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(54) **Martensitic Stainless Steel**

(57) A martensitic stainless steel of this invention, aimed at achieving excellent corrosion resistance and cold workability and a desirable level of toughness, while keeping the hardness equivalent to that of conventional martensitic stainless steel, which consists essentially of, in % by mass, C: less than 0.15%, Si: 0.05% or more and less than 0.20%, Mn: 0.05-2.0%. P: 0.03%

or less, S: 0.03% or less, Cu: 0.05-3.0%, Ni: 0.05-3.0%, Cr: 13.0-20.0%, Mo: 0.2-4.0%, V: 0.01-1.0%, Al: 0.030% or less, Ti: less than 0.020%, O: 0.020% or less, N: 0.40-0.80%. and the balance of Fe and inevitable impurities.

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Description**BACKGROUND OF THE INVENTION**

1. Field of the Invention

[0001] This invention relates to a high-hardness martensitic stainless steel excellent in corrosion resistance.

2. Description of the Related Art

[0002] Martensitic stainless steel such as SUS420J2 and SUS440C have generally been used in fields in need of certain levels of corrosion resistance; hardness and wear resistance, including cylinder liner, shaft, bearing, gear, pin, bolt, screw, roll, turbine blade, mold, die, valve, valve seat, cutting tool and nozzle and so on.

[0003] However, the martensitic stainless steel, which contains a large amount of C in view of ensuring a necessary level of hardness, is inferior to austenitic stainless steel represented by SUS304 and SUS316 in corrosion resistance, and cannot be used under outdoor environments where water drops or aqueous solution may adhere. This is partially solved by providing surface treatment such as plating, but a problem arises in that any scratch or peeling-off of the plated film may allow corrosion to proceed.

[0004] Another problem is that the martensitic stainless steel is extremely low in the cold workability due to eutectic carbide produced therein. On the other hand, the austenitic stainless steel represented by SUS304 and SUS316 are excellent in the corrosion resistance but far inferior to the martensitic stainless steel in the hardness, showing only a hardness of as small as HRC40 or around after cold working.

[0005] The present applicant previously disclosed, in Japanese Laid-Open Patent Publication "Tokkai" No. 2002-256397, a martensitic stainless steel equivalent to or superior to SUS420J2 in terms of cold workability and temper hardness, and equivalent to or superior to SUS316 in terms of corrosion resistance. Our previous martensitic stainless steel has, however, not paid a special consideration on the toughness which would be necessary for use as the mechanical components listed in the above.

[0006] It is therefore an object of the present invention to provide a martensitic stainless steel which is equivalent to the conventional martensitic stainless steel in terms of hardness, excellent in corrosion resistance and cold workability, and also satisfactory in toughness.

SUMMARY OF THE INVENTION

[0007] Aiming at solving the aforementioned problems, a martensitic stainless steel of this invention consists essentially of, in % by mass, C: less than 0.15%, Si: 0.05% or more and less than 0.20%, Mn: 0.05-2.0%, P: 0.03% or less, S: 0.03% or less, Cu: 0.05-3.0%, Ni: 0.05-3.0%, Cr: 13.0-20.0%, Mo: 0.2-4.0%, V: 0.01-1.0%, Al: 0.030% or less, Ti: less than 0.020%, O: 0.020% or less, N: 0.40-0.80%, and the balance of Fe and inevitable impurities.

[0008] This invention makes it possible for a martensitic stainless steel to ensure a necessary level of temper hardness, to improve corrosion resistance and cold workability, and to ensure a necessary level of toughness, by reducing the C content, by increasing the N content, by reducing also the Si, Al and Ti contents, and by adding V. The following paragraphs will describe reasons for the compositional limitations.

C (carbon): less than 0.15%

[0009] C is an interstitial element, and contributes to improvement in the strength, and improvement in the temper hardness through bonding with Cr, Mo, W, V, Nb and Ta, described later. Addition in an amount of 0.01% or more is preferable in view of obtaining these effects. On the other hand, any excessive addition lowers amount of solubility of N, and allows coarse primary carbides to generate, and this not only degrades the cold workability after annealing, corrosion resistance and toughness after hardening-and-tempering, but also increases residual austenite content to thereby result in degraded temper hardness. The amount of addition is therefore limited to less than 0.15%, and more preferably 0.14% or less.

