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(54) SURFACE-CARBONITRIDED STAINLESS STEEL PARTS EXCELLENT IN WEAR RESISTANCE AND METHOD FOR THEIR MANUFACTURE

(57) A steel part according to the present invention is a part in which a surface of an austenitic stainless steel containing 3 to 20 mass % of Mn was carbonitrided to be hardened. By setting Vickers hardness of the surface to 1350 HV or more and setting a depth of a hardened layer having 1000 HV or more from the surface of the steel to 10 μm or more, when the part according to the present invention is applied to a part required for sliding and wear resistance particularly, the service life can be improved significantly. Further, since the manufacturing method is performed by only heating in a gas atmosphere, a large number of parts can be simultaneously treated. Thus the stainless steel parts of the present invention can be adopted to wide fields as stainless steel parts required for wear resistance.

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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to a surface hardened austenitic stainless steel part for improving wear resistance and its manufacturing method.

Background Art

[0002] Austenitic stainless steels have been utilized in various fields, required for corrosion resistance such as food machines, machines for chemical fields, plants and auto-motive engines and others. Among them there are many applications, also required for wear resistance, like sliding machine parts such as shafts and the like, valves and the like, gears and the like and so on. To improve this wear resistance, hardening by heat treatment such as quenching or the like, or surface-hardening such as carburizing, carbonitriding or the like is often applied to machine structural carbon steels, alloy steels and tool steels and the like.

[0003] In a case of austenitic stainless steel it is not hardened by quenching. Thus since sufficient hardness cannot be obtained by carburizing in the austenitic stainless steel, when it is necessary to harden the surface of the stainless steel particularly, wet plating such as hard chromium plating or the like, coating of a hard layer by PVD (Physical Vapor Deposition) or nitriding of the surface or the like is performed. However, coating of a film by plating or PVD or the like has a drawback in adhesive properties of the film with the base material. Particularly, when a surface pressure is increased, the coating cannot be applied stably.

[0004] On the other hand, a surface nitriding treatment is a method in which nitrogen is penetrated through a surface to harden it. Stainless steel containing much Cr (Chromium) is generally difficult to nitride for the sake of the presence of an oxide film. However, the nitriding of the stainless steel becomes easy by use of a hydrochloric acid treatment process, a halide treatment process, or ion-nitriding treatment process or the like. These processes are often utilized as a surface-hardening method of austenitic stainless steel.

[0005] The surface hardening of the austenitic stainless steel is needed for improving its fatigue strength. However, it is further needed for the sake of improving its wear resistance. The improvement of the wear resistance suppresses wear on a sliding surface of a sliding part to improve durability thereof. Additionally the improvement of the wear resistance has such effects that wear loss in a tool for polishing or cutting is reduced and scratching of a surface of a stainless steel part is suppressed.

[0006] Nitriding treatment is not necessary to quench unlike the carburizing treatment. Accordingly, in the nitriding treatment the surface can be hardened by a comparatively low temperature treatment. However, there is the most suitable temperature for increasing the surface hardness, and if the thickness of a hardened layer is increased at the temperature, it takes long time for nitriding. Otherwise, if the temperature is increased the thickness of the hardened layer can be increased. However, the obtained surface hardness is decreased.

[0007] Further, to improve the wear resistance of sliding parts, higher surface hardness of the parts is better. However, when a surface hardening treatment is performed at a decreased temperature, a hard layer such as a compound layer can be produced on the surface layer of the part. Nevertheless, the hard layer is brittle and the wear resistance is not necessarily improved.

[0008] As described above, although the method using the nitriding is important as a surface-hardening method of the austenitic stainless steel, sufficiently satisfactory hardening method cannot be necessarily obtained.

SUMMARY OF THE INVENTION

[0009] The object of the present invention is to provide an austenitic stainless steel part excellent in wear resistance, which is used in a sliding portion or the like, has high surface hardness and has sufficient hardness in a portion just below the surface, and its manufacturing method.

