) SURFACE MODIFIED STAINLESS STEEL

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

Correspondence Address:
DRINKER BIDDLE & REATH (DC)
1500 K STREET, N.W.
SUITE 1100
WASHINGTON, DC 20005-1209 (US)

(73) Assignee: **SANDVIK INTELLECTUAL PROPERTY AB**, Sandviken (SE)

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(57) **ABSTRACT**

A stainless steel, which after nitriding exhibits a hardened surface layer with a hardness of at least 1200 Hv is disclosed. The stainless steel can be in the form of wire, plate, strip, tube and pipe and other geometries, especially complex geometries, particularly useful in applications with high demands on a combination of high strength and/or toughness and wear resistance and as a substrate for coating.

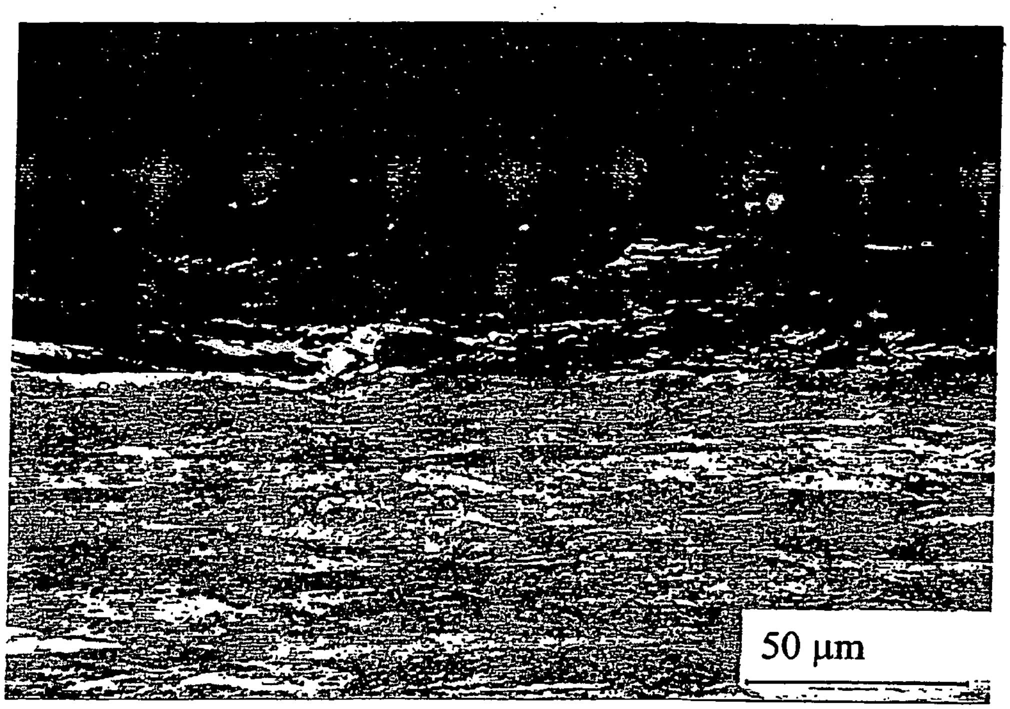


Figure 1

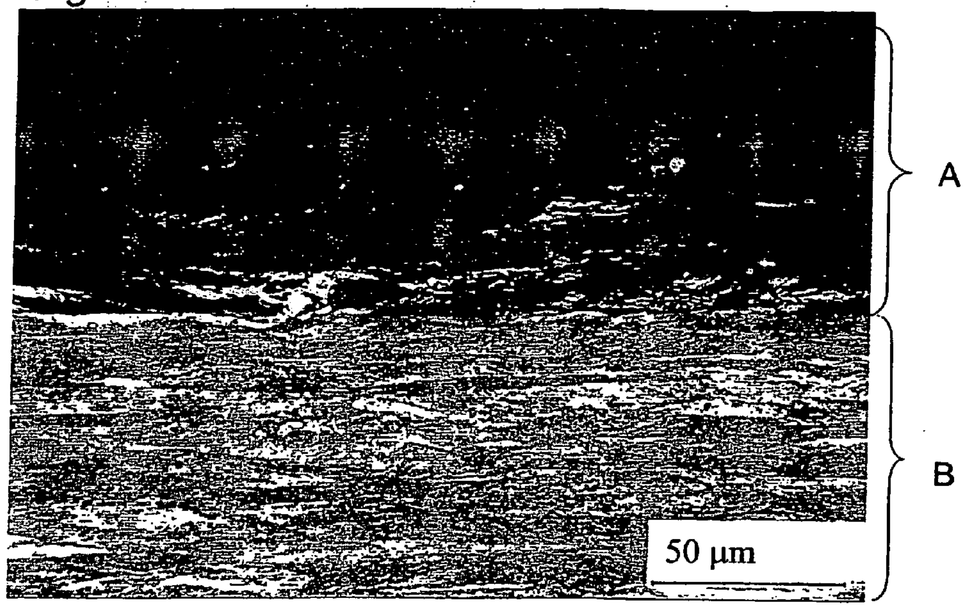
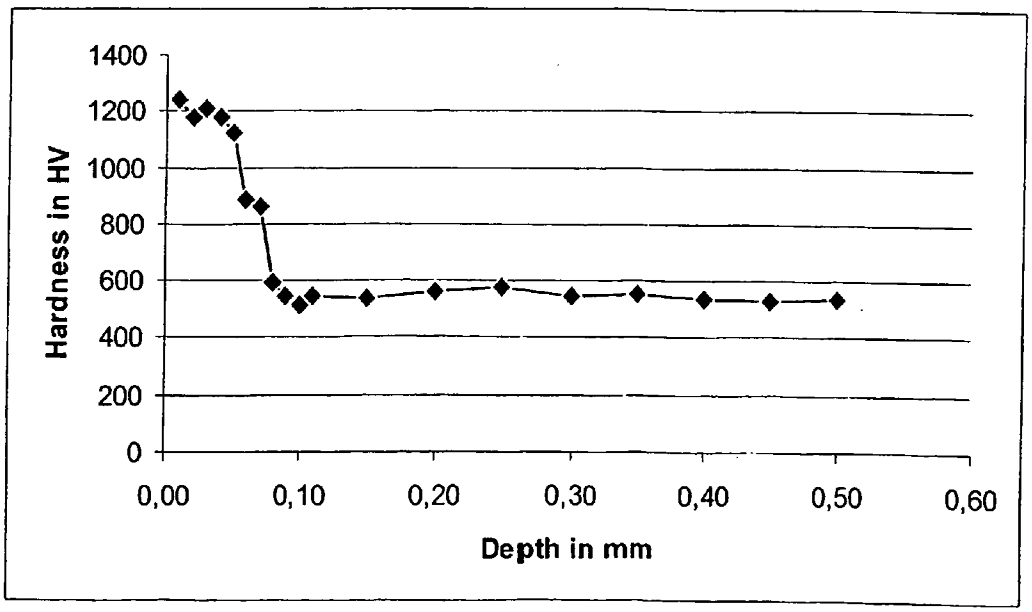



Figure 2



# SURFACE MODIFIED STAINLESS STEEL

## RELATED APPLICATION DATA

[0001] This application is a §371 National Stage Application of PCT International Application No. PCT/SE2003/001159 filed Jul. 2, 2003, which International Application was published by the International Bureau in English on Jan. 15, 2004, the entire contents of which are incorporated herein by reference. This application also claims priority under 35 U.S.C. §119 and/or §365 to Swedish Application No. 0202107-9, filed Jul. 3, 2002, the entire contents of which are incorporated herein by reference.

## FIELD OF THE DISCLOSURE

[0002] The present disclosure relates to a stainless steel, which after nitriding exhibits a hardened surface layer with a hardness of at least 1200 Hv. Such stainless steel is particularly useful, for example, in applications with high demands on a combination of high strength and/or toughness and wear resistance and as a substrate for coating.