Si (silicon): 0.05% or more and less than 0.20%

[0010] Si is a deoxidizer element, and is effective for suppressing Al possibly produces AlN which is causative of an extreme lowering in the toughness and ductility. Addition in an amount of 0.05% or more is necessary in view obtaining these effects. Whereas, any excessive addition not only extremely lowers the toughness and ductility, but also adversely affects the hot workability, so that the amount of addition is therefore limited to less than 0.20, and more preferably

0.18% or less.

Mn (manganese): 0.05-2.0%

[0011] Mn is an element effective for increasing amount of solubility of N, and is also effective as a deoxidizing and desulfurizing element. Addition in an amount of 0.05% or more, and more preferably 0.10% or more, is necessary in view of obtaining these effects. Whereas, any excessive addition not only increases amount of residual austenite content, and this not only degrades the temper hardness but also degrades corrosion resistance. The amount of addition is therefore limited to 2.0% or less, and more preferably 1.0% or less.

P (phosphorus): 0.03% or less

[0012] P is an element possibly lowers the hot workability, grain boundary strength, toughness and ductility, and is preferably suppressed to a lower level. The amount of addition is limited to 0.03% or less. It is to be, however, noted that any effort of excessively lowering in the content will raise the cost.

S (sulfur): 0.03% or less

[0013] S is an element possibly degrades the corrosion resistance, toughness and ductility during cold working, and also degrades the hot workability, and is preferably suppressed to a lower level. The amount of addition of S is set to 0.03% or less, and preferably 0.02% or less. It is to be, however, noted that any effort of excessively lowering in the content will raise the cost.

Cu (copper): 0.05-3.0%

[0014] Cu is an element capable of improving not only the toughness during cold working, but also the corrosion resistance. The addition in an amount of 0.05% or more, and more preferably 0.08% or more, is necessary in view of obtaining these effects. Whereas, any excessive addition increases residual austenite content, and this not only results in lowered temper hardness but also in degraded hot workability. The amount of addition is therefore limited to 3.0% or less, and more preferably 1.0% or less.

Ni (nickel): 0.05-3.0%

[0015] Ni is a potent austenite stabilizing element, and is therefore effective for suppressing nitrogen blow. It also contributes to improvements in the corrosion resistance and toughness. Addition in an amount of 0.05% or more, and more preferably 0.08% or more, is necessary in view of obtaining these effects. Whereas, any excessive addition increases the hardness after annealing, to thereby results in degraded cold workability. It not only extremely lowers the corrosion resistance, toughness and ductility due to increase in the insolubilized Cr carbonitride during hardening, but also lowers the temper hardness due to increase in residual austenite content. The amount of addition is therefore limited to 3.0% or less, and more preferably 1.0% or less.

Cr (chromium): 13.0%-20.0%

[0016] Cr is an element capable of increasing amount of solubility of N, and can therefore contribute to increase not only in the strength, but also in the oxidation resistance and corrosion resistance. It also contributes to increase in the hardness through bonding with C and N during tempering to thereby produce fine carbonitride grains. Addition in an amount of 13.0% or more, and more preferably 14.0% or more, is necessary in view of obtaining these effects. Whereas, any excessive addition increases residual austenite content and thereby lowers the temper hardness. The amount of addition is therefore limited to 20.0% or less, and more preferably 19.0% or less.

Mo (molybdenum): 0.2-4.0%

[0017] Mo increases amount of solubility of N to thereby improve the corrosion resistance, and improves the hardness as a solid solution hardening element. It also contributes to improvement in the hardness through bonding with C and N during tempering. Addition in an amount of 0.2% or more, and more preferably 0.4% or more, is necessary in view of obtaining these effects. Whereas, any excessive addition will make it difficult to ensure an austenitic phase effective for suppressing nitrogen blow, and will also result in degradation of the toughness and ductility due to increase in insolubilized Cr carbonitride during hardening. The amount of addition is therefore limited to 4.0% or less, and more

preferably 3.5% or less.

V (vanadium): 0.01-1.0%

[0018] V contributes to micronization of the crystal grains through bonding with C and N, and contributes also to improvement in the toughness as a solute element. Addition in an amount of 0.01% or more, and more preferably 0.02% or more, is necessary in view of obtaining these effects. Whereas, any excessive addition allows large amounts of carbide, oxide and nitride to remain in the steel, to thereby degrade the toughness. The amount of addition is therefore limited to 1.0% or less, and more preferably 0.8% or less.

