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Espy

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[54] **FERRITIC-AUSTENITIC STAINLESS STEEL**

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[51] **Int. Cl.**..**C22c 39/14**

[58] **Field of Search**..........................75/126 J, 126 B, 75/128 N

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[57] **ABSTRACT**

An austenitic-ferritic stainless steel consisting essentially of up to about 0.06 percent carbon, about 4.0 to less than 11.0 percent manganese, about 19 to about 24 percent chromium, about 0.12 to about 0.26 percent nitrogen, nickel up to about 3.0 percent, and remainder substantially iron except for incidental impurities. The austenite-ferrite balance, ranging between 10 percent and 50 percent austenite, is stable, and the steel exhibits high toughness, corrosion resistance and excellent weldability.

12 Claims, No Drawings

FERRITIC-AUSTENITIC STAINLESS STEEL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a modified chromium stainless steel (low in nickel, copper and cobalt) of stable ferritic-austenitic structure having excellent toughness, ductility, corrosion resistance and welding characteristics. The alloy of the invention, by reason of its compositional balance, achieves a structure of from 10 percent to 50 percent austenite (preferably 20 percent to 30 percent) in a ferritic matrix which resists transformation into martensite despite cold working, heat treatment, or welding.

The stainless steel of this invention has particular utility as weldments in straight chromium steels, for fabrication into fasteners which require cold heading, and a variety of other applications requiring relatively high strength and ductility, good weldability, and high resistance to intergranular corrosion in strongly oxidizing media, as well as good resistance to stress corrosion in chloride media.

2. Description of the Prior Art

Among the numerous alloys developed to offset the scarcity and high cost of nickel are those disclosed in U.S. Pat. No. 2,778,731 issued Jan. 22, 1957, to D. Carney, consisting of 0.06 percent to 0.15 percent carbon, 14 percent to 20 percent manganese, 17 percent to 18.5 percent chromium, 0.05 percent to 1.0 percent nickel, 0.25 percent to 1.0 percent silicon, 0.25 percent to 1.0 percent nitrogen, and remainder iron; B & W CROLOY 299 consisting of 0.20 percent carbon, 15.0 percent manganese, 17.0 percent chromium, 1.5 percent nickel, 0.35 percent nitrogen, and remainder iron; and other fully austenitic steels such as Armco 16-16-1 and Allegheny Ludlum 205.

A fully austenitic stainless steel having excellent physical properties and stress corrosion resistance at cryogenic temperatures, coupled with great tensile strength when drastically cold reduced, is described in copending application Ser. No. 868,893 filed Oct. 23, 1969, in the name of George N. Goller and Ronald H. Espy. This steel is non-magnetic.

Straight chromium stainless steels such as A.I.S.I. Types 430, 442 and 446 have the serious disadvantages of being brittle and subject to corrosion in the heat affected zone of the base metal of a weldment. Further, the unaffected base metal may be low in impact strength at room temperature.

Typical of austenitic stainless steels which transform with cold working to less ductile martensite is A.I.S.I. Type 304, consisting of 0.08 percent maximum carbon, 2.0 percent maximum manganese, 18 percent to 20 percent chromium, 8 percent to 10.50 percent nickel and balance iron.

An alloy developed for cold heading applications which does not transform to martensite is designated as IN 744X. This steel contains about 26 percent chromium and is about half austenitic and half ferritic. Due to the high alloy content the cost is excessively high.

SUMMARY OF THE INVENTION

The principal object of this invention is to provide a magnetic austenitic-ferritic stainless steel essentially consisting of chromium, manganese, carbon and nitrogen which is stable against transformation to martensite regardless of cold working, heat treatment or welding, which has good ductility, toughness and corrosion resistance in its as-welded condition, and high strength, but which nevertheless is relatively low in cost because of lower alloy content than prior art alloys offered for applications requiring the above properties.

According to the invention a stainless steel having a two-phase structure comprising between 10 percent and 50 percent austenite in a ferrite matrix consists essentially of from about 4.0 percent to less than 11.0 percent manganese, about 19 percent to about 24 percent chromium, and about 0.12 percent to about 0.26 percent nitrogen. Carbon is of course present and is limited to a maximum of about 0.06 percent. Phosphorus and sulfur, normally present as impurities, are limited to a maximum of about 0.03 percent each. Silicon is also normally present, in amounts up to 1.0 percent maximum. Nickel may be present, ranging from trace amounts up to about 3.0 percent. Copper and cobalt, if present as residual elements, are limited to a maximum of about 0.5 percent each. The balance is of course iron, together with incidental impurities.

