

[54] **FERRITIC STAINLESS STEEL**

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[22] Filed: **Nov. 9, 1973**

[21] Appl. No.: **414,257**

[52] **U.S. Cl.**..... **148/37**; 75/126 C; 75/126 J;
75/126 L; 75/126 M; 75/128 P; 75/128 N;
75/128 W

[51] **Int. Cl.**²..... **C22C 38/22**; **C22C 38/60**

[58] **Field of Search**..... 75/126 C, 126 L, 128 P,
75/126 J, 128 N; 148/37

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[57]

ABSTRACT

Ferritic, preferably free-machining stainless steel containing 0.08% max. carbon, 0.06–0.20% nitrogen, 2.5% max. manganese, 0.50% max. sulfur (and/or selenium), 17.5–19.5% chromium, 1.5–2.5% molybdenum with the balance iron plus optional elements and incidental impurities, characterized by a unique combination of corrosion resistance and impact toughness, plus free machinability in its preferred form.

12 Claims, No Drawings

FERRITIC STAINLESS STEEL

BACKGROUND OF THE INVENTION

This invention relates to ferritic stainless steel and, more particularly, to a ferritic stainless steel characterized by a unique combination of free machinability, corrosion resistance and toughness, the latter as measured by the V-notch Charpy impact test.

Chromium steels modified with molybdenum and sulfur have hitherto been known. One such steel, here designated Alloy A for convenience, as published, contained, nominally, 18% chromium, 2% molybdenum and 0.20% sulfur. The remainder of Alloy A was 0.15% carbon, 0.30% silicon, 0.80% manganese, a maximum of 0.040% phosphorus, and the balance iron plus incidental impurities. Another such composition, Alloy B, contained a maximum of 0.03% carbon, 17.50–19.50% chromium, a maximum of 1.50% manganese, a maximum of 1.0% silicon, a maximum of 0.04% phosphorus, 0.30–0.35% sulfur, 1.50–2.50% molybdenum, and the balance iron plus incidental impurities. Depending upon how such steels were produced they might contain up to about 0.040% nitrogen as a residual or incidental impurity even though none would be intentionally added. Alloys A and B are essentially the same and are commonly designated as 18 Cr-2 Mo stainless steel with additives for machinability.

We have found that such 18% Cr-2% Mo stainless steels leave much to be desired when, in particular, room temperature toughness or impact strength as measured by the V-notch Charpy impact test and where lower impact transition temperature are wanted in such parts as construction fasteners for the building trade, valves for handling chemicals, machine shafts, food-processing equipment, and generally any screw machine parts, especially where any such parts would be exposed in service to subfreezing temperatures.

SUMMARY OF THE INVENTION

It is, therefore, a principal object of this invention to provide an 18% Cr-2% Mo stainless steel which has improved toughness and good corrosion resistance, and in its preferred form also has good machinability.

In accordance with our invention a ferritic stainless steel is provided which in its annealed condition contains about 5–50 percent, preferably about 5 to 20 percent, highly tempered not fully decomposed martensite, from which such parts as construction fasteners, valves for handling chemicals, machine shafts, food-processing equipment, screw machine parts and others can be made having good corrosion resistance and toughness and which preferably also have good machinability. By way of summary our composition in its broad and preferred ranges contains in weight percent

	Broad	Preferred
C	0.08 Max.	0.06 Max.
N	0.06–0.20	0.08–0.16
Mn	2.5 Max.	1.7–2.2
S	0.50 Max.	0.25–0.4
Cr	17.5–19.5	18.0–19.0
Mo	1.5–2.5	1.7–2.2

and the balance iron plus incidental impurities.

DESCRIPTION OF PREFERRED EMBODIMENTS

By tabulating the ranges of our composition to provide a convenient summary, it is not intended to restrict our alloy to the stated broad and preferred combinations thereof, it being intended to include within the scope of this invention as defined by the claims, elements equivalent to those stated and combinations of one or more of the broad ranges with one or more of the preferred ranges.