Al (aluminum): 0.030% or less

[0019] Al is an element effective as a deoxidizing element, similarly to Si and Mn. Addition in an amount of 0.001% or more is preferable in view of obtaining the effect. This invention is, however, aimed at increasing amount of solubility of N, and any excessive addition thereof is undesirable because it will extremely degrade the toughness and ductility due to production of AlN. The amount of addition is therefore necessarily limited to 0.030% or less, and more preferably 0.025% or less in view of ensuring a desirable level of toughness.

Ti (titanium): less than 0.020%

[0020] Ti allows large amounts of oxide and nitride to remain in the steel, to thereby extremely degrade the corrosion resistance and toughness. Addition in an amount of less than 0.020%, and more preferably 0.018 or less, is necessary in view of ensuring a desirable level of toughness.

O (oxygen): 0.020% or less

[0021] O is preferably suppressed to a lower level because it allows a large amount of oxide to remain in the steel, to thereby extremely degrade the corrosion resistance and toughness. The amount addition is therefore limited to 0.020% or less, and more preferably 0.010% or less.

N (nitrogen): 0.40-0.80%

[0022] N is an interstitial element, and one of most important elements in this invention because it can extremely improve the hardness and corrosion resistance of the martensitic stainless steel, and can further improve the hardness during tempering through formation of fine Cr nitride. Addition in an amount of 0.40% or more, and preferably 0.42% or more, is necessary in view of obtaining these effects. Whereas, any excessive addition induces generation of nitrogen blow, and allows insolubilized Cr carbonitride to remain during hardening. This not only results in an extreme degradation in the corrosion resistance, toughness and ductility, but also results in degradation of the hardness after hardening-and-tempering, due to increased amount of residual austenite. The amount of addition is therefore limited to 0.80% or less, and more preferably 0.70% or less.

[0023] Next, the martensitic stainless steel of this invention can further contain any one or more of steel components which consist of Co: 0.05-4.0%, W: 0.020-0.20%, Ta: 0.020-0.20%, and Nb: 0.010-0.20%. The following paragraphs will describe reasons for the compositional limitations.

Co (cobalt): 0.05-4.0%

[0024] Co is a potent austenite stabilizing element, and is therefore effective for suppressing nitrogen blow. It also contributes to improvements in the corrosion resistance. It is also effective for ensuring a desirable level of hardness during hardening, because it can raise the Ms point to thereby reduce amount of residual austenite. Addition in an amount of 0.05% or more, and more preferably 0.07% or more, is preferable in view of obtaining these effects. Whereas, any excessive addition not only results in increase in the cost, but also in degradation in the corrosion resistance, toughness and ductility, due to increase in the insolubilized Cr carbonitride during hardening. It is therefore preferable to limit the amount of addition to 4.0% or less, and more preferably 2.0% or less.

W (tungsten): 0.020-0.20%

[0025] W contributes to improvement in the hardness as a solid solution hardening element, or through bonding with C and N during tempering. Addition in an amount of 0.020% or more, and more preferably 0.040% or more, is preferable

in view of obtaining the effect. Whereas, any excessive addition may degrade the toughness and ductility. It is therefore preferable to limit the amount of addition to 0.20% or less, and more preferably 0.15% or less.

Ta (tantalum): 0.020-0.20%

[0026] Ta contributes to micronization of the crystal grain through bonding with C and N. Addition in an amount of 0.020% or more, and more preferably 0.040% or more, is preferable in view of obtaining this effect. Whereas, any excessive addition may allow large amounts of carbide, oxide, and nitride to remain in the steel, similarly to Ti, to thereby degrade the toughness. It is therefore preferable to limit the amount of addition to 0.20% or less, and more preferably 0.15% or less.

Nb (niobium): 0.010-0.20%

[0027] Nb contributes to micronization of the crystal grain through bonding with C and N. Addition in an amount of 0.010% or more, and more preferably 0.020% or more, is preferable in view of obtaining this effect. Whereas, any excessive addition may allow large amounts of carbide, oxide, and nitride to remain in the steel, similarly to Ti, to thereby degrade the toughness. It is therefore preferable to limit the amount of addition to 0.20% or less, and more preferably 0.10% or less.

[0028] Next, the martensitic stainless steel of this invention can further contain any one or more of steel components which consist of B: 0.001-0.01%, Mg: 0.001-0.01%, Ca: 0.001-0.01%, and Zr: 0.020-0.20%. The following paragraphs will describe reasons for the compositional limitations.