Molybdenum may be substituted for chromium on a 1:1 basis in amounts up to about 5 percent for improved resistance to corrosion in pitting media.

Columbium may be added in amounts up to about 1 percent for improved weld area corrosion resistance.

The austenite level, preferably 20 percent to 30 percent, is achieved through addition of nitrogen (a strong austenite former) within the range of 0.12 percent and 0.26 percent. Carbon, although maintained at a low level, also contributes to some extent to austenite formation. The austenite is maintained at a stable level by reason of the chromium, manganese and nitrogen relationship. It is thus apparent that the compositional balance among the essential elements is in every sense critical. Unlike prior art austeniticferritic alloys, the nickel, copper and cobalt contents are maintained at low levels, and hence the steel of the invention is not subject to stress corrosion failure when exposed to hot chloride media. The use of manganese to stabilize the austenite balance results in a ductile material which is also resistant to stress cracking in hot chloride media. The low carbon content tends to prevent intergranular corrosion when welded.

At least about 0.12 percent nitrogen is necessary in order to form sufficient austenite. Nitrogen in excess of about 0.26 percent would exceed the solubility limit of this element and hence would result in porosity and unsoundness in the metal.

A minimum of about 4 percent manganese is required in order to balance the chromium and thereby stabilize the austenite. Excessive manganese adversely affects the balance with chromium, increasing the austenite level above the desired range, and the maximum manganese content is thus less than 11.0 percent.

Nickel, if present, is limited to a maximum of about 3.0 percent. It has been found that the stress corrosion resistance of the metal will be adversely affected if the nickel content exceeds 3.0 percent. Within the prescribed range, nickel will of course increase the austenite level and thus cooperates with the nitrogen in this function, without adversely affecting toughness.

PREFERRED EMBODIMENTS OF THE INVENTION

While, as indicated above, in its broad ranges the steel of the invention consists essentially of carbon up to about 0.06 percent, manganese about 4.0 percent to less than 11.0 percent, chromium about 19 percent to about 24 percent, nitrogen about 0.12 percent to about 0.26 percent, nickel up to about 3.0 percent, phosphorus and sulfur up to about 0.03 percent each, silicon up to about 1.0 percent, copper and cobalt up to about 0.5 percent each, and remainder substantially iron, a preferred composition comprises about 0.02 percent carbon, about 6.0 percent manganese, phosphorus and sulfur low, about 0.40 percent silicon, about 21.0 percent chromium, about 0.20 percent nickel, about 0.20 percent nitrogen, copper and cobalt low, and balance substantially iron.

A series of heats was prepared in order to establish parameters for the composition which would achieve the novel combination of properties. The compositions of these heats are set forth in Table I below. Heats designated as B, E, H, I, J, K, L, P and Q are steels of the invention.

TABLE I

Heat No.	C	Mn	P	S	Si	Cr	Ni	N
A	0.12	0.75	Low	0.015	0.50	26.00	0.25	0.20
B	0.106	5.85	0.017	0.023	0.41	21.12	0.14	0.23
C	0.032	6.20	0.019	0.014	0.52	27.26	0.20	0.23
D	0.019	6.09	0.009	0.008	0.30	24.80	0.13	0.24
E	0.020	5.96	0.004	0.008	0.38	21.07	2.58	0.23
F	0.020	5.67	0.005	0.007	0.35	20.42	5.05	0.22
G	0.015	5.92	0.009	0.009	0.33	21.12	0.14	0.11
H	0.017	6.06	0.009	0.006	0.32	21.13	0.13	0.17
I	0.013	6.04	0.009	0.012	0.27	21.12	0.21	0.23
J	0.035	6.05	0.009	0.012	0.26	21.16	0.21	0.24
K	0.013	5.89	0.008	0.009	0.41	22.48	0.74	0.26
L	0.009	5.76	0.009	0.006	0.38	24.10	1.22	0.25
M	0.009	5.96	0.003	0.007	0.33	15.28	0.18	0.22
N	0.007	5.82	0.004	0.007	0.33	17.75	0.18	0.26
O	0.008	3.36	0.006	0.007	0.42	20.57	0.20	0.22
P	0.008	8.77	0.009	0.008	0.40	20.93	0.20	0.25
Q	0.055	5.74	0.007	0.008	0.32	20.99	0.19	0.25

Table II below summarizes the effect of the austenite percentage level on the hardness and toughness of the heats of Table I both in the annealed and austenitized condition. In Table II the heats are listed in the order of increasing austenite content. Heats L, I, B, J and K fall within the preferred austenite levels of 20 percent to 30 percent, and heats I and B have optimum properties.

TABLE II

Ann.=Annealed 788° C.-4 hrs.-A.C.
Aus.=Austenitized 1,038° C.-15 mins.-W.Q.

Effect of Austenite on Properties

(Heats are listed in order of increasing austenite contents)

Heat No.	C	Mn	Cr	N	Rockwell hardness		CVN impact strength, kgm./cm.²		Percent austenite measured		
					Ann.	Aus.	Ann.	Aus.	Ann.	Aus.	Avg.
A	0.12	0.75	26	0.20	------	------	0.4	0.6	2	2	2
G	0.015	5.9	21.1	0.11	B86	B91	1.0	3.2	6	6	6
D	0.019	6.1	24.8	0.24	B91	B95	0.6	2.2	4	10	7
C	0.032	6.2	27.3	0.20	B93	B92	0.6	0.4	9	9	9
H	0.017	6.1	21.1	0.17	B90	B92	2.6	6.4	12	9	11
M	0.009	6.0	15.3	[1] 0.22	C42	C44	1.1	2.8	8	20	14
O	0.008	3.4	20.6	[2] 0.22	B90	B94	0.8	8.3	7	30	18
L	0.009	5.8	24.1	0.25	B94	B96	2.2	11.2	19	21	20
I	0.013	6.0	21.1	0.23	B95	B95	5.4	16.5+	21	20	20
B	0.016	5.8	21.1	0.23	B92	B95	8.6	16.5+	25	25	25
J	0.035	6.0	21.2	0.24	B95	B95	5.3	16.5+	26	24	25
K	0.013	5.9	22.5	0.26	B95	B96	4.3	16.5+	24	32	28
N	0.007	5.8	17.8	[1] 0.26	C31	C30	0.4	1.8	34	32	33
P	0.008	8.8	20.9	0.25	B97	B95	16.5+	16.5+	38	32	35
Q	0.055	5.7	21.0	0.25	B96	B95	5.4	16.5+	37	35	36
E	0.020	6.0	21.1	0.23	B100	B96	16.5+	16.5+	65	58	61
F	0.020	5.7	20.4	0.22	B95	B92	16.5+	16.5+	92	89	90

[1] Low chromium austenite transformed to martensite.
[2] Low manganese austenite transformed to ferrite.

A Charpy V notch impact strength of 2 kgm/cm² in the annealed condition is considered the minimum acceptable toughness.

The austenite percentage was measured on a calibrated permanent magnet gauge known as a MAGNE-GAGE.

The data of Table II indicate that for nitrogen contents over about 0.20 percent, an average of at least 20 percent austenite is needed to impart good toughness. With nitrogen contents less than about 0.20 percent, a minimum average austenite level of 10 percent is sufficient to impart satisfactory toughness.

Tables III through VIII below list certain selected heats and compare the effect on hardness and toughness of variation of chromium, manganese, nitrogen, carbon, nickel, and chromium plus nickel, respectively, all other elements in each Table being substantially constant.

The data on hardness are included to show transformation to martensite. High hardness indicates that transformation to martensite has occurred. The magnetism values measure both ferrite and martensite since both are magnetic, but if the hardness does not increase after annealing or austenitizing, substantially all the magnetic phase remains as ferrite.

TABLE III

Effect of Chromium Content on Properties
(Heats are listed in order of increasing chromium)

Heat No.	Cr	Hardness		CVN impact strength, kgm./cm.²		Percent austenite measured		
		Ann.	Aus.	Ann.	Aus.	Ann.	Aus.	Avg.
M [1]	15.3	C42	C44	1.1	2.8	8	20	14
N [1]	17.8	C31	C30	0.4	1.8	34	32	33
I	21.1	B95	B95	5.4	16.5+	21	20	20
B	21.1	B92	B94	8.6	16.5+	25	25	25
D	25.0	B91	B95	0.6	2.2	4	10	7
C	27.3	B93	B93	0.6	0.4	9	3	6

[1] Much of the austenite in these heats transformed to martensite.

TABLE IV

Effect of Manganese Content on Properties
(Heats are listed in order of increasing manganese)

Heat No.	Mn	Hardness		CVN impact strength, kgm./cm.²		Percent austenite measured		
		Ann.	Aus.	Ann.	Aus.	Ann.	Aus.	Avg.
O [1]	3.4	B90	B94	0.8	8.3	7	30	18
B	5.8	B92	B94	8.6	16.5+	25	25	25
I	6.0	B95	B95	5.4	16.5+	21	20	20
P	8.8	B97	B95	16.5+	16.5+	38	32	35

[1] Some of the austenite in this heat appears to have transformed to ferrite.

From Table III it will be noted that with all other elements substantially constant, chromium contents of less than about 19 percent permit the austenite to

TABLE V

Effect of Nitrogen Content on Properties
(Heats are listed in order of increasing nitrogen)

Heat No.	N	Hardness Ann.	Hardness Aus.	CVN impact strength, kgm./cm.² Ann.	CVN impact strength, kgm./cm.² Aus.	Percent austenite measured Ann.	Percent austenite measured Aus.	Percent austenite measured Avg.
G	0.11	B86	B91	1.0	3.2	6	6	6
H	0.17	B90	B92	2.6	6.4	12	9	11
I	0.23	B95	B95	5.4	16.5+	21	20	20
B	0.23	B92	B94	8.6	16.5+	25	25	25

TABLE VI

Effect of Carbon Content on Properties
(Heats are listed in order of increasing carbon)

Heat No.	C	Hardness Ann.	Hardness Aus.	CVN impact strength, kgm./cm.² Ann.	CVN impact strength, kgm./cm.² Aus.	Percent austenite measured Ann.	Percent austenite measured Aus.	Percent austenite measured Avg.
I	0.013	B95	B95	5.4	16.5+	21	20	20
B	0.016	B92	B95	8.6	16.5+	25	25	25
J	0.036	B95	B95	5.3	16.5+	26	24	25
Q	0.055	B96	B96	5.4	16.5+	37	35	36

the range of 0.013 percent to 0.055 percent increase the austenite content but have little effect on toughness.

Table VII shows the effect of nickel in control of the austenite-ferrite balance. With all other elements substantially constant, nickel contents in the range of 0.14 percent to 5.1 percent increase the austenite from about 20 percent to about 90 percent with good toughness over the entire range.

The effect on toughness of varying the chromium and nickel contents while maintaining a constant austenite level is shown in Table VIII. With all other elements substantially constant, a chromium content of just over 24 percent with 1.2 percent nickel cause a significant decrease in toughness.

Mechanical properties of the steels of the invention are set forth in Table IX below.

TABLE IX

Heat	Annealed U.T.S., MN/m.²	Annealed 0.2% Y.S., MN/m.²	Annealed Percent elong. in 5 cm.	Annealed Percent red. area	Annealed Rockwell hardness	Annealed CVN impact strength, kgm./cm.²	Austenitized U.T.S., MN/m.²	Austenitized 0.2% Y.S., MN/m.²	Austenitized Percent elong. in 5 cm.	Austenitized Percent red. area	Austenitized Rockwell hardness	Austenitized CVN impact strength, kgm./cm.²
B	785	516	40	50	B92	8.6	682	434	40	68	B95	16.5+
E	750	430	48	69	B100	16.5+	746	465	44	71	B96	16.5+
H	710	434	39	51	B90	2.6	646	434	38	69	B92	6.4
I	756	468	38	49	B95	5.4	695	441	39	67	B95	16.5+
J					B95	5.3	710	454	40	68	B95	16.5+
K	744	516	31	57	B95	4.3	710	489	36	68	B96	16.5+
L	724	482	32	56	B94	2.2	724	530	36	65	B96	11.2
P	764	454	47	65	B97	16.5+	703	441	45	74	B95	16.5+
Q	860	427	40	44	B96	5.4	710	441	45	69	B95	16.5+

TABLE VII

Effect of Nickel Content on Properties
(Heats are listed in order of increasing nickel)

Heat No.	Ni	Hardness Ann.	Hardness Aus.	CVN impact strength, kgm./cm.² Ann.	CVN impact strength, kgm./cm.² Aus.	Percent austenite measured Ann.	Percent austenite measured Aus.	Percent austenite measured Avg.
B	0.14	B92	B94	8.6	16.5+	25	25	25
I	0.21	B95	B95	5.4	16.5+	21	20	20
E	2.6	B100	B96	16.5+	16.5+	65	58	61
F	5.1	B95	B92	16.5+	16.5+	92	89	90

TABLE VIII

Effect of Chromium and Nickel Content with Constant Austenite on Properties
(Heats are listed in order of increasing Cr and Ni)

Heat No.	Cr	Ni	Hardness Ann.	Hardness Aus.	CVN impact strength, kgm./cm.² Ann.	CVN impact strength, kgm./cm.² Aus.	Percent austenite measured Ann.	Percent austenite measured Aus.	Percent austenite measured Avg.
B	21.1	0.14	B92	B94	8.6	16.5+	25	25	25
I	21.1	0.21	B95	B95	5.4	16.5+	21	20	20
K	22.5	0.74	B95	B96	4.3	16.5+	24	32	28
L	24.1	1.22	B94	B96	2.2	11.2	19	21	20

transform to martensite, thereby increasing the hardness and reducing the impact strength. Chromium contents greater than about 24 percent decrease the quantity of austenite and the impact toughness.

