

1

3,492,117 CORROSION RESISTANT STAINLESS TYPE ALLOYS

Raymond P. Jackson, Suffern, N.Y., and Jacob Schramm, Ringwood, and Daniel van Rooyen, Ramsey, N.J., assignors to The International Nickel Company, Inc., New York, N.Y., a corporation of Delaware
Filed Oct. 21, 1966, Ser. No. 588,341
Int. Cl. C22c 39/20

U.S. Cl. 75—128

8 Claims

ABSTRACT OF THE DISCLOSURE

Alloys containing iron, nickel, chromium, molybdenum and columbium offer a high degree of resistance to stress corrosion cracking and intergranular attack. The molybdenum and columbium must be correlated within certain ranges when the nickel content is 35% or more.

The present invention relates to corrosion resistant alloys of novel composition, particularly to improved alloys of the stainless type capable of markedly inhibiting the onset of both stress-corrosion cracking and grain boundary sensitization while affording enhanced resistance to crevice corrosion and pitting in various chloride media.

Notwithstanding the many attributes and well established versatility of the austenitic stainless steels, one of the historically old drawbacks thereof has been their acknowledged propensity to undergo stress-corrosion cracking, especially in respect of aggressive chloride corrodents, e.g., boiling magnesium chloride. Numerous solutions to this most difficult problem have been offered, two of the most recent and notable being described in U.S. patents to Copson and Lang, Nos. 3,159,479 and 3,159,480, wherein the background and nature of the problem are also rather extensively treated. The proposals advanced therein concern maintaining the elements phosphorus and nitrogen, inter alia, at low levels in steels containing at least 19% nickel and 15% chromium while utilizing a minimum amount of carbon or silicon (at least 0.07% carbon, 1.7% silicon).

As so often is the case, however, the solution of one problem focuses attention on another. It is well known, for example, that high carbon (and this would include the minimum 0.07% referred to above) renders austenitic stainless steels quite susceptible to intergranular corrosion, i.e., the steels are grain boundary sensitive. Intergranular corrosion, which is particularly troublesome in connection with weldments, can, of course, be minimized in various ways. Ironically, perhaps, one of the most exemplary and accepted procedures is to maintain the carbon content of such steels below about 0.03% as evident from the now standard AISI 304L grade. Too, higher carbon contents can be brought under control through stabilization with columbium, whence evolved AISI 347. AISI 304L and 347 might circumvent intergranular corrosion but in view of the Copson and

2

Lang development involving the use of at least 0.07% carbon, stress-corrosion cracking is accentuated. (High silicon as recommended in the second patent above mentioned is discussed infra.)

Perhaps also noteworthy, both of the aforementioned patents admonish that molybdenum should be kept at an extremely low order of magnitude, less than 0.075%; otherwise, stress-corrosion cracking is aggravated. But adherence thereto precludes obtaining the benefits conferred by the very molybdenum contents (2% to 4%) largely responsible for the development of austenitic stainless steels AISI 316 and 317, steels which, however, are prone to stress-corrosion cracking, and intergranular corrosion at high carbon levels. Data herein confirm that small amounts of molybdenum, say, up to 2%, are subversive, but for reasons presently unexplainable, molybdenum above about 3%, depending on alloy chemistry, begins to restrain rather than promote stress-corrosion attack and upwards of about 5.5% greatly inhibits cracking. This behavioral pattern is illustrated infra. In any event, it would appear that a stainless type alloy was hitherto needed capable of effectively resisting both stress-corrosion cracking and also intergranular corrosion and which would also offer appreciable resistance to crevice corrosion and pitting in chloride media.

It has now been discovered that with special alloys containing controlled amounts of iron, nickel, chromium, molybdenum, columbium, carbon, etc., the foregoing objectives can be accomplished.

It is an object of the invention to provide new corrosion resistant alloys.

Another object is to provide alloys of novel composition resistant to stress-corrosion cracking and intergranular corrosion attack while also offering outstanding resistance to crevice corrosion and pitting.