B (boron): 0.001-0.01%

[0029] B contributes to improvement in the toughness, and is also effective for improving the hot workability. Addition in an amount of 0.001% or more is preferable in view of obtaining this effect. Whereas, any excessive addition may adversely affect the hot workability. It is therefore preferable to limit the amount of addition to 0.01% or less, and more preferably 0.008% or less.

Mg (magnesium): 0.001-0.01%

[0030] Mg is effective for improving the hot workability. Addition in an amount of 0.001% or more is preferable in view of obtaining this effect. Whereas, any excessive addition may adversely affect the hot workability. The amount of addition is preferably limited to 0.01% or less, and more preferably 0.008% or less.

Ca (calcium): 0.001-0.01%

[0031] Ca is effective for improving the hot workability, and also for improving the machinability. Addition in an amount of 0.001% or more is preferable in view of obtaining these effects. Whereas, any excessive addition may adversely affect the hot workability. It is therefore preferable to limit the amount of addition to 0.01 % or less, and more preferably 0.008% or less.

Zr (zinc): 0.020-0.20%

[0032] Zr contributes to improvement in the toughness. Addition in an amount of 0.020% or more, and more preferably 0.030% or more, is preferable in view of obtaining the effect. Whereas, any excessive addition may adversely affect the toughness and ductility. It is therefore preferable to limit the amount of addition to 0.20% or less, and more preferably 0.15% or less.

[0033] Next, the martensitic stainless steel of this invention can further contain either of, or both of steel components which consist of Te: 0.005-0.05% and Se: 0.02-0.20%. The following paragraphs will describe reasons for the compositional limitations.

Te (tellurium): 0.005-0.05%

[0034] Te contributes to improvement in the machinability. Addition in an amount of 0.005% or more, and more preferably 0.01% or more, is preferable in view of obtaining the effect. Whereas, any excessive addition may adversely affect the toughness and hot workability. It is therefore preferable to limit the amount of addition to 0.05% or less, and more preferably 0.04% or less.

Se (selenium): 0.02-0.20%

[0035] Se contributes to improvement in the machinability. Addition in an amount of 0.02% or more, and more preferably 0.05% or more, is preferable in view of obtaining the effect. Whereas, any excessive addition may adversely affect the toughness. It is therefore preferable to limit the amount of addition to 0.20% or less, and more preferably 0.15% or less.

[0036] Next, the martensitic stainless steel of this invention preferably has a value of W_C/W_N of less than 0.30, and more preferably 0.29 or less, where W_C (%) is C content, and W_N (%) is N content. The ratio of contents of C and N, both are interstitial elements, largely affects the hardness and corrosion resistance. A value of W_C/W_N of 0.30 or more may result in a degraded corrosion resistance, and may also fail in ensuring a necessary level of hardness.

[0037] Next, the martensitic stainless steel of this invention preferably has a mean crystal grain size of the prior austenitic grain in the tempered martensitic structure of 50 μm or less, and more preferably 40 μm or less. The size of the prior austenitic grain affects the toughness. A mean crystal grain size exceeding 50 μm may result in a degraded toughness.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0038] The experiments below were conducted in order to confirm the effects of this invention.

[0039] Alloys having chemical compositions listed in Table 1 were melted in a pressurizable high-frequency induction furnace, homogenized under heating, and hot-forged to thereby produce 24-mm diameter round rods. The rods were annealed by being heated at a temperature of $\text{Ac3}+50^\circ\text{C}$ for 4 hours, cooled at a cooling rate of 15°C/h down to 650°C , and then allowed to cool in the air.

[0040] Test samples were collected after these processes, and subjected to measurements of anneal hardness, and limit compressibility for crack generation by compression test.

1. Measurement of Anneal Hardness

[0041] Hardness of the samples after annealing was measured as Rockwell B-scale hardness using a Rockwell hardness test specified by JIS-Z2245.

2. Measurement of Limit Compressibility for Crack Generation

[0042] Limit compressibility for crack generation was measured by a compression test. Compression test pieces were columns of 15 mm in diameter and 22.5 mm high, and were compressed using a 600-t hydraulic press machine. Ten each test pieces were measured under the individual reduction ratios, and a reduction ratio at which the number of test pieces causing crack generation was reduced to 5 or less (50% or less) was defined as limit compressibility for crack generation.