[0010] The present inventors have studied variously to improve the performance of austenitic stainless steel surface-hardened by gas nitriding. Although the surface nitriding process of the stainless steel includes ion nitriding, the nitriding is performed under a reduced pressure and the treatment speed is slow and even the shape to be nitrided can be limited. On the contrary, gas nitriding can be treated in high amounts, and it has been considered that the gas nitriding is suitable for mass production.

[0011] Therefore, regarding the surface hardening of the austenitic stainless steel by gas nitriding, steels having various different compositions were prepared, and influences of the gas compositions and treatment conditions on the surface hardness and hardened depth of the steel by gas nitriding have been studied variously.

[0012] In the case, while using a furnace that can shut out the outside air, gas containing fluoride of 10 volume % of NF_3 and the remaining of N_2 was led to the furnace and the steels were maintained for thirty minutes so that the surfaces of the steels were activated. After that nitriding gas containing NF_3 was injected into the furnace and temperature and time were variously changed for nitriding treatment.

[0013] The surface hardness of the steel by nitriding generally reaches about 1200 to 1300 HV. However, although a harder compound layer can be formed on the surface of the steel by treatment conditions, it is generally considered that the compound layer is so brittle that it cannot be utilized. In examinations using these austenitic stainless steels, steel having a surface hardness of 1350 HV or more at Vickers hardness was found.

[0014] This hard surface layer is not a brittle compound layer, which has been obtained in machine structural steels, ferritic stainless steels and the like, but it has sufficient toughness. Thus, after preparing test pieces for wear tests, wear resistances were checked. As a result, it has been recognized that the wear resistances are extremely excellent.

[0015] Then, the thus hard surface obtained steel members were examined in detail. As a result, the following points have been found.

(a) A compound layer is recognized on the surface layer.
(b) The steel is an austenitic stainless steel containing much Mn (Manganese).
(c) The atmosphere used in nitriding treatment contains, in addition to NH_3, carburizing gas such as RX gas or the like.

[0016] In the case of a machine structural steel or a ferritic stainless steel, a compound layer often appears on the surface layer depending on treatment conditions. It is considered that this compound layer was formed by increasing the content of active nitrogen on the surface layer, produced by decomposition of NH_3 due to the advancing of nitriding, and by nitriding Fe, Cr or the like with the increased nitrogen.

[0017] However, in the case of an austenitic stainless steel such a compound layer does not usually appear. It is considered that the solubility of nitrogen in an austenitic phase of the steel is significantly larger than in a ferritic phase of the steel, and nitrogen is diffused into the steel and an increase of nitrogen on the surface of the steel is difficult to arise whereby a compound layer is not formed.

[0018] However, in the case of an austenitic stainless steel containing much Mn, when it is treated in a nitriding and carburizing atmosphere, a compound layer appears on the steel. The treatment-performed test pieces exhibited excellent wear resistance.

[0019] The reason of such a result is not necessarily clear. However, if the facts of the above-mentioned (a), (b) and (c) are also considered, the following assumption is obtained.

[0020] First, hardening by nitriding treatment which is performed at a lower temperature compared with usual carburizing temperature is obtained by the formation of fine nitride precipitates and an increase of soluble nitrogen. In the cases of the machine structural steel and the ferritic stainless steel, since the steels have ferritic phases and small solubility of nitrogen, a compound layer is liable to be formed. However, since in a portion just below the compound layer the content of nitrogen is not increased, the hardness of the steel is low and there is a large difference of hardness between the compound layer and the portion just below the compound layer.

[0021] Therefore, the steel cannot hold a hard and brittle compound layer sufficiently and the hard compound layer is easily broken by small stress. Thus, only brittleness is prominent and the hard compound layer is not made full use of.