## STATE OF THE ART

[0003] In the discussion of the state of the art that follows, reference is made to certain structures and/or methods. However, the following references should not be construed as an admission that these structures and/or methods constitute prior art. Applicant expressly reserves the right to demonstrate that such structures and/or methods do not qualify as prior art against the present invention.

[0004] Stainless steel alloys are relatively less hard than other steel materials. As a result, in many applications the stainless steel article or part is provided with a hardened surface, often referred to as case hardening. The concept of case hardening is to transform a relatively thin layer of material at the surface of the part by enrichment of carbon or other ingredients to make the surface harder than the matrix of the alloy. The steel thus retains in bulk the desired formality of stainless steel without the softness of the matrix at the modified steel surface.

[0005] Stainless steels are often casehardened by carburization. Carburization is a process by which carbon atoms are diffused in solution into the surface of the article. Known case hardening processes are performed at high temperatures. However, carburization processes performed at temperatures greater than about 540° C. (for stainless steel alloys) can promote the formation of carbides in the hardened surface.

[0006] Plasma nitriding is an alternative case-hardening process. Plasma nitriding is carried out in a glow discharge in a nitrogen gas-containing mixture at a pressure of 100 to 1000 Pa (1 to 10 mbar). This method treats stainless steel surfaces, 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.