Other objects and advantages will become apparent from the following description.

Generally speaking and in accordance with the present invention, alloys contemplated herein contain (in percent by weight) at least 30% nickel, about 17% to 22% chromium, from about 5.5%, e.g., 6%, to 9.25% molybdenum, at least 1%, e.g., at least 1.5%, and up to about 3.25% columbium, up to 0.03% carbon, up to about 1.5% manganese, up to 1% silicon, up to 0.6% titanium, up to 0.6% aluminum, and the balance essentially iron. While vanadium and copper can be present in the alloys, it is preferred that the amounts of these constituents not exceed 2%, respectively, since it has been found that they often detract from corrosion resistance. Elements such as oxygen, nitrogen, phosphorus, sulfur and the like should be kept at low levels consistent with good commercial practice. In this regard, the respective amounts of phosphorus and sulfur should not exceed about 0.02% and 0.03%.

In carrying the invention into practice, the alloys should contain at least 30% nickel lest stress-corrosion cracking be promoted. It has been found that with alloys otherwise in accordance herewith, a range of about 31% to 34% nickel offers excellent resistance to stress-corro-

sion cracking even in the highly aggressive environment of boiling magnesium chloride. Up to 40% nickel can be present, but in amounts above about 35% and to consistently achieve highly satisfactory crevice corrosion resistance, it is quite advantageous that the nickel content be correlated with the molybdenum and columbium as shown in Table I.

TABLE I

Nickel, percent	Molybdenum, percent		Columbium, percent		Molybdenum+Colum- bium, percent	
	A	B	A	B	A	B
35-36.5	6-8.5	6.25-8.25	1.5-3.25	1.75-3.1	8.5-11	8.5-10.5
36.5-38	6.5-9	7-8.75	1.6-3	1.8-3	8.75-11.75	9-11
38-40	7-9.25	8-9.25	1.75-3.25	2-3	9-12	9.25-11.5

Column B denotes most advantageous range.

Molybdenum should not fall below about 5.5%; otherwise resistance to stress-corrosion cracking is endangered and, at best, crevice corrosion resistance is impaired. The data in Table II is of interest in illustrating that although inconsequential amounts of molybdenum are an open invitation to stress-corrosion cracking in magnesium chloride, the reverse is the case with molybdenum levels upwards of 5.5% or 6%. Usual testing procedures were employed, to wit, U-bend specimens (annealed condition). C.) and periodically inspected for a period up to 30 days, the tests thereafter being discontinued.

ly at least 25%, in obtaining the maximum by way of corrosion resistance.

In respect of other constituents, processing of the alloys is facilitated with the presence of 0.1% to 0.5% of either aluminum or titanium or both. Silicon above about 1% can bring about the occurrence of weldability and workability difficulties and it is beneficial that silicon not exceed

20

25

0.25%, it being of advantage to observe a maximum of 0.1%. Manganese preferably does not exceed 1%. While, as indicated above herein, up to 2% each of vanadium or copper can be present, amounts up to 1% and 0.75%, respectively, are satisfactory. Tungsten, if present, should not exceed 1% and tantalum (if any) above 2% is not recommended. Provided at least 1% columbium is present, it is considered that tantalum can be used in lieu of columbium on an atom for atom basis, two parts of tantalum for one part of columbium. Finally, for purposes of good deoxidation, it is most favorable that at least one of the following elements be incorporated in the alloy