[0022] On the contrary, in the case of the austenitic stainless steel an austenitic phase has significantly larger solubility of nitrogen than the ferritic phase. It was seemed that the appearance of a compound layer in the austenitic steel containing much Mn was due to the fact that Ni is small.

[0023] The purpose of causing much Mn to contain into the austenitic stainless steel resizes in suppressing the use of expensive Ni, and when much Mn is contained in the steel, the Ni content is surely low. Ni is said to be an element, which generally prevents nitriding, and since Ni is small, penetration of nitrogen and penetration of carbon become easy. Therefore, it is assumed that the nitrogen content near the surface of the steel during nitriding is further increased as compared with a case where the austenitic stainless steel contains a small amount of Mn and a large amount of Ni.

[0024] Further, when carburizing gas containing CO and CH_4 such as an RX gas exists in a nitriding atmosphere, carburizing advances simultaneously. Thus, nitrogen dissolved in the steel has the same effect as a case where the nitrogen content was increased by the presence of dissolved carbon and a compound is easy to be formed on the surface of the steel. A portion just below a compound layer having an austenitic phase contains dissolved nitrogen and dissolved carbon more than the case of a ferritic phase, since the solubility of the portion just below the compound layer is large.

[0025] Thus, the solubility content of nitrogen is high since the austenitic steel has an austenitic phase, and the penetration of nitrogen is actively performed since Ni content is low. Additionally, a compound layer is easy to be formed by the penetration of carbon. Further, the hardness of the portion just below the compound is significantly increased since large amounts of fine carbide and nitride having high solid solubility content are formed.

[0026] Therefore, it is considered that since the compound layer is held by the lower layer having sufficient strength, the brittleness of the compound layer is compensated, resulting in that the compound layer has become a surface-strengthened layer excellent in wear resistance. In order to improve wear resistance, it is important to have higher surface hardness as well as a suitably-thick strengthened layer having intermediate hardness between the base and the hard surface layer.

[0027] Therefore, various investigations of the compositions of steels, nitriding treatment conditions, various properties of the obtained surface hardened parts and the like were performed with respect to an austenitic stainless steel containing much Mn. Based on the result of a review limits by which such results can be obtained were clarified and the present invention was accomplished. The gist of the present invention is as follows.

(1) A surface-carbonitrided stainless steel part excellent in wear resistance, in which Mn of 3 to 20 mass % is contained in the steel and a surface of the steel was carbonitrided to be hardened, characterized in that Vickers hardnesses of the surface are 1350 HV or more and depths of a hardened layer having 1000 HV or more are 10 µm or more.

(2) A manufacturing method of a surface-carbonitrided stainless steel part excellent in wear resistance according to the above mentioned (1), characterized in that after a stainless steel part containing 3 to 20 mass % of Mn, molded in a required shape, was surface activated in an atmosphere containing halogen gas or halide gas, the obtained stainless steel part is carbonitrided at 430 to 600 °C in an atmosphere containing NH_3 and carburizing gas.

DETAILRED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0028] A steel, which is manufactured to a part of the present invention, is an austenitic stainless steel containing 3 to 20 mass % of Mn. The reason for Mn content of 3 mass % or more is that in a case of an austenitic steel when Mn is decreased, Ni content is increased and surface hardening hardness due to nitriding is not significantly increased. On the other hand, when the Mn content is increased the corrosion resistance for the austenitic stainless steel becomes deteriorated. Thus, the Mn content is set to at most 20 mass %.

[0029] Such stainless steels include for example SUS 201, SUS 202, SUS 304J2, SUH 35, SUH 36 and the like in the JIS standard. The compositions other than Mn are not particularly limited if they are in ranges, which belong to the austenitic stainless steels. Nevertheless, it is preferable that the Ni content is, if possible, smaller than the Mn content since there is a possibility that sufficient surface hardness of the steel cannot be obtained.

