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[54] **CORROSION RESISTANT AUSTENITIC STAINLESS STEEL**

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[52] **U.S. Cl.** ..... **75/125;** 75/126 B; 75/126 C; 75/126 J; 75/128 A; 75/128 N; 75/128 W; 148/38

[51] **Int. Cl.**.. **C22c 39/26;** C22c 39/48; C22c 39/54

[58] **Field of Search** ..... 148/38; 75/125, 126 B, 75/126 C, 126 L, 126 M, 126 J, 128 A, 128 P, 128 N, 128 W

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[57] **ABSTRACT**

An austenitic stainless steel containing 0.25 percent Max. carbon, 15–20 percent manganese, 1% Max. silicon, 16–22 percent chromium, 3 percent Max. nickel, 0.5–3 percent molybdenum, 0.5–2 percent copper, 0.2–0.8 percent nitrogen, and the balance iron which in its annealed condition is substantially fully austenitic and is capable of an ultimate tensile strength in its annealed condition of about 125 ksi, and which can be cold worked to strength levels in excess of 200 ksi in which condition it is substantially fully austenitic and nonmagnetic.

10 Claims, No Drawings

CORROSION RESISTANT AUSTENITIC STAINLESS STEEL

BACKGROUND OF THE INVENTION

This invention relates to austenitic stainless steel having outstanding corrosion resistance and, more particularly, to such steel which contains as essential elements only manganese, chromium, molybdenum, copper, nitrogen and iron, and which has improved corrosion resistance and strength as compared to such nickel-bearing stainless steel alloys as A.I.S.I. Type 304 or Type 316.

Hitherto, efforts have been made to provide nickel-free or low nickel-bearing austenitic stainless steel alloys at least comparable to A.I.S.I. 300 series alloys, such as Type 304 or Type 316, in corrosion resistance and strength, but such efforts have left much to be desired. For example, Dulis and Day U.S. Pat. No. 3,075,839 relates to an alloy containing up to 0.15 percent carbon, 11–14 percent manganese, 14–18 percent chromium, 0.3 to 3 percent molybdenum, 0.15 to 0.55 percent nitrogen and the balance iron. Optional elements include up to 2 percent copper, up to 3 percent silicon, but both are included as essential elements in the preferred composition of the Dulis and Day patent. That patent emphasizes that when manganese is present in amounts substantially greater than about 14 percent, it tends to form ferrite and is, therefore, objectionable in larger amounts even though the amount of nitrogen which can be kept in solution in such steels can be increased by increasing the amount of manganese.

Allen U.S. Pat. No. 3,615,366 relates to a stainless steel alloy consisting of up to 0.15 percent carbon, 3 to 10 percent manganese, 0.15 to 1 percent silicon, 15–19 percent chromium, 3.5 to 6 percent nickel, 0.5 to 4 percent copper, 0.04 to 0.4 percent nitrogen and the remainder iron. Allen, like Dulis and Day, warns against the use of excessive amounts of manganese and points out that excessive manganese results in the formation of ferrite at hot-working temperatures with resultant risk of breakage in the hot mill. Allen also points out that above 10 percent, manganese becomes uneconomical.

Despite the development of those steels and others, it is yet a desirable goal to provide a stainless steel with little or no nickel which has higher strength than A.I.S.I. Types 304 and 316 and which has comparable or better corrosion resistance than those types.

SUMMARY OF THE INVENTION

It is, therefore, a principal object of this invention to provide an austenitic stainless steel containing little or no nickel which can be produced using conventional metallurgical techniques, using less costly alloying elements than alloys such as Type 304 and Type 316 and yet having greater strength and at least comparable corrosion resistance.

A more specific object is to provide such an alloy which contains as essential elements only manganese, chromium, molybdenum, copper, nitrogen and iron, which has greater strength than such alloys as A.I.S.I. Type 304 and Type 316, and which has better resistance to corrosion than such alloys in reducing media such as dilute sulfuric acid and in pitting environments such as chloride-containing media.

The foregoing objects and further advantages of the present invention are attained in a significant measure by providing an alloy consisting essentially of the following elements in about the amounts stated in the broad ranges and are fully attained by providing an alloy consisting essentially of about the more restricted amounts of the elements indicated in the preferred ranges. Here and elsewhere throughout this application by percent is intended weight percent unless otherwise indicated and the balance of each composition is essentially iron plus incidental impurities and such other elements customarily employed in the preparation of such compositions.