As incidental impurities several hundredths percent of one or more of such elements as phosphorus, copper and nickel may be included, but, no more than 0.04% phosphorus, 0.5% copper or 0.5% nickel. Strong stabilizing elements such as titanium and columbium are not desirable additions to our alloy because they tie up nitrogen. Selenium can be substituted for all or part of the sulfur on a 1 for 1 basis, and tungsten can be substituted for all or part of the molybdenum in the ratio of about 1.5 to 1.

Silicon is not an essential alloying addition to our alloy, but it is preferably used in the customary way for deoxidation. With less than 0.2% silicon, deoxidation is not usually carried far enough, and above about 0.6%, the silicon has the objectionable effect of forming undesired silicates and tends to raise the impact transition temperature of the composition. Thus, while up to about 1% silicon is tolerable, 0.2–0.6 percent best favors desired deoxidation and, by its effect on microstructure, optimum mechanical properties.

Both nickel and copper are not desired in our composition. Though each is tolerable in amounts up to about 0.5 percent, neither should be present in excess of that amount because of their adverse effect upon the resistance to cracking while under stress when exposed to such media as hot chlorides.

Carbon, in addition to being a strong austenite former, results in the formation of undesired grain boundary constituents and is, therefore, limited to no more than about 0.08 percent, preferably no more than about 0.06 percent. When carbon is present in an amount of no less than about 0.02 percent, the minimum amount of nitrogen required in accordance with the present invention need not be adjusted. However, if the carbon content is reduced below about 0.01 percent, the minimum of nitrogen required should be adjusted upward from 0.06 percent by an equal amount.

At least about 0.06% nitrogen is required in our composition and preferably at least 0.08 percent to provide the toughness and reduced impact transition temperature of the composition. By impact transition temperature is meant the lowest temperature at which the impact specimens show predominantly ductile fracture. Up to about 0.20% nitrogen can be included to offset the maximum permissible amounts of the ferrite-forming elements which include chromium and molybdenum and thereby ensure the required minimum amount of martensite. Preferably 0.08–0.16% or, better yet, 0.08–0.14% nitrogen is present with the larger amounts of nitrogen being balanced with the larger amounts of chromium and molybdenum so that at least the small but definite amount of martensite required, about 5–20 percent, is present when, following hot working, the material is to be annealed. However, it is to be noted that when the maximum amounts of carbon and nitrogen in the broad range are used together as much as about 50% may be martensite following hot working.

Manganese and sulfur (and/or selenium) work together and are added to provide the best free machinability in our composition. To this end, a minimum of about 1.5 percent, preferably at least 1.60 percent, is included to provide with the sulfur the best free-machining properties characteristic of our alloy. Manganese in excess of about 2.5 percent does not contribute significantly to free machinability. Preferably, manganese is limited to no more than about 2.2 percent, and best results are provided with about 1.7–2.2% manganese. Below about 0.15 percent, sulfur is not present in sufficient quantity to prevent the formation of long stringy chips which tend to clog the machine and cause it to wear excessively. Therefore, at least 0.15% sulfur and preferably about 0.25–0.40 percent is included for best results. Above about 0.50 percent, not enough improvement is obtained to offset the accompanying disadvantages to warrant further additions of sulfur.

Chromium and molybdenum primarily contribute to the corrosion resistance of our composition and, as ferrite formers, work to insure an essentially single phase ferritic microstructure in our composition in its annealed and quenched condition. To this end, both chromium and molybdenum are limited to the critical ranges indicated. To provide the desired resistance to corrosion in oxidizing media, at least about 17.5% chromium is required. Above about 19.5% chromium, insufficient improvement in corrosion resistance is obtained, and larger additions of chromium are not warranted. Beyond that, increasing chromium above 19.5 percent objectionably affects the impact transition temperature by causing it to rise, and also increases the tendency toward 885°F embrittlement. Best results are obtained with about 18.0 to 19.0% chromium.

