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(54) Title: CORROSION-RESISTANT, COLD-FORMABLE, MACHINABLE, HIGH STRENGTH, MARTENSITIC STAINLESS STEEL

(57) Abstract: A corrosion resistant, martensitic steel alloy having very good cold formability is described. The alloy has the following weight percent composition. Carbon 0.10-0.40 Manganese 0.01 -2.0 Silicon 2.0 max. Phosphorus 0.2 max. Sulfur 0.030 max. Chromium 10-15 Nickel 0.5 max. Molybdenum 0.75-4.0 Nitrogen 0.02-0.15 Copper 1 .5-4.0 Titanium 0.01 max. Aluminum 0.01 max. Niobium + 0.10 max. Tantalum Vanadium 0.20 max. Zirconium less than 0.001 Calcium less than 0.001 The balance of the alloy is essentially iron. Nickel and copper are balanced in the alloy such that the ratio Ni/Cu is less than 0.2. A second embodiment of the alloy contains at least about 0.005% sulfur, selenium, or a combination thereof to provide good machinability.

**Corrosion-Resistant, Cold-Formable, Machinable,
High Strength, Martensitic Stainless Steel**

DESCRIPTION

Field of the Invention

[Para 1] This invention relates to martensitic stainless steel alloys, and in particular to a martensitic stainless steel alloy having a composition that is balanced to provide a unique combination of corrosion resistance, cold formability, machinability, and high strength.

Background of the Invention

[Para 2] Many steel components of machines and other devices are machined from bar or rod forms of steel alloys. However, the machining process for making such parts, particularly fasteners, results in significant amounts of wasted material. Therefore, parts that were traditionally machined are now being engineered to be fabricated by cold forming techniques such as cold heading.

[Para 3] The shift to the cold forming of steel parts presents a significant problem when in addition to cold formability, corrosion resistance and high strength are required in the steel parts. Hitherto, when high strength and corrosion resistance are needed in a steel part, precipitation hardenable stainless steels have been used. However, the known precipitation hardenable stainless steels do not provide adequate cold formability because of their high annealed hardness which is typically greater than about 100 HRB. The known martensitic

stainless steels, although providing somewhat better cold formability, leave something to be desired with their corrosion resistance. Austenitic and ferritic stainless steels provide better corrosion resistance than martensitic stainless steels, but do not provide the strength needed for many applications. In addition, some cold-formed parts may also require a small amount of machining to achieve their final shape and dimension. The use of free-machining additives can adversely affect other desired properties in cold-formable steel alloys.

[Para 4] In view of the foregoing comments, a need has arisen for a martensitic stainless steel with a combination of high strength, corrosion resistance, and good cold formability that is better than the known cold formable stainless steels. It would also be desirable to have such a steel that provides good machinability without adversely affecting the cold formability of the alloy.

Summary of the Invention

[Para 5] The drawbacks of the known cold formable stainless steels are solved to a significant degree by a martensitic stainless steel alloy having the following Broad, Intermediate, and Preferred alloy compositions.

[Para 6]	<u>Broad</u>	<u>Intermediate</u>	<u>Preferred</u>
C	0.10–0.40	0.15–0.30	0.20–0.25
Mn	0.01–2.0	0.01–1.0	0.01–0.3
Si	2.0 max.	1.0 max.	0.75 max.
S	0.030 max.	0.005–0.020	0.007–0.015
Cr	10–15	11.5–14.3	13.0–13.8
Ni	0.5 max.	0.35 max.	0.25 max.
Mo	0.75–4.0	1.25–3.0	1.75–2.5
Cu	1.5–4.0	1.75–3.5	2.0–3.0
N	0.02–0.15	0.04–0.10	0.05–0.08

The balance of the alloy is essentially iron together with usual impurities. Nickel and copper are balanced such that the ratio Ni/Cu is less than 0.2, preferably not more than about 0.15, and better yet, not more than about 0.10.

[Para 7] The foregoing tabulation is provided as a convenient summary and is not intended to restrict the lower and upper values of the ranges of the individual elements for use in combination with each other, or to restrict the ranges of the elements for use solely in combination with each other. Thus, one or more of the ranges can be used with one or more of the other ranges for the remaining elements. In addition, a minimum or maximum for an element of a broad, intermediate, or preferred composition can be used with the minimum or maximum for the same element in another preferred or intermediate composition. Here and throughout this specification the term "percent" or the symbol "%" means percent by weight unless otherwise specified.