[0030] The hardness of a carbonitrized surface is set to 1350 HV or more. This is because sufficiently high wear resistance cannot be obtained when the hardness thereof is lower than 1350 HV. Thus, in addition to the surface hardness of 1350 HV or more, the depth of a hardened layer whose hardness is 1000 HV or more is set to 10 µm or more.

[0031] This is because in a case where the hardness of a hardened layer just below a surface compound layer is lower than 1000 HV, when the depth of the hardened layer is less than 10 µm, any surface hardness not only reaches a level lower than 1350 HV, but also a surface compound layer becomes brittle and wear resistance deteriorates.

[0032] The austenitic stainless steel part surface hardened in the above-mentioned conditions cannot be obtained by only nitriding. Thus it is necessary to manufacture the part by carbonitriding. As the surface nitriding of the austenitic stainless steel there is a method in which the surface of the steel is heated in an atmosphere containing halogen gas or halide gas to activate the surface, and nitriding gas containing NH_3 is introduced into a furnace and the heated surface of the steel is nitrided. In the present invention carbonitriding is performed according to the method of using the halogen or halide.

[0033] First, by using a heating container which may be hermetically closed, an austenitic steel is heated at 200 to 550 °C for 10 minutes to 3 hours in atmosphere containing 0.5 to 20 volume % of halogen gas or halide gas such as F_2, Cl_2, HCl or NF_3 and the balance of nitrogen, hydrogen or inactive gas to activate the surface of the steel.

[0034] After the surface of the steel was activated, the surface is carbonitrided by heating at a temperature range of 430 to 600 °C for 20 minutes or more in a mixed gas atmosphere containing NH_3 for nitriding and CO or CH_4 for carbonizing.

[0035] These carbonitriding atmospheric gases include 10 to 95 volume % of NH_3 and 5 to 30 volume % of one of CO or CH_4, or both of them. The reason for 10 volume % or more of NH_3 is that if NH_3 is less than 10 volume %, nitriding cannot be performed sufficiently and a hardened layer cannot be obtained. 100 volume % NH_3 may be used for the purpose of nitriding. However, since it is necessary to use a carbonizing gas, NH_3 is contained by at most 95 volume %.

[0036] For the purpose of carbonizing, 5 volume % or more of one of CO or CH_4 or both of them is needed. However, when these gas ratio is too increased, soot is generated. Accordingly, the gas content is set to at most 30 volume %.

[0037] The carbonitriding atmospheric gas may contain NH_3 and CO or CH_4 by enough contents for nitriding and for carbonizing the surface of the steel, and other components may be inactive gas, hydrogen, nitrogen or other hydrocarbon gases and the like, which are not limited. Further, if the above-mentioned composition ranges are satisfied as in a case where NH_3 is mixed to RX gas, carbonitriding gas may be prepared by mixing carburizing gas, which has been used, with NH_3.

[0038] When the carbonitriding temperature is less than 430 °C or less, surface hardness of 1350 HV or more cannot be obtained. Additionally, a development of a hardened layer of 1000 HV or more becomes insufficient. This is because nitriding advances but carboniding does not advance significantly. When the carbonitriding temperature reaches 430 °C or more, these surface hardness and hardened layer can be obtained. However, when the carbonitriding temperature exceeds 600 °C, not only a surface hardness of 1350 HV or more cannot be obtained, but also corrosion resistance as a stainless steel is reduced.

[0039] Further, when the carbonitriding time is less than 20 minutes, there is a possibility that a surface compound layer cannot be obtained, and a surface hardness of 1350 HV or more cannot be obtained. If the carbonitriding time is 20 minutes or more, the limitation of the time is not needed. Then the carbonitriding time is increased, the thickness in a hardened layer of 1000 HV or more can be increased. However, wear resistance is not improved more than a certain level and it is preferable that the carbonitriding time is within at most 50 hours since corrosion resistance can be deteriorated.

