Jan. 29, 1963 E. J. DULIS ETAL 3,075,839

NICKEL-FREE AUSTENITIC CORROSION RESISTANT STEELS

Filed Jan. 5, 1960 2 Sheets-Sheet 1

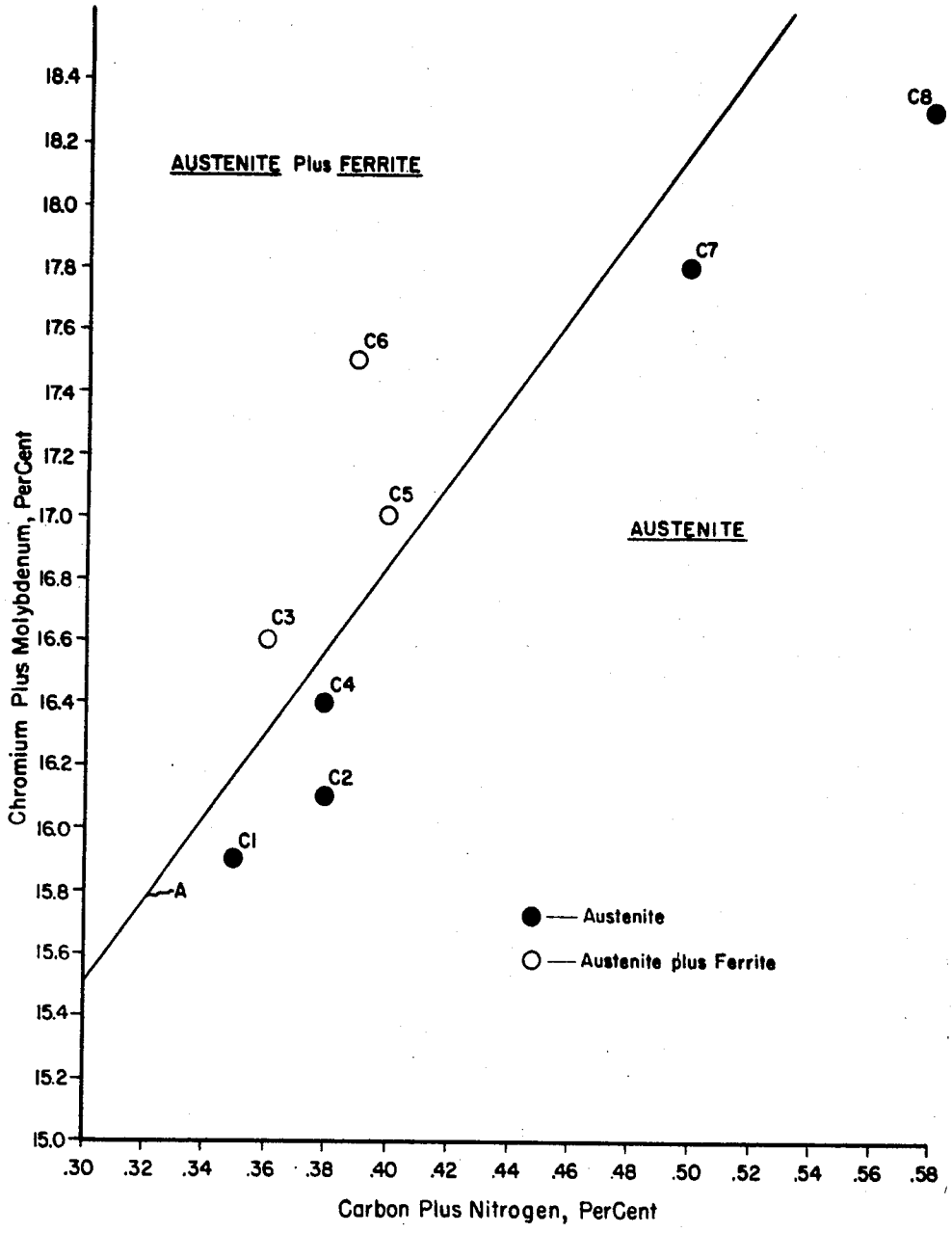