	Broad	Preferred
Carbon	0.25*	0.05–0.15
Manganese	15–20	16–19
Silicon	1*	0.75*
Phosphorus	0.05*	0.03*
Sulphur	0.5*	0.03*
Chromium	16–22	17–19
Nickel	3*	1*
Molybdenum	0.5–3	0.5–1.5
Copper	0.5–2	0.5–1.5
Boron	0.01*	**
Nitrogen	0.2–0.8	0.4–0.65

*Maximum
**Preferably not added or no more than a residual amount

Silicon is present as an incident to the steel making process because of its use as a deoxidizer but other deoxidizing agents such as aluminum though less preferred can also be used. The larger amounts of sulfur indicated in the broad range are used when it is desired to impart greater free machining to the composition and for this purpose other free-machining additives such as up to 0.75 percent selenium could also be used. Thus, by reference to 0.5 percent sulfur it is intended to include appropriate amounts of such other free-machining additives as are used in austenitic stainless steels.

It is to be noted that while the best all-around properties are provided by the preferred composition, it is not intended to restrict the composition of this invention to the ranges indicated in tabular form which was solely for ready reference. It is contemplated that any one or more of the preferred ranges indicated can be used with any one or more of the broad ranges indicated for the remaining elements.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In this composition carbon and nitrogen work as austenite formers with carbon being tolerable in amounts up to a maximum of about 0.25 percent to ensure freedom from ferrite. However, excessive amounts of carbon are undesirable because of impairment of corrosion resistance from the formation of carbides when more carbon is introduced than can be retained in solid solution in the steel. Because of its beneficial effect, from about 0.05–0.15 percent carbon is preferably included in the steel.

As was seen, silicon is not a required alloying addition and is tolerable in an amount up to about 1 percent, but preferably is limited to no more than 0.75 percent. Phosphorus and sulfur are each preferably present, if at all, in an amount no greater than about 0.03 percent although up to a maximum of about 0.05 percent phosphorus can be present. In the case of sulfur as much as 0.5 percent, or as a substitute 0.75 percent se-

lenium, can be present to improve machinability or free-cutting properties when that is desired and any accompanying impairment of corrosion resistance can be tolerated. When used together the combined total of $1.5 \times (\%S) + (\%Se)$ should not be greater than 0.75 percent.

Manganese, like carbon and nitrogen, is an austenite former, but is much less powerful in that regard than carbon or nitrogen each of which is about 60 times stronger on a weight percent basis. Consequently, manganese, by ensuring the solubility of the larger amounts of nitrogen in this composition, has a much greater effect on maintaining the austenitic balance of the composition than it alone could provide while minimizing the possibility that unsound metal may result. For this purpose, at least about 15 percent manganese is required, but above about 20 percent, the benefit attained from further additions of manganese does not appear to be worth the added cost.

Nitrogen not only is a very strong austenite former, but also serves to strengthen this composition. When present in the preferred amount of about 0.4 to 0.65 percent, it ensures that this composition has an ultimate strength in its annealed condition of at least about 120,000 to 130,000 psi. It is, of course, necessary that the nitrogen present be retained in solution during solidification of the melt when the alloy is prepared to avoid blowy or unsound metal. Thus, while from 0.2 to 0.8 percent nitrogen can be present, the larger amounts of nitrogen must be used with the larger amounts of the other alloying elements, particularly, manganese and chromium. Nitrogen is preferably limited to about 0.65 percent, as was seen, and for best results 0.4 to 0.55 percent nitrogen is used.

Chromium is important to provide the minimum desired corrosion resistance in an oxidizing environment, and for this purpose, at least about 16 percent is required. Above about 22 percent, too much of the austenite-forming elements are required to preserve the austenitic balance of this composition. Best results are attained with about 17 to 19 percent chromium.

While nickel is an austenite-forming element, it has an adverse effect on the resistance of the composition to pitting, as for example, in chloride-containing environments. Thus, while some small amount up to a maximum of about 3 percent can be tolerated to help balance the composition as when the smaller amounts of nitrogen are used, preferably no more than residual amounts are permitted which can amount to as much as about 1 percent depending upon the nature of the materials used in making the composition.

Molybdenum contributes to the corrosion resistance of this composition and at least 0.5 percent molybdenum is present for this reason. Preferably no more than about 1.5 percent molybdenum is used because, like chromium, it is a ferrite former although up to as much as 3 percent can be present, particularly with the larger amounts of the austenite-forming elements. Larger amounts of molybdenum would tend to upset the austenitic balance of the alloy. Tungsten can be substituted for all or part of the molybdenum in the ration of 1.5 to 1, that is, 0.75 to 4.5 percent tungsten can be used or part of the molybdenum can be replaced by tungsten in the proportions stated.