[0043] Next, the test pieces were hardened by oil quenching after being kept at 1000 to 1100°C for one hour, subjected to sub-zero treatment in liquid nitrogen, and tempered by being kept at 450°C for one hour and then allowed to cool in the air.

[0044] Test samples were collected after these processes, and subjected to measurement of hardening-and-temper hardness, salt spray test, measurement of pitting corrosion potential, and Charpy impact test. Mean crystal grain size of the prior austenitic grain was also measured.

3. Measurement of Hardening-and-Temper Hardness

[0045] Hardness of the samples after hardening and tempering was measured as Rockwell C-scale hardness using a Rockwell hardness test specified by JIS-Z2245.

4. Salt Spray Test

[0046] The test was conducted conforming to a method specified by JIS-Z2371. After the test, the test pieces were evaluated by a four-level rating based on ratios of corroded area, where A: not corroded, B: corroded only in less than 5% area, C: 5-20%, both ends inclusive, and D: over 20%.

5. Measurement of Pitting Corrosion Potential

[0047] Pitting corrosion potential (mV) was measured conforming to a method specified by JIS-G0577.

6. Charpy Impact Test

[0048] Charpy impact test was conducted using 10R notch test pieces (depth of notch=2 mm, R diameter= 10 mm) cut out from the product, conforming to a method specified by JIS-Z2242, so as to obtain Charpy impact values.

7. Measurement of Mean Crystal Grain Size of Prior Austenitic Grain

[0049] Ten fields of view of 0.1 mm² were randomly observed under an optical microscope (ca. 400x magnification), so as to measure crystal grain sizes of the prior austenitic grain in the tempered martensite structure, and thereby a mean value was determined.

[0050] Similar test was conducted as Comparative Example 1, using SUS440C, a representative of currently-available material. The SUS440C (Comparative Example 1) was melted in a high-frequency induction furnace, homogenized under heating, and hot-forged to thereby produce a 24-mm diameter round rod. The rods were annealed by being heated at 850°C for 4 hours, cooled at a cooling rate of 15°C/h down to 650°C, and then allowed to cool in the air. The rods were then hardened by oil quenching after being kept at 1050°C for one hour, subjected to sub-zero treatment in liquid nitrogen, and tempered by being kept at 200°C for one hour and then allowed to cool in the air.

[0051] Similar test was also conducted as Comparative Example 13, using SUS316. The SUS316 (Comparative Example 13) was melted in a high-frequency induction furnace, homogenized under heating, and hot-forged to thereby produce a 24-mm diameter round rod. The rod was then solution-treated by keeping it at 1050°C for one hour and by water quenching. Test samples were collected after these processes, and subjected to the above-described salt spray test and measurement of pitting potential.