Fig. 1

Jan. 29, 1963 E. J. DULIS ETAL 3,075,839
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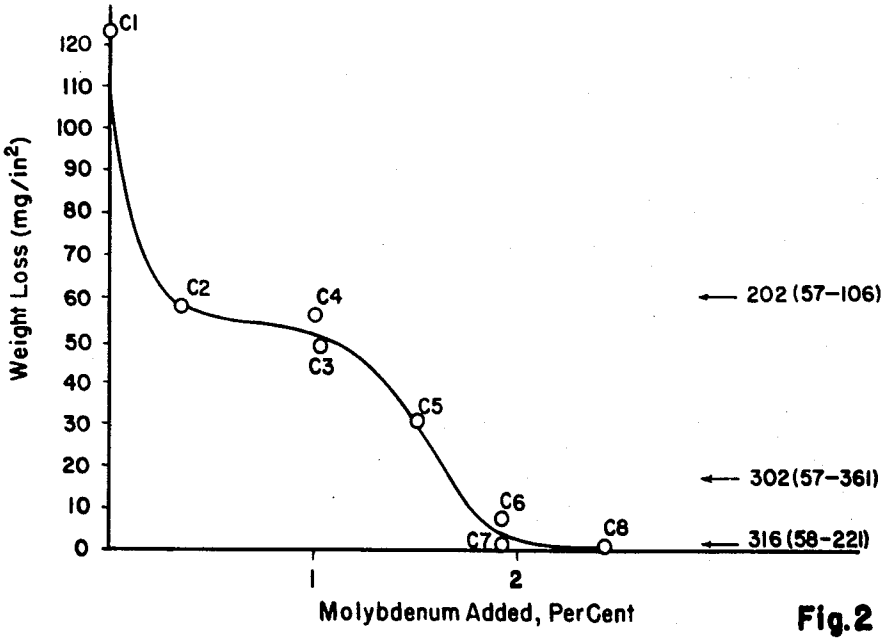