[0040] Examples of stainless steel parts, which are required for wear resistance and to which the present invention is effectively applied, are described as follows. Those are sliding mechanical parts including an engine valve, a compressor shaft, a compressor vane, a piston ring, a bearing ball, a micro motor shaft, a motor shaft, and the like. Further, fluid wear resistant parts include a filter mesh, a nozzle, a valve, a piping joint, a reducer, a pump and the like. Furthermore, fastening parts include a bolt, a nut, a screw, a tapping screw, and the like. Further, tools and the like include a dresser, a cutting saw, a wire saw, a saw, a drill and the like. The stainless parts can also be applied to an extrusion mold, a die cast mold, an injection die and the like.

(Examples)

[0041] Stainless steels having compositions shown in Table 1 were used. First, they were cut to prepare disk-shaped test pieces of 35 mm in diameter and 10 mm in thickness. In a case where the test piece is used as a rotating test piece for an Amsler wear test, the circumferential surface of the disk is further polished in a mirror surface to remove edges. The obtained test pieces were heated at 300 °C and the heating was maintained in an atmosphere containing NF_3 to perform nitriding or carbonitriding thereby hardening the surfaces of the test pieces. The atmospheric gases, temperatures and treatment time during surface-nitriding are shown in Table 2.

[0042] In reference to surface hardened test pieces the surface hardness was measured at Vickers hardness (HV0.1) of test force of 0.9806 N, and the hardness distribution in cross-section was measured at Vickers hardness (HV0.05) of test force of 0.4903 N. The concave mark obtained after the measurement of surface hardness, was observed with an optical microscope at 100 fold and when generation of chipping or a crack was recognized, the test piece was determined to be brittleness failure.

[0043] Amsler wear test was performed as follows. In two cylindrical rolling abrasion testers circumferential surfaces of the above-mentioned test pieces were pressed against cylindrical metal surfaces (made of SKH52) of 35 mm and 50 mm in diameter at 150 kg, and the abrasion testers were rolled in the same direction in sliding portions. Then the sliding speed was set to 0.12 m/sec and specific abrasion wear [mg/(m · sec)] was obtained without lubrication.

Table 1

Steel Mark	Chemical Composition (Mass %) [Balance: Impurities and Fe]							Remarks
	C	Si	Mn	Cr	Ni	Mo	N	
A	0.05	0.2	9.5	13.5	2.5	1.0	0.15	Range of the present invention
B	0.05	0.5	10.0	11.0	5.0	1.0	0.05	Range of the present invention
C	0.05	0.5	10.0	22.0	5.0	2.0	0.10	Range of the present invention
D	0.03	0.5	*2.5	25.0	7.0	3.5	0.30	Out of the range

Mark * shows out of range defined in the present invention.

[0044] The results of the abrasion test are shown in Table 2 on the next page. The test pieces of test Nos. 1 to 3 in which an austenitic stainless steel of a sufficiently high Mn content was used and carbonitriding was performed as a surface hardening treatment, exhibit excellent low specific abrasion wear. This is assumed to be the facts that the steel has a high surface hardness, which exceeds 1400 HV, and a hardened layer depth having 1000 HV or more.

Table 2

Test No.	Steel Mark	Surface Hardened Treatment			Surface Hardness (HV0.05)	Hardened Depth of 1000 HV or more (μm)	Surface Hardened Layer Brittleness	Specific Abrasion Wear [mg/(m·s)]	Remarks
		Atmosphere	Temperature (°C)	Time (h)					
1	A	50% NH_3 + 50% RX	570	3.0	1500	50	Good	0.1	Example of the present invention
2	B	50% NH_3 + 50% RX	540	2.0	1450	18	Good	0.1	Example of the present invention
3	C	50% NH_3 + 50% RX	570	3.0	1500	50	Good	0.1	Example of the present invention
4	*D	50% NH_3 + 50% RX	570	3.0	*1200	50	Good	0.5	Comparative example
5	A	50% NH_3 + 50% RX	*410	48.0	*1330	7	Bad	0.5	Comparative example
6	A	*100% NH_3	570	3.0	*1300	50	Bad	0.6	Comparative example

Mark * shows out of range defined in the present invention.