[0007] Plasma nitriding is a recently developed surface hardening procedure. The process can replace traditional nitriding methods, such as gas nitriding and nitrocarburation (short-term gas nitriding, bath nitriding and tenifer treatment) as similar thermo-chemical conditions can be established in this process. Plasma nitriding achieves higher hardness and wear resistance, while creating lower distortion.

[0008] Plasma 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., under some conditions even galvanizing and hard-chrome plating, may not be necessary.

[0009] Plasma nitriding is performed in a vacuum furnace. Treatment temperatures in the range of 400 to 580° C. are employed subject to the requirements of the process at hand. Typical treatment temperatures are in the range of 420 to 500° C. Commonly used process gases are ammonia, nitrogen, methane, and hydrogen. Oxygen and carbon dioxide are used in the corrosion protective step of post-oxidation. Aside from the type of process gas used, pressure, temperature, and time are the main parameters of the treatment process. By varying these parameters, the plasma nitriding process can be fine tuned to achieve the exact desired properties in any treated component.

[0010] Any iron-based material can be subjected to plasma nitriding. The process does not require the use of special types of nitriding steel. The results achieved through plasma nitriding can be accurately reproduced. This is especially important in the manufacture of serial products. U.S. Pat. No. 5,632,826 discloses a precipitation hardened martensitic alloy in which the strengthening is based on the precipitation of particles. The strengthening particles have a quasicrystalline structure, said structure being essentially obtained at aging times up to 1000 h and tempering treatments up to 650° C. This strengthening involves an increase in tensile strength of at least 200 MPa. It has now surprisingly been found that if steel according to U.S. Pat. No. 5,632,826 is nitrided on the surface, an unexpected further increase in surface hardness is obtained compared to the matrix of said stainless steel.

## SUMMARY

[0011] An exemplary embodiment of a stainless steel comprises a composition (in weight-%):

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

[0012] Iron balance and

normally occurring usual steelmaking additions and impurities, wherein said stainless steel after nitriding exhibits a hardened surface layer with a hardness of at least 1200 Hv.

[0013] An exemplary method for making a surface modified stainless steel comprises subjecting a stainless steel to a nitriding process at a temperature of 450 to 580° C. for a time period of 1 to 40 hours in a plasma nitriding atmosphere, the stainless steel having a composition comprising:

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

[0014] Iron balance and

normally occurring usual steelmaking additions and impurities.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0015] The following detailed description of preferred embodiments can be read in connection with the accompanying drawings in which like numerals designate like elements and in which:

[0016] **FIG. 1** is a light-optical micrograph showing the microstructure of an exemplary embodiment of the surface modified stainless steel in 500×, where A is the nitrided surface layer and B is the stainless steel matrix.

[0017] **FIG. 2** is a graph showing the hardness (in Hv) plotted over the depth (in mm) from the surface.

## DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0018] A stainless steel alloy characterized by increased hardness at the surface of said alloy after modification of the surface at the same time as the hardness of the matrix of the stainless steel is also increased is provided. In addition, products made of said surface modified stainless steel are provided. Further, a stainless steel substrate for coating with wear resistant layers is provided.

[0019] In exemplary embodiments, the stainless steel substrate before surface modification has the following composition (in weight-%):

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

[0020] Iron balance

and normally occurring usual steelmaking additions and impurities.

[0021] Said stainless steel contains quasicrystalline particles in the martensitic microstructure as a result of a precipitation hardening.

[0022] Plasma nitriding is a surface hardening process, which utilizes the properties of gas plasma, i.e., an ionized gas, to achieve desirable mechanical properties at the surface of the work piece. The main influential parameters in nitriding are pressure, temperature, and time of treatment as well as the chemical composition of the ionized process gas. Plasma nitriding typically takes place at a vacuum pressure between 0.3 to 10 mbar. The actual treatment pressure chosen is governed by the geometry of the part and the desired surface layer structure.

[0023] The treatment temperature in the range of 400 to 580° C. is selected according to the type of material and pre-treatment of the part and the desired layer structure. Treatment time varies between 10 minutes and 70 hours, and depends on the part to be treated as well as the desired structure and thickness of the layers formed. Plasma nitriding uses ammonia or gas mixtures containing methane, nitrogen, and hydrogen as the process gas. The process gas used is selected subject to the nature of the part to be treated and the required layer structure.

[0024] In exemplary embodiments, a material treated with the disclosed method can be in the form of wire, plate, strip, tube and pipe and other geometries, especially complex geometries for use in applications with high demands on a combination of high strength and/or toughness and wear resistance, such as, e.g., wear parts of engines and other engine components, impact loads, such as safety devices, cam followers, cam follower pads, valve stems, valve stem guides, piston pins, piston shafts, hydraulic pistons, ejector pins, safety protection plates, lock cylinders and other locking devices, blocking elements, thief-proof equipment or the like.