Fig. 2

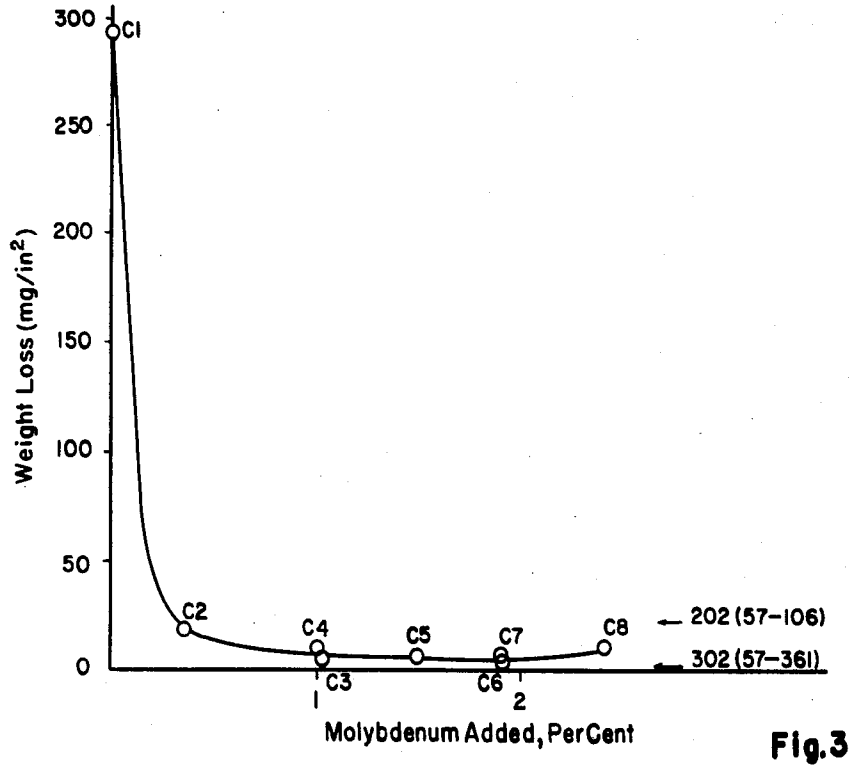


Fig. 3

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NICKEL-FREE AUSTENITIC CORROSION RESISTANT STEELS

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This invention relates to nickel-free austenitic stainless steels and more particularly to a highly corrosion resistant steel of this type which contains as essential elements, in addition to iron, only chromium, manganese, molybdenum, nitrogen and carbon, and preferably also copper and silicon, each within critically restricted ranges and in balanced proportions so as to impart a wholly austenitic structure together with good mechanical properties and excellent resistance to corrosion.

Nickel has often been in scarce supply, particularly during times of national emergency and, therefore, efforts have been made in the past to develop stainless steels wherein the nickel content is substantially reduced or eliminated. Thus, A.I.S.I. type 201 and 202 steels have been developed having reduced, but appreciable, nickel contents and possessing, respectively, the following typical analyses: 6.5 Mn–4.5 Ni–17 Cr–0.25 N max.–0.15 C max. and 9 Mn–5 Ni–18 Cr–0.25 N max.–0.15 C max.–1 Si max.

There have also been developed substantially completely nickel-free steels such as those disclosed in U.S. Patent No. 2,862,812 to E. J. Dulis and P. Payson. These steels constitute a marked improvement over prior art attempts to produce nickel-free steels and, with respect to their mechanical properties, are comparable to existing corrosion resistant steels such as A.I.S.I. types 302, 304, and 316, containing relatively large amounts of nickel. Although the steels in accordance with the aforesaid patent have good corrosion resistance as compared to that of plain carbon steel, their corrosion resistance is not as great as that of the austenitic chromium-nickel alloy steels.

We have now found that the corrosion resistance of austenitic nickel-free stainless steels of the type disclosed in U.S. Patent No. 2,862,812 can be improved in a marked fashion by the addition thereto of critical amounts of molybdenum and by balancing the composition of such steels to maintain a fully austenitic structure. Thus, we have found that when molybdenum is substituted, in a critical range, for a portion of the chromium of such steels, the corrosion resistance of the steels is unexpectedly increased to such an extent that the steels of the invention are much superior, in respect to corrosion resistance to austenitic chromium-nickel steels such as A.I.S.I. type 202 and possess a corrosion resistance rivaling or exceeding that of other steels of that type having higher nickel contents such as A.I.S.I. types 302, 304, and 316.

The steels of this invention retain all of the desirable mechanical properties of the nickel-free steels containing no molybdenum, that is, they can be annealed at about 1950–2050° F. and, as annealed, have yield strengths of about 50,000 p.s.i., tensile strengths of about 145,000 p.s.i. and tensile elognations of about 45%. When subjected to 30% cold reduction, the steels may have yield strengths of about 140,000 p.s.i., tensile strengths of about 145,000 p.s.i. and tensile elongations of about 15%. Accordingly, the steels of the invention possess excellent forming properties by reason of their low yield strengths combined with high ductilities as annealed, and by reason of their retention of high ductilities after as much as 30% cold reduction.

Moreover, the steels of this invention by reason of their enhanced corrosion resistance, lend themselves to a variety of applications wherein resistance to atmospheric and chemical corrosion is a prerequisite. For example, the steels of this invention are admirably suited for the fabrication of processing apparatus for use in the chemical industry, the pulp and paper industry, etc., as well as for use in exterior structural and decorative applications. The steels of the invention may be welded by ordinary welding techniques without undue loss of mechanical properties or corrosion resistance in the vicinity of the weld.