Detailed Description

[Para 8] Carbon is present in this alloy because it benefits the high strength provided by the alloy. Carbon is also beneficial for the good phase balance of the alloy. For those reasons, the alloy contains at least about 0.10%, better yet at least about 0.15%, and preferably at least about 0.20% carbon. Too much carbon results in the excess formation of primary carbides in this alloy which adversely affect the corrosion resistance and the cold formability of the alloy. Therefore, the alloy contains not more than about 0.40% carbon, better yet not more than about 0.30% carbon, and preferably not more than about 0.25% carbon.

[Para 9] Manganese is an element that is beneficial to the phase balance of this alloy because it promotes the formation of austenite and inhibits the formation of ferrite. To that end, the alloy contains up to about 2.0% manganese. In order to obtain the benefit provided by manganese, the alloy contains at least about 0.01% manganese. When sulfur is added to this alloy to benefit its machinability, manganese sulfides can form which adversely affect the corrosion resistance provided by the alloy. Therefore, when more than about 0.005% sulfur is present in the alloy, manganese is restricted to not more than about 1.0% and preferably to not more than about 0.3%. Restricting the formation of manganese sulfides by keeping manganese at such low levels promotes the formation of chromium sulfides which benefit machinability, but do not adversely affect the corrosion resistance provided by this alloy.

[Para 10] A small amount of sulfur can be present in this alloy to benefit the machinability of the alloy when desired or needed. Therefore, when good machinability is needed, the alloy contains at least about 0.005% sulfur and preferably at least about 0.007% sulfur. Too much sulfur adversely affects the hot workability and cold formability of the alloy. Also, as described above, sulfur combines with available manganese to form manganese sulfides which adversely affect the corrosion resistance of the alloy. Therefore, when present, sulfur is limited to not more than about 0.030%, better yet not more than about 0.020% , and preferably not more than about 0.015% . Selenium can be substituted for some or all of the sulfur on a 1:1 weight percent basis because selenium also benefits the machinability of this alloy.

[Para 11] For applications where the best cold formability is needed, sulfur is preferably restricted to not more than 0.010%, better yet to not more than about 0.007%, and for best results, to not more than about 0.005%.

[Para 12] Chromium is present in this alloy to benefit the corrosion resistance provided by the alloy. Accordingly, the alloy contains at least about 10% chromium, better yet at least about 11.5% chromium, and preferably at least about 13.0% chromium. Too much chromium results in the formation of ferrite in the alloy in an amount that adversely affects the corrosion resistance and hot workability of the alloy. Therefore, chromium is restricted to not more than about 15% chromium, better yet to not more than about 14.3% chromium, and preferably to not more than about 13.8% chromium in this alloy.

[Para 13] This alloy contains at least about 0.75% molybdenum because it benefits the corrosion resistance of the alloy, particularly in chloride-containing environments. Preferably the alloy contains at least about 1.25% molybdenum and preferably at least about 1.75% molybdenum for that purpose. Like chromium, molybdenum promotes the formation of ferrite in the alloy and too much ferrite adversely affects the general corrosion resistance and the hot workability of the alloy. Therefore, the alloy contains not more than about 4.0% molybdenum, better yet not more than about 3.0% molybdenum, and preferably not more than about 2.5% molybdenum.

[Para 14] Copper is present in this alloy to benefit the cold formability of the alloy. Copper also helps provide an acceptable phase balance in the alloy and contributes to the machinability of the alloy when sulfur is present. The advantages provided by copper are realized when the alloy contains at least about 1.5%. Preferably the alloy contains at least about 1.75% copper and better yet, at least about 2.0% copper. Too much copper can result in hot shortness in the alloy which adversely affects its hot workability. Therefore, copper is restricted to not more than about 4.0%, better yet to not more than about 3.5%, and preferably to not more than about 3.0% in this alloy.

[Para 15] Up to about 0.5% nickel can be present in this alloy to benefit the phase balance of the alloy. Preferably nickel is restricted to not more than about 0.35% and better yet to not more than about 0.25% because nickel increases the annealed strength of the alloy which adversely affects its cold formability. In order to provide a good

combination of low annealed hardness, which is essential for good cold formability, and proper phase balance, which is beneficial for corrosion resistance and hot workability, nickel and copper are balanced in this alloy such that the ratio of nickel to copper (Ni/Cu) is preferably less than 0.2, better yet, not more than about 0.15, and preferably, not more than about 0.10.

[Para 16] This alloy contains at least about 0.02% nitrogen, better yet at least about 0.04% nitrogen, and preferably at least about 0.05% nitrogen because nitrogen contributes to the high strength provided by the alloy. Nitrogen also benefits the phase balance and the corrosion resistance provided by this alloy. Too much nitrogen in the alloy results in blowy ingots and adversely affects the cold formability and hot workability of the alloy. Therefore, nitrogen is restricted to not more than about 0.15%, better yet to not more than about 0.10% nitrogen, and preferably to not more than about 0.08% nitrogen.