Molybdenum enhances corrosion resistance and crevice corrosion resistance in reducing or pitting media, e.g., sulfuric acid, dilute ferric chloride, or salt water. It also tends to raise the impact transition temperature. For these reasons, molybdenum in an amount ranging from about 1.5–2.5 percent is used and for best results about 1.7–2.2% molybdenum should be used.

Our alloy is prepared and shaped using customary metallurgical practices suitable for the making and shaping of ferritic stainless steel containing about 18% chromium. Hot working is carried out at about 1,800° to 2,200°F, preferably between about 1,900° to 2,100°F, the higher hot working temperature, e.g., from about 1,950° to 2,200°F being best suited for initially breaking down the composition containing the larger amounts of nitrogen.

Following hot working, the shapes are cooled in air, and some martensite is formed, but at a temperature (M_s) below 1,000°F with the result that the intermetallic phases, e.g., nitrides and carbides are not formed, the carbon and nitrogen being retained in solution in the martensite (body centered tetragonal) formed from the austenite which had been present at the hot work temperature. The material is heat treated by annealing at about 1,200° to 1,600°F, preferably between about 1,300° to 1,500°F, and better yet between about 1,400° to 1,500°F. Depending upon the thickness of the section, the parts are held at the annealing temperature for up to about 4 hours, shorter times of 1 to 2 hours or less being preferred. Following annealing and quenching, the martensite is seen as highly tempered, not fully decomposed martensite. By highly tempered, not fully, that is partially, decomposed martensite is meant the ferritic structure obtained by quenching from the an-

nealing temperature and in which no trace of the acicular structure characteristic of tempered martensite can be found, but the relatively fine nitrides remain to identify the prior location of tempered martensite. In practice, an excessively high annealing temperature leads to undesired agglomeration of the nitrides and other intermetallic phases that may be present.

Best results are obtained when the quenching following annealing is carried out more rapidly than can be done in air except for relatively small cross-sections or for parts containing the larger amounts of nitrogen with or without the larger amounts of carbon contemplated herein. In any event, whether in air or in faster quenching media such as oil or water, quenching should be sufficiently rapid to prevent or minimize precipitation of undesired phases, e.g., a plate-like nitride, in the grain boundaries.

Examples 1–6 prepared as small experimental heats are illustrative of our invention and had the composition indicated in Table I with the balance iron and incidental impurities which included small amounts of but less than 0.005% phosphorus, less than 0.2% nickel, and less than 0.2% copper.

TABLE I

Ex. No.	C	Mn	Si	S	Cr	Mo	N
1	.011	1.83	.40	.35	18.41	2.01	.092
2	.038	1.80	.40	.35	18.44	2.01	.092
3	.057	1.80	.37	.34	18.43	2.02	.085
4	.012	1.88	.41	.35	18.59	2.03	.139
5	.041	1.88	.41	.35	18.60	2.02	.139
6	.056	1.83	.36	.35	18.45	2.01	.130

Examples 1–6 were melted under an argon atmosphere to facilitate controlling the nitrogen content for experimental purposes. Examples 1 to 2 were poured and cast as ingots from the same heat, but with added carbon in Example 2. Similarly, Examples 3 and 6 and Examples 4 and 5 were formed from split heats, the variation between Examples 3 and 6 being in the nitrogen content and between Examples 4 and 5 being in the carbon content.

The thus formed 2% inch ingots were forged from 2,000°F to 1½ inch square bars, reheating being carried out at 1½ inch square. After hot working, annealing for ½ hour at 1,500°F followed by water quenching was carried out before the 1½ inch square bars were shaped into test specimens. Standard tensile test specimens having a 0.252 inch gage diameter and a 1-inch gage length were formed as well as standard V-notch Charpy impact test specimens. The results of room temperature (72°F) mechanical property tests are given in Tables II and III. In Table II, the 0.2 percent yield strength in thousands of pounds per square inch is given under 0.2YS (KSI), the ultimate tensile strength is given under UTS (KSI), and the percent elongation and percent reduction in area are given under % EL and % RA respectively. The data tabulated is, in each instance, an average of two tests.