The broad and preferred ranges of analyses of our steels are:

Element	Composition, percent	
	Broad	Preferred
Chromium	14–18	15.5–16.5.
Molybdenum	0.3–3	0.35–2.5.
Manganese	11–14	11.5–13.5.
Carbon	Up to 0.15	0.05–0.15.
Nitrogen	0.15–0.55	0.25–0.40.
Carbon plus nitrogen	0.075 [(Cr+Mo)= 15.5]+0.3.	0.075 [(Cr+Mo)= 15.5]+0.3.
Copper	Up to 2	0.5–1.5.
Silicon	Up to 3	0.15–1.5.
Iron	Balance	Balance.

By balancing iron in the steels of the invention is meant iron except for impurities within commercial tolerances, e.g., phosphorus and sulfur about 0.04 max. each and nickel about 0.5 percent max.

The addition of copper in the stated percentages to our steels is preferred because of the desirable effect of that element in improving the resistance of our steels to work hardening and to corrosion.

Manganese, within our broad range of about 11–14%, acts to stabilize the austenitic structure of our steels but, if present in amounts substantially greater than about 14%, it tends to form ferrite.

Similarly, chromium above about 17 or 18% tends to produce a ferritic structure. Molybdenum is also a ferrite former and may be substituted, in part, for chromium. We have found that the critical molybdenum substitution for chromium, in order to achieve the desired results, is in the ratio of 1:1. This finding is contrary to prior art determinations of the molybdenum equivalent of chromium in forming ferrite. Thus, prior art investigations had established the chromium equivalent of molybdenum at values of from 2.0 to 4.2. We have found, however, that, with such high equivalent values, it is not possible to obtain fully austenitic steels of the type contemplated by this invention. Accordingly, we substitute molybdenum for chromium on a 1:1 basis and limit the amount of molybdenum so introduced in our compositions to a maximum of 3%, since, as will appear hereinafter, we have found that the corrosion resistance of our steels is materially enhanced by the addition of molybdenum up to such maximum amounts. A particularly desired group of steels are those wherein the (Cr+Mo) content is between about 15.5% and about 18.5%.

Despite the restriction of the amounts of manganese, chromium and molybdenum to the above-stated values, our steels will not have a completely austenitic structure in the absence of the strong austenite stabilizers, carbon and nitrogen, in critical amounts. For assurance of a completely austenitic structure, we have found that the minimum carbon plus nitrogen content should be related to the (Cr+Mo) content as follows:

(1) Percent (C+N) min.=0.075 [(percent Cr+Mo)—15.5]+0.3

According to the above formula, the minimum carbon plus nitrogen content necessary to assure a completely

austenitic structure increases with the (Cr+Mo) content. Thus, for a typical steel containing 16% (Cr+Mo) for example, 14% chromium and 2% molybdenum, the minimum carbon plus nitrogen is about 0.34% and for a typical steel containing 18% (Cr+Mo), for example, 17.65% chromium and 0.35% molybdenum, the minimum carbon plus nitrogen is 0.49%.

It is necessary to place a maximum value upon carbon content in order to prevent reaction of carbon with chromium to form chromium carbide. Precipitation of the latter material, when steels containing excess carbon are welded, is made possible by the extraction of chromium from areas adjacent the welds and results in a lowered corrosion resistance of such areas. Accordingly, we limit our carbon to about 0.15% on the high side.

The maximum amount of nitrogen is limited by the solubility of nitrogen in the steel. If present in excessively large amounts, nitrogen will evolve in gaseous form from the steel as it solidifies and thereby produce unsound material. According to the above-mentioned Equation 1, a steel of our invention having a combined (Cr+Mo) content of 18.5% and a carbon content of 0.15% would require about 0.38% nitrogen to maintain a completely austenitic structure. We, therefore, prefer an upper limit of nitrogen of about 0.4% although larger quantities about to 0.55% may be utilized, especially in those steels having a manganese content near the high end of the specified broad range. Although the amount of nitrogen which can be kept in solution can be increased by increasing the amount of manganese, this is an undesirable procedure since, as pointed out hereinabove, increasing amounts of manganese tend to produce a ferritic structure in the steel.