TABLE II

Alloy	Ni, percent	Cr, percent	C, percent	Mo, percent	Si, percent	Mn, percent	Al, percent	Ti, percent	Cu, percent	Days to failure
A-----	41.8	18.3	0.07	n.a.	0.58	0.69	n.d.	n.d.	0.05	O.K.
B-----	34.1	21.0	0.08	n.a.	0.61	0.81	0.10	0.26	0.41	O.K.
C-----	34.2	20.5	0.03	n.a.	0.71	0.83	0.23	0.44	0.41	6.
D-----	32.6	19.1	0.07	0.15	0.63	0.15	<.01	0.06	0.06	13.
E-----	34.4	20.1	0.07	0.33	0.57	0.13	<.01	0.015	0.06	5.
F-----	34.2	20.3	0.08	0.48	0.62	0.14	<.01	0.019	0.06	12.
G-----	33.8	20.4	0.026	0.25	0.70	0.82	0.19	0.39	0.41	9.
H-----	41.2	18.7	0.02	1.7	0.82	0.86	<0.1	0.13	0.48	1.
J-----	41.0	18.1	0.02	3.3	0.8	0.84	0.14	0.20	0.50	16, O.K.
K-----	32.9	18.8	0.03	2.1	0.66	0.79	0.20	0.25	0.40	5, 6.
L-----	35.7	18.8	0.02	2.1	0.80	0.80	0.14	0.24	0.50	5, 8.
M-----	33.0	18.5	0.02	3.3	0.62	0.75	0.32	0.26	0.51	11, 15.
N-----	39.2	17.7	0.036	3.2	0.71	0.72	0.26	0.23	0.51	O.K., O.K.
P-----	38.1	17.7	0.02	4.9	0.71	0.81	0.26	0.20	0.52	11, O.K.

n.a.=Not added.

n.d.=Not detected.

Balance of alloys iron and impurities.

In respect of the data in Table II, molybdenum-free, high carbon Alloys A and B serve as controls. Reducing the carbon content (Alloy C) confirms the ease with which cracking occurs. Alloys D through G illustrate the destructive influence exerted by small amounts of molybdenum, including high carbon Alloys D, E, and F (alloys which otherwise would be expected to be virtually crack-free under test). A comparison of Alloys H and J, K, L and M and N and P reflect that, generally speaking, molybdenum above about 3% reverses its role as a subversive.

Columbium potentially contributes to crevice corrosion resistance provided at least 1% is present in the alloys and that it is correlated with the nickel and molybdenum contents as set forth herein. Low amounts of columbium, e.g., 0.2% or 0.5%, are not effective and it is most advantageous that at least 1.5% be present in the alloys irrespective of nickel content. Amounts above 3.25% are unnecessary and but serve to increase cost. To this might be added that cracking occurred when rolling an ingot at 2100° F. concerning an alloy containing 5% columbium, the alloy otherwise being within the invention. Chromium below 17% adversely affects resistance to crevice corrosion and amounts above 22% contribute to workability problems. The alloys beneficially contain at least 18% chromium with 21.5% being a preferred maximum. It is to be emphasized that the sum of the chromium plus molybdenum should be at least 24%, most advantageous-

50

55

60

65

70

75

melts; up to 0.08% magnesium, up to 0.005% boron, up to 0.05% calcium and up to 0.02% zirconium.

In order to give those skilled in the art a better understanding of the invention, the following illustrative description and data are given:

Nickel, iron, chromium (vacuum grade), and carbon were charged into a magnesium oxide crucible. Upon melting under an argon blanket, columbium, molybdenum and manganese were then added, the melt being brought to a temperature of about 2900° F. Upon cooling to 2850° F., aluminum, titanium and, excepting Alloy Q, calcium-silicon or magnesium was then added. The melts were poured at about 2800° F. and cast into ingots which were then hot rolled at about 2100° F. to specimens ¼ inch thick.

Specimens were then subjected to at least one of two well known tests, the first consisting of cold rolling to strip about 0.075 inch thick (a cold reduction of about 75%) and thereafter annealing at 1950° F. for about one hour. These specimens (1" x 1½") were machined and then immersed for about 72 hours in 10% ferric chloride solution, rubber bands being wrapped therearound to form crevices. The data obtained on a number of alloys are given in Table III wherein in contrast to Alloys 1 through 6, Alloys Q through Y are outside the invention. Included are various commercially produced prior art alloys, to wit, Z and AA through DD.