[Para 17] Silicon can be present in this alloy in an amount that is effective to deoxidize the alloy during melting. However, too much silicon promotes the formation of excess ferrite in the alloy which adversely affects the corrosion resistance and the hot workability of the alloy. Therefore, the alloy may contain up to about 2.0% silicon for use as a deoxidizer. However, silicon is preferably limited to not more than about 1.0%, and better yet to not more than about 0.75% in this alloy.

[Para 18] The balance of the alloy is iron except for the usual impurities and additives found in similar grades of martensitic stainless steel alloys intended for the same or similar use or service. In this

regard the alloy contains up to about 0.2% phosphorus, better yet up to about 0.1%, and preferably not more than about 0.05% phosphorus. Also, the alloy contains up to about 0.20%, but preferably not more than about 0.10% vanadium. Up to about 0.10%, preferably not more than about 0.01% of niobium and tantalum combined can be present in this alloy. Further, the alloy contains less than about 0.01% each of titanium, aluminum, and zirconium. The alloy may contain up to about 0.003% boron. Small, trace amounts, typically less than 0.001% each of calcium and zirconium may also be present in the alloy.

[Para 19] No special techniques are required for melting and refining this alloy. Arc melting followed by argon–oxygen decarburization (AOD) can be used. However, vacuum induction melting (VIM) is preferred when better alloy cleanliness is needed. This alloy is suitable for use in continuous casting processes and, when desired, can be made by powder metallurgy techniques. After being cast, an ingot of this alloy is preferably furnace cooled at a rate that is slow enough to prevent ingot cracking.

[Para 20] An ingot of the alloy according to the present invention is preferably hot worked from a furnace temperature of about 2000–2300°F (1093–1260°C), preferably about 2100–2250°F (1149–1232°C), with reheating as necessary after intermediate reductions. In large section sizes, the alloy is hot worked to size in which it can be hot rolled to a cross-sectional dimension in which it can be cold drawn. Intermediate anneals are carried out at about 1650–1700°F (900–927°C) for about 4 hours followed by a furnace cool preferably at about 30F°

per hour to 1200°F (649°C). The alloy is then cooled in air to room temperature.

[Para 21] The alloy is preferably hot rolled to a cross-sectional dimension that is suitable for cold drawing. Hot rolling is preferably conducted from a starting temperature of about 2150–2250°F (1177–1232°C). After hot rolling, the alloy is annealed at about 1450–1550°F (788–843°C) for about 2 hours. Preferably, the alloy is furnace cooled at about 20F° per hour from the annealing temperature down to about 1200°F (649°C) and then air cooled to room temperature.

[Para 22] The alloy is cold drawn to final dimension in one or more passes depending on the amount of reduction needed. Prior to cold drawing, the alloy can be shaved, polished, and precoated. After cold drawing to the desired size, the wire is cleaned to remove residual drawing compound and any other surface contamination. The alloy wire is then annealed with the same or similar cycle described above. The alloy wire can be coated with a surface layer of copper or other coating to prevent galling during cold forming operations.

[Para 23] The alloy is cold formed, as by cold heading, into a desired shape and dimension. Cold formed products include fasteners such as screws, bolts, and nuts. The final product form is hardened by austenitizing it at about 1750–2000°F (954–1093°C), preferably at least about 1900°F (1038°C) for about 1 hour, followed by quenching. The alloy is preferably heated at the austenitizing temperature in vacuum for about 1 hour and quenched by rapid gas cooling to protect against

thermal scaling (oxidation). The alloy can be tempered at about 300–900°F (149–482°C) for about 2 hours and then cooled in air.

[Para 24] The alloy of the present invention can be formed into a variety of shapes for a variety of uses. However, the alloy is preferably formed into rod or wire which can be cold formed into useful articles as described above.

[Para 25] It will be recognized by those skilled in the art that changes or modifications may be made to the above-described embodiments without departing from the broad inventive concepts of the invention. It is understood, therefore, that the invention is not limited to the particular embodiments that are described, but is intended to cover all modifications and changes within the scope and spirit of the invention as described above and set forth in the appended claims.