It thus will be seen that, in order to maintain the desired structure, it is necessary to properly balance all of the elements of the composition within critically restricted ranges. Moreover, by substituting molybdenum, in the specified ratio, for a portion of the chromium, it is not only possible to maintain a completely austenitic structure but, surprisingly, it is also possible to produce steels having greatly enhanced corrosion resistance as compared to the same steels without molybdenum, and as compared to prior art steels containing substantial quantities of nickel. These critical relationships, and the improved results, will become more readily apparent from the following description and examples when considered in connection with the accompanying drawings wherein:

FIGURE 1 is a phase diagram showing the relation between minimum carbon plus nitrogen content versus combined chromium and molybdenum content of the steels necessary for maintaining a completely austenitic structure;

FIGURE 2 is a diagram showing the effect, on weight loss, of the addition of molybdenum to steels upon exposure to a ferric chloride environment, and

FIGURE 3 is a diagram showing the effect, on weight loss, of the addition of molybdenum to steels upon exposure to a sulfuric acid environment.

Experimental 10-pound heats consisting of several compositions, including the steels of this invention, were induction melted and cast into slab ingots 3 inches x 1½ inches x 2 inches. Chemical analyses of these experimental compositions are shown in Table I below.

TABLE I

Chemical Analyses of Experimental Material

Material	Serial or Bar No.	C	Mn	Si	Ni	Cr	Mo	N	Cu
Cr-Mn-Cu-N-C(C)	C1	0.072	11.46	0.81	-------	15.86	------	0.28	1.17
C+0.3% Mo	C2	0.091	11.80	0.80	-------	15.75	0.35	0.29	1.13
C+1% Mo	C3	0.077	11.77	0.80	-------	15.60	1.03	0.28	1.14
C+1% Mo	C4	0.068	11.87	0.86	-------	15.40	1.01	0.31	1.11
C+1.5% Mo	C5	0.070	11.66	0.80	-------	15.51	1.51	0.33	1.10
C 2% Mo	C6	0.069	11.63	0.80	-------	15.58	1.92	0.32	1.09
C 2% Mo	C7	0.066	11.32	0.80	-------	15.88	1.93	0.45	1.09
C 2.4% Mo	C8	0.072	11.30	0.80	-------	15.86	2.42	0.51	1.10
AISI 302	57-361	0.09	1.91	0.57	8.86	17.92	0.27	0.06	------
AISI 304	3394	0.047	1.31	0.45	9.03	19.06	------	------	------
AISI 316	58-221	0.025	1.70	0.50	12.96	17.21	2.57	0.06	------
AISI 316	57-252	0.06	1.77	0.66	13.30	17.95	2.30	------	------
AISI 202	57-106	0.088	9.07	0.55	5.14	17.02	0.03	0.17	------

Each of the ingots was sectioned and prepared, in the usual fashion, for metallographic examination by visual microscopic inspection which showed that experimental compositions C3, C5 and C6 contained some ferrite in an austenite matrix. Magnetic testing of the compositions showed these three compositions to be slightly magnetic thereby confirming the presence of some small quantity of ferrite. The ingots were then cut into pieces 3 inches x 1½ inches x 2 inches and hot rolled to sheet. Metallographic examination after rolling showed all of the compositions C1 through C8 to be free of ferrite with the exception of composition C6 which contained a very small amount of ferrite.

In FIG. 1, the graph A represents the relation between that chromium plus molybdenum content, plotted as ordinate, and carbon plus nitrogen, plotted as abscissa, which is necessary to avoid the formation of delta ferrite in the as-cast steel. Graph A is a graphic illustration of Equation 1 which is derived therefrom and which defines the relationship between these elements in the steels contemplated by this invention. The minimum carbon plus nitrogen contents required by Equation 1 for the various chromium plus molybdenum contents of the respective compositions were calculated in accordance with Equation 1 and compared with the actual measured carbon plus nitrogen values of the experimental steels. These comparative values are set out in Table II.