TABLE III

Alloy	Ni, percent	Cr, percent	Mo, percent	C, percent	Cb, percent	Al, percent	Ti, percent	Fe, percent	Weight loss, milligrams
1-----	30.1	21.8	6.5	0.029	2.2	.07	.15	Bal.	2.5
2-----	32.4	21.6	6.5	0.021	2.1	.18	.24	Bal.	0.4
3-----	33.5	21.2	6.4	0.01	2.1	.25	.20	Bal.	0.1
4-----	35.5	20.0	6.3	0.025	2.2	.26	.25	Bal.	10.75
5-----	35.8	20.2	7.3	0.031	3.1	.18	.24	Bal.	0.0
6-----	39.7	19.9	9.1	0.017	2.2	.25	.21	Bal.	0.7
Q-----	36.3	20.3	0.7	0.023	0.14	.25	2.45	Bal.	416.5
R-----	39.3	19.8	6.3	0.019	-----	.37	.28	Bal.	208.7
S-----	40.0	20.0	6.25	0.032	1.16	.30	.26	Bal.	101.9
T-----	39.0	22.0	6.15	0.030	2.18	.35	.24	Bal.	113.4
U-----	38.5	20.0	6.2	0.054	2.2	.33	.26	Bal.	154.3
V-----	39.0	20.0	4.35	0.025	2.1	.22	.24	Bal.	176.1
W-----	44.2	19.9	6.15	0.10	2.1	.32	.25	Bal.	101.2
X ² -----	43.5	21.6	6.6	0.038	2.34	.31	.26	Bal.	88.0
Y-----	60.8	20.2	6.0	0.04	2.1	.30	.27	Bal.	97.4
Other percent									
Z-----	45.9	21.8	6.56	0.04	1.96	0.32 W, 0.81 Co-----		Bal.	16.3
AA-----	44.5	21.5	6.69	0.03	-----	1.19 Cu, 2.25 Ta, 1.06 Co-----		Bal.	9.2
BB-----	43.2	20.0	3.03	0.03	-----	1.75 Cu, 1.04 Ti	29.9		544.2
CC-----	33.8	20.1	2.3	0.05	-----	3.41 Cu-----		Bal.	260
DD-----	52.5	19.0	3.0	0.04	5.2	0.1 Cu-----		18.0	80.6

Bal.=Balance plus impurities with manganese not more than about 1%.

¹ Average of 2 specimens.

² Contained 2.0% copper.

In respect of the data in Table III, Alloys Q through V are without the invention primarily by reason of the fact that the correlation of the percentages of molybdenum and columbium and nickel content is quite inconsistent with that set forth in Table I. Alloy 6 illustrates particularly well (compare with Alloy S, for example), that nickel between 35% and 40% can be successfully employed provided the aforesaid relationship is observed. It will also be observed that the alloys within the invention compared more than favorably with the commercial alloys Z and AA through DD.

The second test involved the extremely severe boiling magnesium chloride test referred to above herein. Test results are reported in Table IV regarding Alloys 1, 2, 3, 5 and 7 each of which is within the invention (Alloys 4 and 6 were not exposed to the magnesium chloride test).

TABLE IV

Alloy	Ni, percent	Cr, percent	Mo, percent	C, percent	Cb, percent	Mn, percent	Fe, percent	Days to failure
1-----	30.1	21.8	6.5	0.029	2.20	0.70	Bal.	>30
2-----	32.4	21.6	6.5	0.021	2.10	0.60	Bal.	>30
3-----	33.5	21.2	6.4	0.010	2.10	0.70	Bal.	>30
5-----	35.8	20.2	7.3	0.031	3.10	0.61	Bal.	>30
7-----	35.9	19.7	6.1	0.020	2.36	0.70	Bal.	>30

It will be observed that each of the alloys of Table IV resisted cracking for the full period of test. Alloys containing 35% to 40% nickel resist stress-corrosion cracking and also manifest excellent resistance to crevice corrosion when the nickel is properly related to molybdenum and columbium in accordance herewith.