【Table 1】

	C	Si	Mn	P	S	Cr	Mo	Co	W	V	Al	Ti	Nb	U	N	B	Mg	Ca	Fe	Zr	Te	Sr	C/N
Inventive Example 1	0.08	0.08	0.08	0.019	0.002	0.11	0.17	0.102		0.14	0.017	0.010		0.003	0.71								0.11
Inventive Example 2	0.03	0.12	0.15	0.016	0.003	0.15	0.22	0.2	1.52	0.61	0.022		0.048	0.004	0.59				0.090				0.05
Inventive Example 3	0.01	0.15	0.49	0.020	0.005	0.58	0.60	0.9		0.02	0.008		0.050	0.003	0.50								0.02
Inventive Example 4	0.14	0.14	0.11	0.021	0.006	0.09	0.13	0.4	0.98	0.10	0.29	0.008	0.048	0.003	0.51		0.003						0.27
Inventive Example 5	0.05	0.18	0.30	0.019	0.004	0.09	0.14	0.5	1.54	0.49	0.007		0.051	0.004	0.52	0.003		0.003					0.10
Inventive Example 6	0.10	0.18	0.18	0.022	0.005	0.20	0.19	0.1	1.99	0.21	0.027		0.051	0.004	0.50		0.003	0.003					0.17
Inventive Example 7	0.01	0.10	0.01	0.022	0.005	0.17	0.22	0.5	1.02	0.32	0.023	0.015		0.003	0.53			0.003			0.02	0.09	0.02
Inventive Example 8	0.03	0.15	0.51	0.018	0.002	0.11	0.17	0.4	2.01	0.14	0.017		0.006	0.003	0.48	0.002	0.003						0.08
Inventive Example 9	0.04	0.10	0.51	0.019	0.007	0.11	0.18	0.1	1.51	0.20	0.022		0.006	0.003	0.44						0.11	0.05	
Inventive Example 10	0.03	0.15	0.15	0.023	0.004	2.47	0.08	0.5	0.98	0.05	0.06	0.008	0.070	0.004	0.42	0.003	0.002	0.003	0.10	0.11	0.02		0.28
Inventive Example 11	0.10	0.18	0.13	0.021	0.001	0.12	2.48	0.4	0.49	0.07	0.31	0.020	0.050	0.004	0.45	0.003		0.003	0.11				0.14
Inventive Example 12	0.13	0.14	0.15	0.020	0.005	0.15	0.15	0.1	1.99	0.02	0.008			0.004	0.55								0.14
Inventive Example 13	0.08	0.14	0.17	0.021	0.007	0.15	0.15	0.1	1.99	0.76	0.008			0.004	0.55								0.14
Comparative Example 1	1.01	0.20	0.40	0.020	0.041	0.10	0.15	0.3	0.02					0.003	0.49	0.003	0.003						0.43
Comparative Example 2	0.21	0.15	0.31	0.018	0.008	0.21	0.21	0.5	0.100	0.03	0.009			0.002	0.59			0.003					0.15
Comparative Example 3	0.09	0.24	0.30	0.017	0.009	0.18	0.16	0.1	0.49	0.02	0.008			0.006	0.34						0.10	0.15	
Comparative Example 4	0.05	0.15	0.51	0.017	0.009	0.18	0.16	0.1	0.01	0.02	0.009			0.006	0.34			0.003	0.12				0.09
Comparative Example 5	0.03	0.14	0.32	0.028	0.008	0.17	0.17	0.6	0.02		0.008			0.006	0.52	0.003			0.11	0.11			0.07
Comparative Example 6	0.04	0.15	0.30	0.017	0.011	0.18	0.16	0.1	0.44	0.02	0.009			0.003	0.53						0.03	0.12	0.10
Comparative Example 7	0.08	0.14	0.12	0.023	0.013	0.18	0.10	0.1	0.52	0.04	0.011	0.051		0.004	0.52						0.11	0.04	
Comparative Example 8	0.02	0.15	0.25	0.021	0.012	0.19	0.20	0.1	0.50	0.04	0.010			0.004	0.54		0.003						0.13
Comparative Example 9	0.08	0.15	0.13	0.018	0.009	0.20	0.21	0.5	0.11	0.03	0.010			0.003	0.53	0.003			0.12				0.08
Comparative Example 10	0.03	0.14	0.31	0.019	0.010	0.21	0.21	0.1	0.49	0.03	0.010			0.003	0.52								0.06
Comparative Example 11	0.03	0.10	0.10	0.021	0.010	0.12	3.60	0.5	0.52	0.02	0.009			0.003	0.51			0.10		0.03	0.11	0.06	
Comparative Example 12	0.08	0.13	0.37	0.019	0.017	0.13	0.14	0.5	0.05	1.32	0.009			0.003	0.50			0.11	0.10				0.16
Comparative Example 13	0.04	0.34	1.12	0.021	0.010	0.21	0.11	0.60	0.12					0.003	0.50								2.00

Results of the measurements are shown in Table 2.

[Table 2]

	Anneal hardness (HRB)	Limit compressibility for crack generation (%)	Hardening and-temper hardness (HRC)	Salt spray test	Pitting potential (mV)	Impact value (J/cm ²)	Mean crystal grain size (μ m)
Inventive Example 1	92	>80	61	A	0.52	15	22
Inventive Example 2	90	>80	59	A	0.66	18	24
Inventive Example 3	92	>80	58	A	0.42	22	31
Inventive Example 4	90	>80	60	A	0.45	15	22
Inventive Example 5	91	>80	59	A	0.49	17	24
Inventive Example 6	91	>80	61	A	0.61	15	26
Inventive Example 7	88	>80	59	A	0.52	15	22
Inventive Example 8	87	>80	58	A	0.58	17	38
Inventive Example 9	90	>80	59	A	0.49	17	21
Inventive Example 10	92	>80	58	A	0.52	18	48
Inventive Example 11	90	>80	58	A	0.41	15	22
Inventive Example 12	91	>80	58	A	0.50	21	23
Inventive Example 13	91	>80	61	A	0.54	16	25
Comparative Example 1	85	45	60	D	-0.11	20	24
Comparative Example 2	89	55	57	D	-0.09	4	47
Comparative Example 3	85	65	60	C	0.28	2	43
Comparative Example 4	82	>80	51	D	0.08	18	48
Comparative Example 5	90	70	60	A	0.45	3	98
Comparative Example 6	88	65	58	C	0.11	3	32
Comparative Example 7	90	60	58	C	0.17	2	23
Comparative Example 8	89	70	62	A	0.39	9	42
Comparative Example 9	90	65	60	D	-0.08	3	45
Comparative Example 10	89	>80	55	A	0.38	15	47
Comparative Example 11	120	>80	61	A	0.35	19	45
Comparative Example 12	88	70	61	C	0.12	3	24
Comparative Example 13	-	-	-	A	0.41	-	-