TABLE II

Relationship Between Composition and Structure

Steel	Cr	Mo	Cr+Mo	C	N	C+N	Required C+N Eq. 1	Structure [1]	
								As-cast	Hot-rolled
C1	15.9	------	15.9	.07	.28	.35	.33	A	A
C2	15.75	.35	16.1	.09	.29	.38	.34	A	A
C3	15.6	1.03	16.6	.08	.28	.36	.38	A+F	A
C4	15.4	1.01	16.4	.07	.31	.38	.36	A	A
C5	15.5	1.51	17.0	.07	.33	.40	.41	A+F	A
C6	15.6	1.92	17.5	.07	.32	.39	.45	A+F	A+F
C7	15.9	1.93	17.8	.07	.45	.52	.47	A	A
C8	15.9	2.42	18.3	.07	.51	.58	.51	A	A

[1] A=austenite, F=ferrite.

It will be noted that the actual (C+N) contents of the experimental steels in general conform quite closely to those required by Equation 1.

Specimens were cut from the rolled steels for corrosion testing purposes. The specimens were solution annealed for two hours at 1950° F. and water quenched after which they were surface ground or sandblasted and

then given the standard 120-grit finish. The specimens were then exposed to various corrosive media in order to study the effect of the addition of molybdenum on the corrosion resistance of the steels.

Ferric chloride tests constitute a method for determining the resistance of stainless steels to pitting. Such tests are of particular value herein since a major benefit accruing from the addition of molybdenum is the enhancement of the resistance of the steels to pitting. Although it is not uncommon practice to utilize pit count, i.e., the number, size and/or depth of pits per unit area of surface of the test specimen, for evaluating the results of corrosion tests, the great number of pits formed and the range in size of pits from microscopic to quite large often make pit count impractical for evaluation. We have found weight loss, although not ordinarily used in evaluating pitting tests, to correlate well in these tests with appearance and with pit counts made with specimens having pits of fairly uniform size. In performing the corrosion tests in the presence of ferric chloride, a test specimen of each of the compositions to be tested, i.e., C1, a nickel-free, molybdenum-free stainless steel, C2–C8, nickel-free stainless steels containing varying quantities of molybdenum and A.I.S.I. types 202, 302 and 316, were suspended in an aqueous test solution containing 10.8% by weight ferric chloride and held at a temperature of about 30° C. for four hours. The test specimens were weighed before being immersed in the test solution and, after exposure, were rinsed with distilled water, dried and re-weighed. The results of such tests are given in FIG. 2 from which it may be seen that the addition of as little as about 0.3% molybdenum appreciably increases corrosion resistance. Further additions of molybdenum up to about 1% do not substantially further increase corrosion resistance, but resistance is greatly enhanced upon still further additions of molybdenum of 1.5, 2 and 2.5%. Thus, the addition of 0.3% molybdenum produces steels which, although having substantially no nickel content, exhibit a resistance to corrosion, as measured by the ferric chloride test, better than that shown by A.I.S.I. type 202 which contains about 5% nickel. An increase in molybdenum content to 2 or 2.5% further increases the corrosion resistance of the nickel-free steels of the invention to the point where the corrosion resistance is superior to A.I.S.I. type 302 (having about 9% nickel) and about equal to that of type 316 (having about 16% nickel).

Similar tests were also performed in a more corrosive, 15% by weight ferric chloride aqueous solution, the results of such tests being given in Table III.

TABLE III

Ferric Chloride (15%) Pitting Test (4 Hours at 30° C.)