TABLE II

Ex. No.	.2YS (KSI)	UTS (KSI)	% EL	% RA
1	55.5	77	27	51
2	58.9	81.5	27.5	50.5
3	61	84.5	27.5	56
4	60.5	84	25.5	48
5	61.5	85	27	53
6	62.5	88	26	49

In Table III are set forth hardness (Rockwell R_b) and V-notch Charpy (VNC) impact strength data, each being an average of two tests.

TABLE III

Ex. No.	HARDNESS (R_b)	VNC IMPACT STRENGTH (FT. LBS.)
1	88	11.5
2	89.5	11.5
3	90.5	17
4	90.5	19.5
5	89	24.5
6	92	16

The machinability of the specimens of each of the examples as annealed and quenched was determined as the average depth of penetration in inches into the specimens under carefully controlled conditions. While there is no generally accepted standard for measuring machinability, the free machining values were obtained by measuring the depth of penetration into the specimens by a quarter-inch drill in a time interval of 15 seconds with the drill rotating at or very close to 670 r.p.m. under constant torque. Before the start of each drilling operation, the drill mounted in a conventional drill press was brought against the surface of the specimen where it was maintained by a constant weight of 100 pounds. The results of the tests are recorded in Table IV under drill penetration (DRILL PENE.) and each is an average of two sets of 3 hole tests. The carbon and nitrogen contents are included for easy reference.

TABLE IV

DRILL MACHINABILITY DATA			
Ex. No.	% C	% N	DRILL PENE. (INCHES)
1	.011	.092	.456
2	.038	"	.432
3	.057	.085	.482
4	.012	.139	.457
5	.041	"	.453
6	.056	.130	.472

To demonstrate the effect of nitrogen on the impact transition temperature, standard V-notch Charpy test specimens were prepared from Examples 2 and 4 and tested at 32°, 72°, 150°, and 200°F. In addition, standard V-notch Charpy specimens were prepared for comparison of an Alloy C having the following composition:

Carbon	w/o
Manganese	0.037
Silicon	1.92
Sulfur	0.43
Chromium	0.36
Molybdenum	18.00
Nitrogen	2.05
	0.039

and the balance iron plus incidental impurities. These and the test specimens yet to be referred to herein prepared from Alloy C were made from bars hot worked, annealed and quenched as was described in connection with Examples 1-6. Except in the case of

Example 2 where the transition temperature was determined by interpolation, the determination of the transition temperature was based on the measured impact strengths and the appearance of the fractures at the temperature indicated, the impact transition temperature being based on the lowest temperature to give a predominately ductile fracture appearance. The transition temperature for Example 2 was found to be at about 110°F, for Example 4 it was found to be about room temperature (72°F), and for Alloy C it was found to be at about 150°F.

It should also be noted that Alloy C tensile specimens when prepared and tested as was described in connection with Examples 1-6 gave a 0.2 percent yield strength of 53 KSI, an ultimate tensile strength of 74.5 KSI, an elongation of 29.5 percent and a reduction in area of 57 percent. The annealed and quenched hardness was R_b90 and the V-notch Charpy impact strength was 7 ft. lbs., all being averages of two tests.

Corrosion rates of duplicate test coupons formed from the forged and heat treated bars prepared as was previously described herein of each of Examples 1-6 and Alloy C and immersed for five 48-hour periods each in boiling 65% by weight nitric acid were found to have lost metal at the calculated average rate in mils per year (MPY) as indicated in Table V.