[0052] It is found from Table 2 that all of the steels of Inventive Examples according to this invention are excellent in the corrosion resistance and cold workability, and are satisfactory in the toughness, while keeping the hardness equivalent to that of the conventional martensitic stainless steel. In other words, the steels of Inventive Examples are far superior to SUS440C (Comparative Example 1) in the cold workability, equivalent or superior to SUS 316 (Comparative Example 13), an austenitic stainless steel, in the corrosion resistance, and equivalent to SUS 440C (Comparative Example 1) in the impact value, while keeping the temper hardness of HRC58 or above.

[0053] Next, the hardening conditions in Example 3 and Example 6 were altered in three ways so as to vary the mean crystal grain sizes, and impact values of the individual samples were measured. Results are shown in Table 3.

[Table 3]

	Mean crystal grain size μ m	Impact value J/cm ²
Inventive Example 3(a)	24	21
Inventive Example 3(b)	31	22
Inventive Example 3(c)	98	13
Inventive Example 6(a)	22	17
Inventive Example 6(b)	26	15
Inventive Example 6(c)	92	10

[0054] It is known from Table 3 that examples (a) and (b), having mean grain sizes of the prior austenitic grain smaller than those in examples (c) were found to have large impact values and therefore have excellent toughness.

[0055] It is to be understood that the embodiments described in the foregoing paragraphs are merely for explanatory purposes, and that this invention can of course be embodied in any types of improvements and modifications based on knowledge of those skilled in the art without departing from the spirit of the invention.

[0056] As is obvious from the above, the martensitic stainless steel of this invention is suitable for use as components

in need of certain levels of, hardness, wear resistance, corrosion resistance, cold workability and toughness, including cylinder liner, shaft, bearing, gear, pin, bolt, screw, roll, turbine blade, mold, die, valve, valve seat, cutting edge and nozzle.

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Claims

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1. A martensitic stainless steel consisting essentially of, in % by mass, C: less than 0.15%, Si: 0.05% or more and less than 0.20%, Mn: 0.05-2.0%, P: 0.03% or less, S: 0.03% or less, Cu: 0.05-3.0%, Ni: 0.05-3.0%, Cr: 13.0-20.0%, Mo: 0.2-4.0%, V: 0.01-1.0%, Al: 0.030% or less, Ti: less than 0.020%, O: 0.020% or less, N: 0.40-0.80%, and the balance of Fe and inevitable impurities.

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2. The martensitic stainless steel as claimed in Claim 1, further containing any one or more of steel components which consist of Co: 0.05-4.0%, W: 0.020-0.20%, Ta: 0.020-0.20%, and Nb: 0.010-0.20%.

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3. The martensitic stainless steel as claimed in Claim 1 or 2, further containing any one or more of steel components which consist of B: 0.001-0.01%, Mg: 0.001-0.01%, Ca: 0.001-0.01%, and Zr: 0.020-0.20%.

4. The martensitic stainless steel as claimed in any one of Claims 1 to 3, further containing any one of or both of steel components which consist of Te: 0.005-0.05% and Se: 0.02-0.20%.

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5. The martensitic stainless steel as claimed in any one of Claims 1 to 4, having a value of W_C/W_N of less than 0.30, where W_C (%) is C content, and W_N (%) is N content.

6. The martensitic stainless steel as claimed in any one of Claims 1 to 5, having a mean crystal grain size of the prior austenitic grain in the tempered martensitic structure of 50 μ m or less.

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Application Number
EP 05 10 1695

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