Material	Serial or Bar No.	Weight loss (g./in.²)	Degree of pitting "Appearance ranking"
Cr-Mn-Cu-N-C+2.42% Mo	C8	0.0003	1
A.I.S.I. 316	58-221	0.0034	2
Cr-Mn-Cu-N-C+1.93% Mo	C7	0.0023	3
A.I.S.I. 302	57-361	0.0428	4-5
Cr-Mn-Cu-N-C+1.03% Mo	C3	0.0819	4-5

From Table III it will be seen that the steel of the invention containing about 2.5% molybdenum is greatly superior to the high nickel content A.I.S.I. type 316 steel. The addition of about 2% molybdenum results in a steel which is considerably less resistant to corrosion than that with about 2.5% molybdenum, but which is still superior to the A.I.S.I. type 316 steel and much superior to the A.I.S.I. type 302 steel. The addition of about 1% molybdenum results in a composition which is considerably less corrosion resistant than A.I.S.I. type 302 steel although a composition with this relatively low molybdenum content would still be considerably more corrosion resistant than A.I.S.I. type 202, as shown in FIG. 2.

Sulfuric acid is representative of a number of non-oxidizing and non-reducing acids. The Cr-Mn-Cu-N-C steels such as disclosed in Patent No. 2,862,812 are considerably less resistant to attack by such acids than are the austenitic chromium-nickel steels such as A.I.S.I. types 202, 302 and 316. However, it has been found the addition of molybdenum to such nickel-free steels significantly increases their resistance to sulfuric acid attack. To show this effect of molydbenum, samples were prepared as previously described and tested in a fully aerated, aqueous solution containing 10% sulfuric acid. The test specimens were exposed for a period of three hours and the test solution was held at about 30° C. The results of these tests are shown in FIG. 3. From FIG. 3 it may be seen that the addition of as little as 0.3% molybdenum increases the sulfuric acid corrosion resistance of our nickel-free steels to the point where they are equal to or superior to type 202. The addition of up to 2% molybdenum further increases the resistance to sulfuric acid attack but not to the point where the steels are equal in that respect to type 302. Thus, the addition of molybdenum to our nickel-free steels results in about a hundred fold increase in their resistance to attack by dilute sulfuric acid.

A further series of tests was performed to determine the effect of molybdenum on the resistance of nickel-free austenitic steels to corrosive attack by glacial acetic acid which constitutes an important corrosive organic environment. Test specimens were specimens were prepared as previously described and the specimens were immersed in boiling glacial acetic acid for 48 hours. For some of the compositions, the tests were continued for a total of 120 hours. The results of these tests are shown in Table IV.

TABLE IV

Boiling Glacial Acetic Acid Test

Material	Serial or Bar No.	Weight loss (g./in.²) 48-hour test	Weight loss (g./in.²) 120-hour test
Cr-Mn-Cu-N-C(C)	C1	0.0317	0.0590
C+0.3% Mo	C2	0.0023	
C+1% Mo	C3	0.0002	0.0026
C+2% Mo	C6	0.0009	
C+2.4% Mo	C8	0.0003	0.0017
AISI 304	3394	0.0342	
AISI 316	57-252	0.0001	0.0036

It may be seen from Table IV that the addition of molybdenum in amounts from 0.3% to about 2.4% increases the corrosion resistance of the nickel-free austenitic steels to the point where they are superior in such respect to A.I.S.I. type 304 although they generally are still inferior in corrosion resistance to type 316. A major improvement in corrosion resistance was obtained by the addition of as little as 0.3% molybdenum while the maximum resistance to corrosion was found at the 1% molybdenum level and the steel having that molybdenum content was substantially equal to type 316.