TABLE V

Ex. No.	% C	% N	MPY
1	.011	.092	31
2	.038	.092	45.5
3	.057	.085	49.5
4	.012	.139	39
5	.041	.139	76
6	.056	.130	67
Alloy C	.037	.039	31.5

From the data in Table V, it is apparent that the addition of nitrogen in accordance with the present invention does not adversely affect the corrosion resistance of our composition in such media as 65 percent by weight boiling nitric acid.

Further important advantages of our composition reside in that its corrosion resistance is at least as good as that of A.I.S.I. Type 303 as measured by such tests as salt spray corrosion resistance, resistance to nitric acid, and other media. The machinability of our composition is superior to that of Type 303 both when measured by the drill test and also when measured on a lathe.

When the unique combination of free machinability with good impact toughness and corrosion resistance of our alloy is not required, the elements manganese and sulfur become optional and need not be present in amounts any greater than usual depending upon the manner in which the steel is made. In the case of steel manufactured in air under a slag, manganese can be as low as 0.2 percent although even smaller amounts may be present when vacuum melting practices are used. And sulfur would not exceed about 0.03 percent.

The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof,

but it is recognized that various modifications are possible within the scope of the invention claimed.

We claim:

1. A ferritic stainless steel consisting essentially in weight percent of about

Carbon	0.08 Max.
Manganese	2.5 Max.
Silicon	1 Max.
Phosphorus	0.04 Max.
Sulfur	0.50 Max.
Chromium	17.5-19.5
Molybdenum	1.5-2.5
Nickel	0.5 Max.
Copper	0.5 Max.
Nitrogen	0.06-0.20

the balance being essentially iron and incidental impurities, in which selenium can be substituted for all or part of the sulfur on a 1 for 1 basis and tungsten can be substituted for all or part of the molybdenum in the ratio of about 1.5% tungsten to 1% molybdenum, and said stainless steel when annealed at about 1,200°-1,600°F and quenched after having been hot worked from about 1,800°-2,200°F contains about 5 to 50% highly tempered partially decomposed martensite free of acicular structure.

2. Ferritic stainless steel as set forth in claim 1 containing 0.25-0.4% sulfur.

3. Free-machining ferritic stainless steel as set forth in claim 2 containing about 0.06% maximum carbon, about 1.7-2.2% manganese and about 0.08-0.16% nitrogen.

4. Free-machining ferritic stainless steel as set forth in claim 3 containing about 18.0-19.0% chromium.

5. Free-machining ferritic stainless steel as set forth in claim 3 containing about 1.7-2.2% molybdenum.

6. Free-machining ferritic stainless steel as set forth in claim 4 containing about 1.7-2.2% molybdenum.

7. Free-machining ferritic stainless steel as set forth in claim 6 containing about 0.08-0.14% nitrogen.

8. Free-machining ferritic stainless steel as set forth in claim 7 containing about 5 to 20 percent highly tempered partially decomposed martensite.

9. Free-machining ferritic stainless steel as set forth in claim 3 containing about 1.8% manganese, about 0.4% silicon, 0.35% sulfur, about 18.4 to 18.6% chromium, about 2% molybdenum, about 0.085-0.14% nitrogen, and about 5 to 20 percent highly tempered partially decomposed martensite.

10. Free-machining ferritic stainless steel as set forth in claim 9 containing about 0.130-0.140% nitrogen.

11. A stainless steel article formed from a ferritic stainless steel having the composition set forth in claim 1 hot worked from about 1,800°-2,200°F, annealed at about 1,200°-1,600°F and quenched so as to contain about 5 percent to 50 percent highly tempered, partially decomposed martensite free of acicular structure.

12. The stainless steel article set forth in claim 11 formed from a ferritic stainless steel containing 0.25-0.4% sulfur, about 1.7-2.2% manganese, about 0.08-0.16% nitrogen, about 18.0-19.0% chromium, about 1.7-2.2% molybdenum, a maximum of about 0.06% carbon, and about 5 to 20 percent highly tempered, partially decomposed martensite free of acicular structure.

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