Copper is an austenite-forming element, but cannot be tolerated in amounts greater than about 2 percent in this composition because of its detrimental effect on the hot workability of the composition. Preferably 0.5 to 1.5 percent copper is used because of its beneficial effect in improving corrosion resistance and also resistance to pitting in chloride-containing environments. However, as the amount of copper present is increased above about 1.5 percent, its adverse effect upon hot workability becomes apparent. Furthermore, when the amount of manganese in this composition is increased above about 18 percent, the amount of copper should be kept below 1.5 percent and preferably to no more than about 1 percent to favor hot workability.

Molybdenum and copper work together in this composition to provide better corrosion resistance than either element in a like amount can provide alone. For example, when about 1 percent each of molybdenum and copper is present, the improvement obtained is significantly greater than when about 2 percent molybdenum and no copper is present or when about 2 percent copper and no molybdenum is present.

Boron is preferably not added to this composition, and is preferably not present in amounts greater than as a residual element introduced incidentally by the materials or equipment used in the steel making process. However, if desired, up to about 0.01 percent can be included for its beneficial effect on hot workability of the composition.

The alloy of this invention can be made and shaped using essentially the same equipment, processes and temperatures normally used in the making and shaping of the A.I.S.I. 300 series austenitic stainless steels. Thus, the composition can be hot worked from a starting temperature of about 2000° to 2300°F and annealing is carried out from about 1850° to 2050°F. The balance of the alloy is maintained such that it is fully austenitic, that is no more than about 5 percent ferrite, both at room temperature and when being hot worked. The composition can be hardened and strengthened by cold reduction as is customary with the 300 series grades.

Because of its unique combination of high strength and corrosion resistance and because large amounts of nickel, a costly alloying addition present in the 300 series alloys, are not used in this composition, it is especially well suited for use in making parts, particularly, stressed parts such as turbine shafting, for use in chemical processing or other corrosive environments. This alloy is also well suited for use in making valves and load lifting members such as cables for use in handling loads to be immersed in corrosive media.

Thus, the alloy of this invention is readily prepared and worked in accordance with good standard commercial practice. The following examples of this invention were melted as small experimental ingots using an induction furnace without vacuum. Bars three-fourths in. sq. were forged from the ingots using a starting temperature of about 2150°F. Test sample blanks were cut from the bars, annealed at about 1950°F for one-half hour, water quenched and then machined into standard test specimens. In Table I, the composition of specific examples is given, the balance of each being iron and the usual incidental impurities including less than 0.015 percent phosphorus and less than 0.015 percent sulfur.

TABLE I

Ex. No.	C	Mn	Si	Cr	Ni	Mo	Cu	N
1	.09	16.07	.44	17.96	.17	.96	.99	.50
2	.09	16.07	.44	17.96	2.19	.96	.99	.47
3	.1	18.04	.36	18.03	.35	.96	.94	.65

Metallographic examination of each of the examples in the annealed condition showed each to be fully austenitic with a grain size of about A.S.T.M. 5–6. Mechanical properties obtained from standard 0.252 inch diameter tensile specimens are listed in Table II. In the table, the 0.2 percent yield strength and ultimate tensile strength are indicated in thousands of pounds per square inch (ksi) under "0.2%YS" and "UTS" respectively. The percent elongation and reduction in area are indicated under "El" and "RA" respectively, and the V-notch Charpy impact strength in foot pounds is indicated under "VNC." The results of two tests are given.

TABLE II

Ex. No.	.2%YS (ksi)	UTS (ksi)	El (%)	RA (%)	VNC (Ft. Lbs.)
1	68.1	126.8	62.3	75.7	229
	73.6	128.3	60.0	73.3	>240
2	66.8	121.2	58.0	74.9	208
	68.5	123.9	62.5	74.3	191
3	80.2	137.7	55.7	75.3	—
	77.7	135.5	55.6	75.3	—

Duplicate test specimens of each of Examples 1–3 each 1 ½ in. × ½ in. ⅛ in. with a three-sixteenths in. hole prepared as was described hereinabove were immersed in a 5 weight percent aqueous solution of ferric chloride ($FeCl_3$) at room temperature. After 3 hours the weight loss in grams was determined and found to be 0.0043 g. and 0.0045 g. for the specimens of Example 1, 0.0025 g. and 0.0033 g. for the specimens of Example 2, and 0.0014 g. and 0.0013 g. for the specimens of Example 3. Despite the apparent good result obtained in that experiment with the specimens of Example 2, nickel nevertheless has been found to be harmful to the pitting resistance of the composition and causes erratic behavior in such media.