[0045] On the contrary, even if a test piece of test No. 6 is the austenitic stainless steel of the high Mn content, the surface hardening treatment is not carbonitriding. Accordingly, the surface hardness of the test piece of test No. 6 is not sufficient and is brittle. Next, in a test piece of test No. 5 since a carbonitriding temperature is low a hardened depth of 1000 HV or more is 7 µm, which is shallow. Further, although a surface hardening treatment of carbonitriding in a test piece of test No. 4 was performed, since the test piece of test No. 4 is an austenitic stainless steel of a low Mn content, the surface hardness is less than 300 HV All cases of test Nos. 4 to 6 exhibit large specific abrasion wear and worse results as compared with the cases of test Nos. 1 to 3 according to the present invention.

[0046] As described above, by applying the parts of the present invention to various mechanical parts, to which austenitic stainless steel is applied, particularly to parts required for sliding and wear resistance, their service life can be improved significantly.

INDUSTRIAL APPLICABILITY

[0047] According to the surface carbonitrided stainless steel part of the present invention and its manufacturing method, by setting a Vickers hardness of the surface to 1350 HV or more and setting a depth of a hardened layer having 1000 HV or more from the surface of the steel to 10 µm or more, when the part according to the present invention is applied to a part required for sliding and wear resistance particularly, the service life can be improved significantly. Further, since the manufacturing method is performed by only heating in a gas atmosphere, a large number of parts can be simultaneously treated. Thus the stainless steel parts of the present invention can be adopted to sliding mechanical parts, fluide wear resistant parts, fastening parts and tools and the like as stainless steel parts required for wear resistance. Therefore, the present invention can be applied to wide fields.

Claims

1. A surface-carbonitrided stainless steel part excellent in wear resistance, in which 3 to 20 mass % of Mn is contained in the steel and a surface of the steel was carbonitrided to be hardened, **characterized in that** a Vickers hardness of the surface is 1350 HV or more and a depth of a hardened layer having 1000 HV or more from the surface of said steel is 10 µm or more.

2. A manufacturing method of a surface-carbonitrided stainless steel part excellent in wear resistance according to claim 1, **characterized in that** after a stainless steel part containing 3 to 20 mass % of Mn, molded in a required shape, was surface activated in an atmosphere containing halogen gas or halide gas, the obtained stainless steel part is carbonitrided at 430 to 600 °C in an atmosphere containing NH_3 and carburizing gas.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP03/12806

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl^7 C23C8/32, C23C8/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl^7 C23C8/32, C23C8/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Toroku Jitsuyo Shinan Koho	1994-2004
Kokai Jitsuyo Shinan Koho	1971-2004	Jitsuyo Shinan Toroku Koho	1996-2004

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 58-5456 A (Nippon Piston Ring Co., Ltd.), 12 January, 1983 (12.01.83), (Family: none)	1,2
A	JP 62-278258 A (Chuo Hatsujo Kabushiki Kaisha), 03 December, 1987 (03.12.87), (Family: none)	1,2
A	JP 63-171855 A (Kobe Steel, Ltd.), 15 July, 1988 (15.07.88), (Family: none)	1,2
A	JP 11-200010 A (Kabushiki Kaisha Hirata), 27 July, 1999 (27.07.99), (Family: none)	1,2

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"&" document member of the same patent family

Date of the actual completion of the international search 21 January, 2004 (21.01.04)	Date of mailing of the international search report 03 February, 2004 (03.02.04)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP03/12806

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1193413 A1 (NSK LTD.), 03 April, 2002 (03.04.02), & JP 2001-330038 A & US 2003/0094215 A1 & WO 01/69100 A1	1,2

Form PCT/ISA/210 (continuation of second sheet) (July 1998)