It can be seen from the foregoing test results that the addition of about 0.3 to 0.35% molybdenum to the contemplated nickel-free Cr-Mn-Cu-N-C austenitic steels produces highly advantageous results in the increased resistance of such steel to pitting and other corrosive attack by acids. Accordingly, the compositions of this invention are much superior to similar compositions wherein the molybdenum is omitted, especially in those applications where contact with acids is probable. Accordingly, the steels of the invention rival or exceed, in corrosion resistance, many high nickel stainless steels of commerce, in many corrosive environments. The steels of the invention possess considerable utility for exterior construction in marine or other chloride-bearing environments

where pitting might be a problem. In acid environments, additions of molybdenum above about 0.35% do not result in drastic increases in corrosion resistance but higher additions of molybdenum up to about 3% are advantageous where optimum resistance to pitting is desired.

It is to be understood that the foregoing description and examples are merely illustrative of the principles of the invention and that various modifications and improvements may be made within the scope of the appended claims.

We claim as our invention:

1. An austenitic stainless steel consisting essentially of about 14 to 18% chromium, 0.3 to 3% molybdenum, 11 to 14% manganese, 0.5 to 1.5% copper, up to 0.15% carbon, 0.15 to 0.55% nitrogen, the minimum carbon plus nitrogen content being related to the chromium plus molybdenum content in accordance with the equation, percent (C+N) min.=0.075 ((percent Cr+Mo)—15.5) +0.3, balance substantially iron, said alloy being characterized by a wholly austenitic structure as quenched from 1950° F. and by improved corrosion resistance to acid and chloride environments.

2. An alloy steel consisting essentially of about 15.5 to 16.5% chromium, 0.35 to 2.5% molybdenum, 11.5 to 13.5% manganese, 0.5 to 1.5% copper, 0.15 to 1.5% silicon, 0.05 to 0.15% carbon, 0.25 to 0.40% nitrogen, the minimum carbon plus nitrogen content being related to the chromium plus molybdenum content in accordance with the equation, percent (C+N) min.=0.075 ((percent Cr+Mo)—15.5)+0.3, balance substantially all iron, said alloy being characterized by a wholly austenitic structure as quenched from about 1950° F. and improved corrosion resistance.

3. An alloy steel consisting essentially of 15.5 to 16.5% chromium, 0.3 to 3.0% molybdenum, 11 to under 14% manganese, 0.5 to 2% copper, up to 3% silicon, up to 0.15% carbon, 0.15 to 0.55% nitrogen, the minimum carbon plus nitrogen content being related to the chromium plus molybdenum content in accordance with the equation, percent (C+N) min.=0.075 ((percent Cr+Mo)—15.5)+0.3, balance substantially iron, said alloy being characterized by a wholly austenitic structure as quenched from 1950° F. and improved corrosion resistance.

4. An austenitic, corrosion resistant, substantially nickel-free stainless steel consisting essentially of about 14 to 16.5% chromium, 0.3 to 3% molybdenum, 11 to 14% manganese, 0.5 to 2% copper, up to 3% silicon, 0.05 to 0.15% carbon, 0.15 to 0.4% nitrogen, the minimum carbon plus nitrogen content being related to the chromium plus molybdenum content in accordance with the equation, percent (C+N) min.=0.075 ((percent Cr+Mo)—15.5)+0.3, balance substantially all iron.

5. An alloy steel consisting essentially of about 0.35 to 2.45% molybdenum, 15.5 to 18.5% total amount of chromium plus molybdenum, 11 to 12% manganese, 0 to 1% silicon, 0.5 to 1.5% copper, 0.05 to 0.1% carbon, 0.15 to 0.5% nitrogen, minimum carbon plus nitrogen content being related to the chromium plus molybdenum content in accordance with the following equation, percent (C+N) min.=0.075 ((percent Cr+Mo)—15.5) +0.3, and balance substantially iron.

6. An alloy steel consisting essentially of from about 14 to 18% chromium, 0.3 to 3% molybdenum, 11 to 14% manganese, 0.05 to 0.15% carbon, 0.15 to 0.55% nitrogen, 0.5 to 2% copper, up to 3% silicon, balance substantially iron, said steel being characterized by enhanced resistance to corrosion and to work hardening.

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