## EXAMPLE 1

[0025] A stainless steel substrate as described herein was subjected to a surface modification by a plasma nitriding process at 450 to 580° C. during a period of time of 1 to 40 hours. This process obtains a hardening of the surface between 0.05 and 0.5 mm. The hardening process can be carried out on wire, plate, strip, tube and pipe and parts with a wide variation of geometries, especially complex geometries. It is a special advantage of the stainless steel substrate used according to the disclosed process, that very complex geometries can be formed without any changes in dimension. The hardness of the surface is at least twice the hardness of the substrate 0.5 mm into the matrix. The hardness of the surface is 1200 Hv, alternatively at least 1100 Hv.

[0026] **FIG. 2** is a graph illustrating the hardness profile from the surface of the substrate into the matrix. It unexpectedly shows that the hardening effect is visible down to about 0.5 mm into the matrix. It is therefore considered a big advantage of this combination of substrate and the method of surface treatment, that creates a surface modified material with a deep-hardened surface zone.

[0027] Exemplary embodiments of the surface modified stainless steel according to the present invention is particularly well suited for use as substrate for the deposition of a wear resistant coating.

[0028] Although the present invention has been described in connection with preferred embodiments thereof, it will be appreciated by those skilled in the art that additions, deletions, modifications, and substitutions not specifically described may be made without department from the spirit and scope of the invention as defined in the appended claims.

**1**. A stainless steel comprising a composition (in weight-%):

| | |
|---|---|
| Carbon | max 0.1 |
| Nitrogen | max 0.1 |
| Copper | 0.5–4 |
| Chromium | 10–14 |
| Molybdenum | 0.5–6 |
| Nickel | 7–11 |
| Cobalt | 0–9 |
| Tantalum | max 0.1 |
| Niobium | max 0.1 |
| Vanadium | max 0.1 |
| Tungsten | max 0.1 |
| Aluminum | 0.05–0.6 |
| Titanium | 0.4–1.4 |
| Silicon | max 0.7 |
| Manganese | ≦1.0 |

Iron balance and

normally occurring usual steelmaking additions and impurities, wherein said stainless steel after nitriding exhibits a hardened surface layer with a hardness of at least 1200 Hv.

**2-5**. (canceled)

**6**. The stainless steel according to claim 1, wherein the stainless steel includes quasicrystalline particles in a martensitic microstructure.

**7**. The stainless steel according to claim 6, wherein the quasicrystalline particles in the martensitic microstructure are a result of a precipitation hardening process.

**8**. The stainless steel according to claim 1, wherein a hardness at a surface of the stainless steel is at least twice that of a hardness of at 0.5 mm into a matrix of the stainless steel.

**9**. The stainless steel according to claim 1, wherein the hardened surface layer has a thickness of about 0.5 mm.

**10**. The stainless steel according to claim 1, wherein the stainless steel is formed into one or more of a wire, a plate, a strip, tube and a pipe.

**11**. The stainless steel according to claim 1, wherein the stainless steel is formed into a complex geometry for use in an application with a high demand on a combination of high strength and/or toughness and wear resistance.

**12**. The stainless steel according to claim 11, wherein the complex geometry is a wear part of an engine, an engine component, or an impact load.

**13**. The stainless steel according to claim 11, wherein the complex geometry is a cam follower, a cam follower pad, a valve stem, a valve stem guide, a piston pin, a piston shaft, a hydraulic piston, an ejector pin, a safety protection plate, a lock cylinder and other locking devices, a blocking element, or a thief-proof equipment

**14**. A material comprising a wear resistant coating deposited on the stainless steel according to claim 1.

**15**. A method for making a surface modified stainless steel, the method comprising:

subjecting a stainless steel to a nitriding process at a temperature of 450 to 580° C. for a time period of 1 to 40 hours in a plasma nitriding atmosphere, the stainless steel having a composition comprising:

| | |
|---|---|
| Carbon | max 0.1 |
| Nitrogen | max 0.1 |
| Copper | 0.5 to 4 |
| Chromium | 10 to 14 |
| Molybdenum | 0.5 to 6 |
| Nickel | 7 to 11 |
| Cobalt | 0 to 9 |
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| Vanadium | max 0.1 |
| Tungsten | max 0.1 |
| Aluminum | 0.05 to 0.6 |
| Titanium | 0.4 to 1.4 |
| Silicon | max 0.7 |
| Manganese | ≦1.0 |

Iron balance and

normally occurring usual steelmaking additions and impurities.

**16**. The method according to claim 15, wherein said stainless steel after nitriding exhibits a hardened surface layer with a hardness of at least 1200 Hv.

**17**. The method according to claim 15, wherein the surface modified stainless steel does not change dimension from the nitriding process.

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