In the cold worked condition alloys in accordance herewith manifest high strength. Alloy 6, for example, when cold reduced to a wire (a reduction of over 90%) was characterized by an ultimate tensile strength of about 305,000 p.s.i. Equally important, the wire was sufficiently ductile to pass the "kink" test (a test wherein the wire is formed into a loop and the ends are drawn together to tightly close the loop). Thus, a particularly suitable use for such alloys would be for marine cable applications.

Conventional processing procedures well known to those skilled in the art can be employed. Air melting practices as well as vacuum techniques are quite suitable. Hot working operations can be carried out over a temperature range of about 1800° F. to 2300° F. and satisfactory annealing temperatures are from about 1900° F. up to about 2150° F.

While alloys of the subject invention are useful in resisting the corrosive effects of various chloride media in general, specific applications include vessels, containers, tubing, piping, valves and the like, employed in the chemi-

cal and other fields, e.g., marine, petroleum, etc. The alloys can be produced in various mill forms, including bar, rod, sheet, plate, strip, wire, etc.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A stainless alloy resistant to both stress-corrosion cracking and intergranular corrosion and consisting essentially of from 30% to 40% nickel, about 17% to 22% chromium, from 5.5% to 9.25% molybdenum, at least

50 1% and up to 3.25% columbium, the nickel, molybdenum and columbium being correlated as follows when the nickel content is from 35% to 40% up to 0.03% carbon,

Nickel, percent	Molybdenum, percent	Columbium, percent	Molybdenum + Columbium, percent
35-36.5	6-8.5	1.5-3.25	8.5-11
36.5-38	6.5-9	1.6-3	8.75-11.75
38-40	7-9.25	1.75-3.25	9-12

60 up to 1.5% manganese, up to 1% silicon and the balance essentially iron, said alloy being further characterized by enhanced resistance to crevice corrosion and pitting.

2. A stainless alloy in accordance with claim 1 in which the sum of the chromium plus molybdenum is at least 24%.

65 3. A stainless alloy in accordance with claim 1 containing at least 18% chromium and in which the nickel, molybdenum and columbium are correlated as follows:

Nickel, percent	Molybdenum, percent	Columbium, percent	Molybdenum + Columbium, percent
35-36.5	6.25-8.25	1.75-3.1	8.5-10.5
36.5-38	7-8.75	1.8-3	9-11
38-40	8-9.25	2-3	9.25-11.5

75

4. A stainless alloy in accordance with claim 2 containing 6% to 9% molybdenum.

5. A stainless alloy in accordance with claim 4 containing 1.5% to 3% columbium.

6. A stainless alloy in accordance with claim 5 containing 18% to 21.5% chromium and in which the sum of the chromium plus molybdenum is at least 25%.

7. A stainless alloy in accordance with claim 1 containing 31% to 34% nickel, 18% to 21% chromium, 6% to 9% molybdenum and 1.5% to 3% columbium.

8. A stainless alloy in accordance with claim 1 and containing up to 0.6% titanium, up to 0.6% aluminum, up to 2% of vanadium, up to 2% copper, up to 1%

tungsten, up to 2% tantalum, up to 0.08% magnesium, up to 0.005% boron, up to 0.05% calcium and up to 0.02% zirconium.

References Cited

UNITED STATES PATENTS

5	2,777,766	1/1957	Binder	75—134
	3,159,480	12/1964	Copson	75—128
	3,168,397	2/1968	Scharfstein.	
10	3,183,084	5/1968	Heydt	75—128.9

HYLAND BIZOT, Primary Examiner

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,492,117 Dated January 27, 1970

Inventor(s) RAYMOND P. JACKSON, JACOB SCHRAMM & DANIEL van ROOYEN

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 8, for "agravated" read --aggravated--.

Column 3, line 59, for "potentially" read --potently--.

Column 6, line 52 (Claim 1, line 7), after "40%" insert a colon (:) and delete remainder of line.

Column 6, line 60 (Claim 1, line 14), before "up to 1.5% manganese" insert --up to 0.03% carbon,--.

SIGNED AND
SEALED
NOV 17 1970

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents