United States Patent [19]

Espy

[11] **3,753,693**

[45] **Aug. 21, 1973**

[54] **CHROMIUM-NICKEL-MANGANESE-NITROGEN AUSTENITIC STAINLESS STEEL**

[75] Inventor: **Ronald H. Espy**, Randallstown, Md.

[73] Assignee: **Armco Steel Corporation,** Middletown, Ohio

[22] Filed: **May 6, 1971**

[21] Appl. No.: **141,005**

[52] **U.S. Cl.** .... **75/128 A,** 75/128 N, 75/125

[51] **Int. Cl.** **C22c 39/20**

[58] **Field of Search** .... 75/128 A, 128 N

[56] **References Cited**

UNITED STATES PATENTS

2,138,289	11/1938	Becket	75/128 A
2,225,440	12/1940	Becket	75/128 A
3,112,195	11/1963	Souresny	75/128 A
3,183,081	5/1965	Clarke	75/128 A
3,192,041	6/1965	Kanter	75/128 A
3,306,736	2/1967	Rundell	75/128 N

Primary Examiner—Hyland Bizot
Attorney—Melville, Strasser, Foster & Hoffman

[57] **ABSTRACT**

An austenitic stainless steel having good austenite stability, a very low work hardening rate and excellent weld ability by fillerless fusion welding techniques comprising from 17 to 19 percent chromium, from 4 to 10 percent nickel, from 11 to 13 percent manganese, from 0.01 to 0.16 percent nitrogen, 0.06 maximum carbon, up to 1 percent silicon, up to 2 percent molybdenum, up to 1.5 percent copper, and remainder iron except for incidental impurities. The 0.2 percent yield strength of the steel in the annealed condition ranges from about 172.5 to 345 MN/m² (25 to 50 ksi). The alloys have particular utility in applications involving cold heading.

9 Claims, No Drawings

CHROMIUM-NICKEL-MANGANESE-NITROGEN AUSTENITIC STAINLESS STEEL

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an austenitic chromium-nickel-manganese-nitrogen stainless steel having good austenite stability, a very low work hardening rate (specifically, a cold work hardening factor (hereinafter abbreviated as CWHF) of less than about 110 by the compression test reported in *Transactions Of The A.S.M.*, Vol. 39, pp 843–864, by F. K. Bloom et al.) and excellent weldability. The 0.2 percent yield strength of the steel of the invention in the annealed condition ranges from about 172.5 to about 345 MN/m² (about 25 to about 50 ksi). Although not so limited, the alloys of the invention find particular utility in applications involving cold heading, and in fusion welding techniques where hot cracking is a problem when using conventional stainless steel alloys.

2. Description of the Prior Art

Presently available stainless steel alloys having .2% yield strengths ranging from about 172.5 to 345 MN/m² which are stable austenitic alloys frequently cannot be welded by fillerless fusion welding techniques; conversely alloys readily weldable by fillerless fusion welding are not low strength, stable austenitic alloys which have a low work hardening rate.

AISI Types 305 (containing 17 – 19 percent chromium, 10 – 13 percent nickel, 2 percent maximum manganese, 0.12 percent maximum carbon and 1 percent maximum silicon) and 310 (containing 24 – 26 percent chromium, 19 – 22 percent nickel, 2 percent maximum manganese, 0.25 percent maximum carbon, and remainder substantially iron) produce fully austenitic welds which are very prone to microfissuring.

AISI Type 304 (containing 18 – 20 percent chromium, 8 – 12 percent nickel, 2 percent maximum manganese, 0.08 percent maximum carbon, 1 percent maximum silicon, and remainder substantially iron) and the high nitrogen equivalent Type 304N produce satisfactory weldments but work harden rapidly because of some transformation to martensite.

A proprietary alloy ARMCO 21-6-9 (containing 21 percent chromium, 6 percent nickel, 9 percent manganese, 0.3 percent nitrogen, 0.05 percent carbon and remainder substantially iron) is weldable and stable but has a 0.2 percent yield strength of about 448.5 MN/m² (65 ksi), which is substantially in excess of that which can be tolerated for many cold forming applications such as cold heading.

Copending U.S. Patent application Ser. No. 868,893, filed Oct. 23, 1969, in the name of George N. Goller and Ronald H. Espy, discloses an austenitic stainless steel of high stability, high strength and good toughness at cryogenic temperatures, containing 15.5 – 20 percent chromium, 1.1 – 4 percent nickel, 11 – 15 percent manganese, 0.28 – 0.38 percent nitrogen, 0.01 – 0.11 percent carbon, 1 percent maximum silicon, up to 3.5 percent molybdenum, and remainder substantially iron. While this alloy is weldable and stable, again the 0.2 percent yield strength is about 448.5 MN/m², which is substantially in excess of that which can be tolerated for many forming operations.

An alloy developed by U.S. Steel Corporation for cryogenic application (containing 18 percent chromium, 5.5 percent nickel, 15 percent manganese, 0.38 percent nitrogen, 0.08 percent carbon, 0.4 percent silicon and remainder substantially iron) exhibits yield strength in the annealed condition in the neighborhood of about 483 MN/m² at room temperature, which again is far above that which can be tolerated for many forming operations. Moreover, there is no indication that this alloy can be welded by fillerless fusion welding techniques (See *Metals Engineering Quarterly*, *ASM*, August 1969, pages 1–5, C. E. Spaeder, Jr. et al.)

In *Transactions Of The A.S.M.*, Vol. 39, pp 843–864, F. K. Bloom, G. N. Goller and P.G. Mabus describe a special compression test for determining cold work hardening of chromium-nickel and plain chromium stainless steels. Data presented in this article indicate that at chromium levels of 15 – 20 percent the CWHF drops rapidly as the nickel content increases to about 10 to 12 percent. For chromium-nickel steels containing about 17 – 19 percent chromium, CWHF values below 100 were attained only in alloys containing more than 10 percent nickel. The article further indicates that in the 17 percent chromium - 7 percent nickel alloy an increase in the nitrogen content (between 0.019 percent and 0.094 percent) decreases the CWHF substantially while in the 18 percent chromium - 12 percent nickel alloy an increase in the manganese content (between 0.42 percent and 3.68 percent) decreases the CWHF very slightly. On the other hand, in the 18 percent chromium - 8 percent nickel alloy an increase in the carbon content (between 0.03 percent and 0.16 percent) increases the CWHF very sharply up to 0.10 percent carbon and has much less effect thereabove. With a nickel content of about 6.5 – 8.5 percent an increase in the chromium content (between 15 and 19 percent) gradually decreases the CWHF, the variation being linear at constant nickel levels.

It is thus apparent that there is not presently available an alloy having the combination of properties of an annealed 0.2 percent yield strength in the range of 172.5 to 345 MN/m², good austenite stability, a CWHF of less than 110 and preferably below 105, and ready weldability by fillerless fusion welding techniques without danger of microfissuring.

SUMMARY

It is a principal object of this invention to provide a stable austenitic stainless steel possessing the novel combination of properties set forth above, which is not presently attainable in any conventional alloy. In its broadest aspect the steel of the present invention consists essentially of from 17.0 to 19.0 percent chromium, from 4.0 to 10.0 percent nickel, from 11.0 to 13.0 percent manganese, from 0.01 to 0.16 percent nitrogen, 0.06 percent maximum carbon, up to 1.0 percent silicon, up to 2.0 percent molybdenum, up to 1.5 percent copper, up to 0.04 percent phosphorus, up to 0.04 percent sulfur, and remainder substantially iron except for incidental impurities.

The nickel equivalent (according to the formula: Ni equiv. = %Ni + 30 × %N + 27 × %C) of the alloy of the invention is between about 10 and 12. Balancing of the nickel, nitrogen and carbon contents is critical in order to obtain a wrought product which is 100 percent austenitic and has high stability, so that cold working will not result in any substantial transformation of austenite to martensite. Such a material has a very low work hardening rate; moreover, control of the carbon and nitrogen contents achieves a 0.2 percent yield strength in the annealed condition within the desired range of 172.5 – 345 MN/m², thereby producing a material which is ideal for cold heading operations and the like.

Balancing of the carbon, chromium, nickel, manganese and nitrogen contents within the ranges of the present invention results in an alloy which is readily weldable by fusion welding techniques without suffering from hot cracking, by reason of the formation of from 2 to 5 percent ferrite in an as-welded weld deposit.

In the steel of this invention chromium is essential within the range of about 17 to about 19 percent. With less than 17 percent chromium, corrosion resistance suffers, while more than 19 percent chromium would upset the austenite balance. When nickel is present in the range of about 4 to 7 percent, a minimum of about 17 percent chromium is needed to ensure a low working hardening rate.

At least about 4 percent nickel is essential for its function as an austenite former. More than about 10 percent nickel would upset the control of the desired percentage of ferrite in a weld deposit. Moreover, it has been found that a low work hardening rate is achieved in the steels of the invention with a nickel content not exceeding 10 percent. This is not predictable from the above Bloom et al. article.

Manganese must be present within the range of about 11 to about 13 percent in order to provide austenite stability during cold working without adversely affecting the strength and weldability of the alloy. Manganese is also a ferrite former in the sense that the formation of delta ferrite is promoted during solidification of weld metal. The range of about 11 to about 13 percent permits the formation of the desired small percentage of ferrite in the as-solidified weld metal which in turn prevents hot cracking or microfissuring.

Nitrogen within the range of 0.01 to 0.16 percent is necessary both for its role as an austenite former and in controlling the yield strength and work hardening rate within the desired limits.

Carbon is of course present in the steel of the invention and preferably amounts to about 0.04 percent. A maximum of about 0.06 percent carbon can be tolerated, and it cooperates with the nitrogen in functioning as an austenite former and in providing the desired strength. However, carbon above 0.06 percent is not desirable as an austenite former because it has a detrimental effect on the corrosion resistance of heat-affected zones adjacent welds. On the other hand, if the carbon content is below about 0.015 percent, there is a danger that the austenite stability will suffer, permitting some transformation to martensite to occur with consequent increase in work hardening rate.

Up to about 1.0 percent silicon does not adversely affect the properties of the steel. Similarly, phosphorus and sulfur may be present as impurities in amounts up to about 0.04 percent each.

Molybdenum may be substituted for chromium on a 1:1 basis in amounts up to about 2.0 percent for improved corrosion resistance in chloride containing media.

Copper may be substituted for nickel on a 3:1 basis in amounts up to about 1.5 percent for improved corrosion resistance in sulfuric acid media.

From the above discussion it will be apparent that a balancing of the nickel, nitrogen and carbon contents

results in attainment of the desired strength levels and the fully austenitic structure of the wrought steel. On the other hand, manganese does not function to any substantial extent as an austenite former, but rather as an austenite stabilizer. For this reason, the necessary nickel equivalent of 10 to 12 is calculated solely on the basis of the nickel, nitrogen and carbon contents as set forth above.

While there are other stable austenitic alloys, such as that of the aforementioned Göller and Espy application Ser. No. 868,893, the yield strength of that alloy is so high at the outset that it would be extremely difficult to effect cold heading on such material due to its high initial strength. Moreover, the work hardening factor is substantially in excess of the preferred maximum of about 105 CWHF for alloys of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

While the benefits of the present invention are attained by the broad composition set forth above, it is possible to control the yield strength within even narrower limits so as to obtain a steel having the desired strength for a particular end use and particular fabricating properties, by balancing the composition within preferred limits. More specifically, a lower strength alloy is obtained with a lower nitrogen content, with the nickel content increased proportionately to offset the decreased nitrogen and maintain the desired austenitic structure. The converse is also true.

A preferred steel of the invention having an annealed 0.2 percent yield strength within the range of 172.5 to 276 MN/m² (20 to 40 ksi), which also possesses good austenite stability, a CWHF not above about 100, and excellent weldability consists essentially of from 17.0 to 19.0 percent chromium, from greater than 7.0 to 10.0 percent nickel, from 11.0 to 13.0 percent manganese, from 0.01 to 0.07 percent nitrogen, 0.06 percent maximum carbon, up to 1.0 percent silicon, up to 2.0 percent molybdenum, up to 1.5 percent copper, up to 0.04 percent phosphorus, up to 0.04 percent sulfur, and remainder substantially iron except for incidental impurities.

A more preferred composition having an annealed 0.2 percent yield strength of about 207 MN/m² (30 ksi) consists essentially of about 18.0 percent chromium, about 9.0 percent nickel, about 12.0 percent manganese, about 0.020 percent nitrogen, about 0.04 percent carbon, about 0.40 percent silicon, about 0.015 percent phosphorus, about 0.015 percent sulfur, and remainder substantially iron except for incidental impurities.

A preferred composition having an annealed 0.2 percent yield strength in the range of 276 to 345 MN/m² (40 to 50 ksi), along with good austenite stability, a CWHF not above about 110, and excellent weldability consists essentially of from 17.0 to 19.0 percent chromium, from 4.0 to 7.0 percent nickel, from 11.0 to 13.0 percent manganese, from greater than 0.07 to 0.16 percent nitrogen, 0.06 percent maximum carbon, up to 1.0 percent silicon, up to 2.0 percent molybdenum, up to 1.5 percent copper, up to 0.04 percent phosphorus, up to 0.04 percent sulfur, and remainder substantially iron except for incidental impurities.

A more preferred composition having an annealed 0.2 percent yield strength of about 310 MN/m² (45 ksi) consists essentially of about 18.0 percent chromium, about 5.0 percent nickel, about 12.0 percent manganese, about 0.13 percent nitrogen, about 0.04 percent carbon, about 0.40 percent silicon, about 0.015 percent phosphorus, about 0.015 percent sulfur, and remainder substantially iron except for incidental impurities.

In these preferred and more preferred compositions, the nickel equivalent, calculated according to the formulation above set forth, ranges between about 10 and about 12.

From a comparison of the above compositions it will be apparent that the desired yield strength is obtained by balancing the nickel and nitrogen contents, in inverse proportion to one another, with other elements remaining constant. More specifically, for a yield strength in the range of 172.5 to 276 MN/m^2 (25 to 40 ksi) the nickel content of from greater than 7.0 to 10 percent (particularly from 8.0 to 10 percent) is varied inversely with from 0.01 to about 0.07 percent nitrogen. Similarly, for a yield strength in the range of 276 to 345 MN/m^2 (40 to 50 ksi) the nickel content of from 4.0 to 7.0 percent (particularly from 4.0 to 6.0 percent) is varied inversely with from greater than 0.07 to 0.16 percent nitrogen.

In the steels of the invention the CWHF values increase with an increase in the nitrogen content, contrary to the findings of the above-mentioned Bloom et al. article. Even though all these alloys are stable and do not transform to martensite upon cold deformation, the crystalline lattice is strengthened by the generation of dislocations. The maintenance of a high manganese content in the steels of this invention contributes to the austenite stability, thereby preventing transformation to martensite upon cold forming and assuring a low work hardening rate, while permitting variation in the yield strength (between 172.5 and 345 MN/m^2) by variation of the nitrogen and nickel contents relative to one another.

The steel of this invention may be prepared by melting in the electric furnace, under either air or vacuum conditions. It may be further refined, as by vacuum degassing, and poured into ingots or continuously cast into slabs. It is then usually hot worked and cold reduced into plate, sheet, strip, bar, rod, and the like. In some instances the steel may be used in the cast or forged condition, as well as fabricated into articles which may involve welding.

For purposes of comparison the compositions of two heats of steels of the invention, together with samples of AISI Types 304 and 305, and a sample of the steel disclosed in the above-mentioned Ser. No. 868,893, are set forth in Table I below. Table II compares the mechanical properties of these steels, while Table III compares the welding properties and corrosion resistance of weldments of the same steels.

TABLE I.—COMPOSITION, WEIGHT PERCENT

Sample	Type	Cr	Ni	Mn	C	N	Si	P	S
1*	18-9-Mn	18.34	9.25	11.12	0.018	0.016	0.34	0.017	0.010
2*	18-5-Mn	18.66	5.33	11.13	0.038	0.13	0.33	0.016	0.009
3	18-3-Mn	17.50	2.94	12.54	0.056	0.33	0.42	0.009	0.009
4	AISI 305	17.56	11.05	1.03	0.032	0.010	0.38	0.014	0.013
5	AISI 304	18.19	8.81	0.77	0.053	0.030	0.37	0.019	0.029

*Steels of the present invention.

TABLE II

Sample	Type	U.T.S. K.s.i.	U.T.S. MN/m.^{2}	.2% Y.S. K.s.i.	.2% Y.S. MN/m.^{2}	Percent elong. 2" (5 cm.)	Percent red. area	CWHF compression test [1]
1*	18-9-Mn	76	524	30	207	60	72	96
2*	18-5-Mn	91	628	43	297	55	71	103
3	18-3-Mn	108	745	63	435	50	70	122
4	AISI 305	72	497	26	179	63	69	115
5	AISI 304	86	593	[2] 45	310	59	69	125

*Steels of the present invention.
[1] Trans. A.S.M., vol. 39, pp. 843–864, Bloom et al.
[2] Straightened after anneal.

TABLE III

Sample	Type	Fillerless fusion welds: Percent ferrite weld metal	Fillerless fusion welds: Condition of weld	Corrosion in 65% boiling HNO_3 as welded weldment: Inches/min.	mm./min.	Heat affected zone attack
1*	18-9-Mn	5	Sound and free of defects	0.0005	0.0127	Very light.
2*	18-5-Mn	5	do	0.0010	0.0254	None.
3	18-3-Mn	3	do	0.0020	0.0508	Do.
4	AISI 305	0	Few crater cracks	0.0006	0.0132	Do.
5	AISI 304	3	Sound and free of defects	0.0009	0.0237	Very light.

*Steels of the present invention.

From the above data it is apparent that the present invention provides a stainless steel which has high austenite stability, a yield strength ranging between 172.5 and 345 MN/m^2, which retains good fillerless weld deposit soundness throughout the entire strength range, and which has a CWHF ranging between about 95 and 105. The nitrogen and nickel contents are adjusted in order to obtain a proper weld deposit structure from fusion of the base metal (i.e. from 2 to 5 percent ferrite). The relatively high manganese content maintains the austenite stability needed for low work hardening in cold heading and other cold deformation. The high austenite stability also improves notch tensile and notch fatigue properties, desired for service applications. These properties are achieved by maintaining the carbon, chromium and silicon contents within the ranges hereinabove disclosed.

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

1. Cold formed stainless steel products having a fully austenitic structure produced from an alloy consisting essentially of from about 17.0 to 19.0 percent chromium, from greater than 7.0 percent to about 10.0 percent nickel, from about 11.0 to about 13.0 percent manganese, from about 0.01 to about 0.07 percent nitrogen, the nitrogen varying inversely with the nickel content, about 0.06 percent maximum carbon, up to about 1.0 percent silicon, up to about 2.0 percent molybdenum, up to about 1.5 percent copper, up to about 0.04 percent phosphorus, up to about 0.04 percent sulfur, and remainder substantially iron except for incidental impurities, said alloy having a cold work hardening factor of less than 100.

2. An austenitic stainless steel consisting essentially of from about 17.0 to about 19.0 percent chromium, from about 4.0 to about 10.0 percent nickel, from about 11.0 to about 13.0 percent manganese, from about 0.01 to about 0.16 percent nitrogen, about 0.06 percent maximum carbon, up to about 1.0 percent silicon, up to about 2.0 percent molybdenum, up to about 1.5 percent copper, up to about 0.04 percent phosphorus, up to about 0.04 percent sulfur, all percentages being by weight, and remainder substantially iron, the nickel, nitrogen and carbon being balanced to give a nickel equivalent of about 10 to 12 according to the formula

$$\text{Ni equiv.} = \%\text{Ni} + 30 \times \%\text{N} + 27 \times \%\text{C},$$

and wherein nitrogen is varied inversely from 0.16 to greater than 0.07 percent for nickel contents ranging from 4.0 to 7.0 percent and from 0.07 to 0.01 percent for nickel contents ranging from greater than 7.0 to 10.0 percent, whereby said steel is fully austenitic in the wrought condition and contains from about 2 to about 5 percent ferrite in an as-welded weld deposit.

3. The steel claimed in claim **2**, containing from greater than about 7.0 to about 10.0 percent nickel, and from about 0.01 to about 0.07 percent nitrogen, wherein the 0.2 percent yield strength in the annealed condition ranges between about 172 and about 276 MN/m^2 (about 25 and about 40 ksi).

4. The austenitic stainless steel claimed in claim **3**, consisting essentially of about 18.0 percent chromium, about 9.0 percent nickel, about 12.0 percent manganese, about 0.020 percent nitrogen, about 0.04 percent carbon, about 0.40 percent silicon, about 0.015 percent phosphorus, about 0.015 percent sulfur, and remainder substantially iron.

5. The steel claimed in claim **2**, containing from about 4.0 to about 7.0 percent nickel, and from greater than about 0.07 to about 0.16 percent nitrogen, wherein the 0.2 percent yield strength in the annealed condition ranges between about 276 and about 345 MN/m^2 (about 40 and about 50 ksi).

6. The steel claimed in claim **5**, consisting essentially of about 18.0 percent chromium, about 5.0 percent nickel, about 12.0 percent manganese, about 0.13 percent nitrogen, about 0.04 percent carbon, about 0.40 percent silicon, about 0.015 percent phosphorus, about 0.015 percent sulfur, and remainder substantially iron.

7. The steel claimed in claim **2**, wherein molybdenum is substituted for chromium on a 1:1 basis in amounts up to about 2.0 percent.

8. The steel claimed in claim **2**, wherein copper is substituted for nickel on a 3:1 basis in amounts up to about 1.5 percent.

9. Filler wire for welding stainless steel articles, said wire consisting essentially of from about 17.0 to about 19.0 percent chromium, from about 4.0 to about 7.0 percent nickel, from about 11.0 to about 13.0 percent manganese, from greater than 0.07 to about 0.16 percent nitrogen, the nitrogen varying inversely with the nickel content, about 0.06 percent maximum carbon, up to about 1.0 percent silicon up to about 2.0 percent molybdenum, up to 1.5 percent copper, up to about 0.04 percent phosphorus, up to about 0.04 percent sulfur, and remainder substantially iron, the nickel, nitrogen and carbon being so balanced as to cause formation of from about 2 to about 5 percent ferrite in a weld deposit.

* * * * *