Similar duplicate specimens were immersed in 5 weight percent sulfuric acid at a temperature of 80°C and the average corrosion rate in mils per year (mpy) after exposure of each of two specimens was calculated and found to be 2.3 mpy and 2.2 mpy for Example 1, 3.8 mpy and 0.9 mpy for Example 2, and 1.8 mpy for each of the specimens of Example 3.

Similar duplicate test specimens of each of Examples 1–3 were immersed in boiling 65 weight percent nitric acid. The average corrosion rate in mils per year after 5 48-hour periods for each specimen was calculated and found to be 42.7 mpy and 45.6 mpy for Example 1, 29.7 mpy and 29.9 mpy for Example 2, and 40.5 mpy and 42.6 mpy for Example 3.

For comparison corresponding specimens were prepared of A.I.S.I. Type 316 containing 0.05 percent carbon, 1.86 percent manganese, 0.68 percent silicon, 0.023 percent phosphorus, 0.013 percent sulfur, 17.80 percent chromium, 12.26 percent nickel, 2.19 percent molybdenum, 0.23 percent copper, and the balance iron plus incidental impurities which included about 0.025 percent nitrogen. Room temperature tensile properties were 35 ksi 0.2 percent YS, 85 ksi UTS, 60 percent El and 70 percent RA. Weight lost after 3 hours in 5 weight percent ferric chloride at room temperature was 0.0060 g., the average corrosion rate in 5 weight percent sulfuric acid at 80°C after 3 48-hour periods was found to be 20.8 mpy and 22.5 mpy. Specimens of Type 316 were not subjected to the boiling 65 w/o nitric acid test, but from past experience with Type 316 it would be expected to give an average corrosion rate of about 10 mpy.

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 corrosion resistant austenitic stainless steel alloy which is substantially fully austenitic and nonmagnetic in its annealed condition and in its cold worked condition, consisting essentially in weight percent of about

Carbon	0.25 Max.
Manganese	15–20
Silicon	1 Max.
Phosphorus	0.05 Max.
Sulfur	0.5 Max.
Chromium	16–22
Nickel	3 Max.
Molybdenum	0.5–3
Copper	0.5–2
Boron	0.01 Max.
Nitrogen	0.2–0.8

the balance being essentially iron and incidental impurities, in which up to 0.75 percent selenium can be substituted for all or part of the sulfur, and in which tungsten can be substituted for all or part of the molybdenum in the proportion of 1.5 percent tungsten for 1 percent molybdenum.

2. The alloy as set forth in claim **1**, in which copper is limited to no more than about 1 percent when the amount of manganese present is greater than about 18 percent.

3. The alloy as set forth in claim **1** containing about 0.4–0.65 percent nitrogen.

4. The alloy as set forth in claim **3** containing about 16–19 percent manganese.

5. The alloy as set forth in claim **4** containing about 17–19 percent chromium.

6. The alloy as set forth in claim **5** containing about 0.05–0.15 percent carbon, no more than about 1 percent nickel, no more than about 1.5 percent molybdenum, and no more than about 1.5 percent copper.

7. The alloy as set forth in claim **6** containing no more than about 1 percent copper when the amount of manganese exceeds about 18 percent.

8. The alloy as set forth in claim **7** containing no more than about 0.55 percent nitrogen.

9. A corrosion resistant austenitic stainless steel alloy which is substantially fully austenitic and nonmagnetic in its annealed condition and which has a room temperature ultimate tensile strength of at least about 120,000

psi in its annealed condition, said alloy consisting essentially in weight percent of about

Carbon	0.05–0.15
Manganese	16
Chromium	18
Molybdenum	1
Copper	1
Nitrogen	0.4–0.55

the balance essentially iron and incidental impurites with no more than 1 percent silicon, no more than 0.03 percent phosphorus, no more than 0.03 percent sulfur, and no more than 1 percent nickel.

10. A corrosion resistant austenitic stainless steel alloy which is substantially fully austenitic and nonmagnetic in its annealed condition and in its cold worked condition and which has a room temperature ultimate tensile strength of at least about 120,000 psi in its annealed condition, said alloy consisting essentially in weight percent of about

Carbon	0.05–0.15
Manganese	18
Chromium	18
Molybdenum	1
Copper	1
Nitrogen	0.4–0.55

and the balance essentially iron and the incidental impurities with no more than 1 percent silicon, no more than 0.03 percent phosphorus, no more than 0.03 percent sulfur, and no more than 1 percent nickel.

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