What is claimed is:

[Claim 1] A corrosion resistant, martensitic steel alloy consisting essentially, in weight percent, about

Carbon	0.10–0.40
Manganese	0.01–2.0
Silicon	2.0 max
Phosphorus	0.2 max
Sulfur	0.030 max
Chromium	10–15
Nickel	0.5 max
Molybdenum	0.75–4.0
Nitrogen	0.02–0.15
Copper	1.5–4.0
Titanium	0.01 max
Aluminum	0.01 max
Niobium+Tantalum	0.10 max
Vanadium	0.20 max
Zirconium	less than 0.001
Calcium	less than 0.001

and the balance is essentially iron, wherein Ni/Cu is less than 0.2.

[Claim 2] A corrosion resistant, martensitic steel alloy as set forth in Claim 1 containing not more than about 14.3% chromium.

[Claim 3] A corrosion resistant, martensitic steel alloy as set forth in Claim 1 containing at least about 1.75% copper.

[Claim 4] A corrosion resistant, martensitic steel alloy as set forth in Claim 1 containing not more than about 3.0% molybdenum.

[Claim 5] A corrosion resistant, martensitic steel alloy as set forth in Claim 1 containing at least about 0.04% nitrogen.

[Claim 6] A corrosion resistant, martensitic steel alloy as set forth in Claim 2 containing at least about 11.5% chromium.

[Claim 7] A corrosion resistant, martensitic steel alloy as set forth in Claim 1 containing not more than about 0.35% nickel.

[Claim 8] A corrosion resistant, martensitic steel alloy as set forth in Claim 7 containing at least about 2.0% copper.

[Claim 9] A corrosion resistant, martensitic steel alloy as set forth in Claim 8 containing not more than about 0.25% nickel.

[Claim 10] A corrosion resistant, martensitic steel alloy as set forth in Claim 1 containing at least about 0.005% of sulfur, selenium, or a combination thereof.

[Claim 11] A corrosion resistant, martensitic steel alloy consisting essentially, in weight percent, about

Carbon	0.15–0.30
Manganese	0.01–1.0
Silicon	1.0 max
Phosphorus	0.1 max
Sulfur	0.020 max
Chromium	11.5–14.3
Nickel	0.35 max
Molybdenum	1.25–3.0
Nitrogen	0.04–0.10
Copper	1.75–3.5
Titanium	0.01 max
Aluminum	0.01 max
Niobium + Tantalum	0.10 max
Vanadium	0.20 max
Zirconium	less than 0.001
Calcium	less than 0.001

and the balance is essentially iron, wherein Ni/Cu is not more than about 0.15.

[Claim 12] A corrosion resistant, martensitic steel alloy as set forth in Claim 11 containing not more than about 13.8% chromium.

[Claim 13] A corrosion resistant, martensitic steel alloy as set forth in Claim 11 containing at least about 2.0% copper.

[Claim 14] A corrosion resistant, martensitic steel alloy as set forth in Claim 11 containing not more than about 2.5% molybdenum.

[Claim 15] A corrosion resistant, martensitic steel alloy as set forth in Claim 11 containing at least about 0.05% nitrogen.

[Claim 16] A corrosion resistant, martensitic steel alloy as set forth in Claim 13 containing at least about 13.0% chromium.

[Claim 17] A corrosion resistant, martensitic steel alloy as set forth in Claim 11 containing not more than about 0.25% nickel.

[Claim 18] A corrosion resistant, martensitic steel alloy as set forth in Claim 11 containing at least about 0.005% sulfur, selenium, or a combination thereof.

[Claim 19] A corrosion resistant, martensitic steel alloy consisting essentially, in weight percent, about

Carbon	0.20–0.25
Manganese	0.01–0.3
Silicon	0.75 max
Phosphorus	0.05 max
Sulfur	0.015 max
Chromium	13.0–13.8
Nickel	0.25 max
Molybdenum	1.75–2.5
Nitrogen	0.05–0.08

Copper	2.0-3.0
Titanium	0.01 max
Aluminum	0.01 max
Niobium + Tantalum	0.10 max
Vanadium	0.20 max
Zirconium	less than 0.001
Calcium	less than 0.001

and the balance is essentially iron, wherein Ni/Cu is not more than about 0.10.

[Claim 20] A corrosion resistant, martensitic steel alloy as set forth in Claim 20 which contains at least about 0.007% sulfur, selenium, or a combination thereof.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER INV. C22C38/00		
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) C22C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
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"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	
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Date of the actual completion of the international search <p style="text-align: center; font-weight: bold;">13 November 2006</p>	Date of mailing of the international search report <p style="text-align: center; font-weight: bold;">27/11/2006</p>	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer <p style="text-align: center; font-weight: bold;">Gavriliu, Alexandru</p>	

INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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