Table IV indicates that with all other elements substantially constant manganese contents of less than about 4 percent result in a transformation of austenite to ferrite.

Table V shows the effect of nitrogen in control of the austenite-ferrite balance. Nitrogen contents of less than about 0.12 percent, with all other elements substantially constant, result in too low an austenite content to provide good toughness.

The effect of carbon in control of the austenite-ferrite balance is shown in Table VI. With all other elements substantially constant, carbon contents within

Weld area corrosion tests were conducted on samples of Heat B, a preferred composition of the invention, with the following results:

$CuSO_4$ A393 Ann.	$CuSO_4$ A393 Aus.	65% Boiling HNO_3 Ann.	65% Boiling HNO_3 Aus.	Boiling $MgCl_2$ 240 Hours Ann.	Boiling $MgCl_2$ 240 Hours Aus.
No corrosion	No corrosion	.0020 IPM No accel. corr.	.0014 IPM No. accel corr.	No Cracks	No Cracks

The boiling HNO_3 tests comprised 3 48-hour periods.

From the above data it is apparent that there is provided a stainless steel which, by reason of its composition and critical balance of essential elements, achieves the objectives hereinbefore stated.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A stainless steel having a two-phase structure comprising between 10 percent and 50 percent austenite in a ferrite matrix, consisting essentially of up to about 0.06 percent carbon, about 4.0 percent to less than 11.0 percent manganese, about 19 percent to about 24 percent chromium, about 0.12 percent to about 0.26 percent nitrogen, nickel up to about 3.0 percent, phosphorus and sulfur up to about 0.03 percent each, silicon up to about 1.0 percent, copper and cobalt up to about 0.5 percent each, and remainder substantially iron.

2. The stainless steel of claim 1, containing about 0.02 percent carbon, about 6.0 percent manganese, about 21.0 percent chromium, about 0.20 percent nitrogen, about 0.20 percent nickel, and about 0.40 percent silicon.

3. The stainless steel of claim 1, wherein carbon is present in an amount of about 0.02 percent.

4. The stainless steel of claim 1, wherein manganese is present in the amount of about 6.0 percent.

5. The stainless steel of claim 1, wherein chromium is present in the amount of about 21.0 percent.

6. The stainless steel of claim 1, wherein nitrogen is present in the amount of about 0.20 percent.

7. The stainless steel of claim 1, wherein nickel is present in the amount of about 0.20 percent.

8. The stainless steel of claim 1, wherein molybdenum is substituted for chromium on a 1:1 basis in amounts up to about 5 percent.

9. The stainless steel of claim 1, including columbium in amounts up to about 1 percent.

10. A stainless steel having a two-phase structure comprising between 20 percent and 30 percent austenite in a ferrite matrix, consisting essentially of about 0.02 percent carbon, about 6.0 percent manganese, about 21.0 percent chromium, about 0.20 percent nitrogen, about 0.20 percent nickel, phosphorus and sulfur low, about 0.40 percent silicon, copper and cobalt low, and balance substantially iron.

11. Welded articles having a two-phase structure comprising between 10 percent and 50 percent austenite in a ferrite matrix, consisting essentially of up to about 0.06 percent carbon, about 4.0 percent to less than 11.0 percent manganese, about 19 percent to about 24 percent chromium, about 0.12 percent to about 0.26 percent nitrogen, nickel up to about 3.0 percent, phosphorus and sulfur up to about 0.03 percent each, silicon up to about 1.0 percent, copper and cobalt up to about 0.5 percent each, and remainder substantially iron.

12. Cold headed fasteners having a two-phase structure comprising between 10 percent and 50 percent austenite in a ferrite matrix, consisting essentially of up to about 0.06 percent carbon, about 4.0 percent to less than 11.0 percent manganese, about 19 percent to about 24 percent chromium, about 0.12 percent to about 0.26 percent nitrogen, nickel up to about 3.0 percent, phosphorus and sulfur up to about 0.03 percent each, silicon up to about 1.0 percent, copper and cobalt up to about 0.5 percent each, and remainder substantially iron.

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