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[54] **FREE-MACHINING AUSTENITIC STAINLESS STEEL**

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[58] **Field of Search** ..... 148/38; 75/128 P, 128 W, 75/128 R

[56] **References Cited**

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[57] **ABSTRACT**

A free-machining austenitic stainless steel and machined products thereof comprising, by weight percent, 0.035% maximum carbon, 17 to 19% chromium, 8 to 10% nickel, 0.5% maximum manganese, 0.25 to 0.65% sulfur, up to 1% silicon, up to 0.20% phosphorus, up to 0.6% molybenum, and balance substantially iron. In the passivated condition the steel is resistant to corrosion, by reason of the critically low manganese content, in environments containing dilute citric, acetic, phosphoric and/or carbonic acids. The combination of machinability and corrosion resistance provides utility for machined fittings used in the beverage and food industry.

5 Claims, No Drawings

FREE-MACHINING AUSTENITIC STAINLESS STEEL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a free-machining austenitic stainless steel which in the passivated condition has excellent resistance to corrosion in environments containing dilute citric, acetic, phosphoric and/or carbonic acids. The steel of the invention has particular utility for fabrication into fittings used in the processing, packaging and/or dispensing of beverage and food products containing dilute solutions of the above acids.

2. Description of the Prior Art

AISI Type 303 is a widely-used free-machining austenitic stainless steel which, in common with some other free-machining stainless steels, obtains good machining properties by reason of the formation of manganese sulfide particles dispersed uniformly throughout the steel. The melting specifications of Type 303 are as follows:

Carbon	—	0.15% maximum
Manganese	—	2.00% maximum
Phosphorus	—	0.20% maximum
Sulfur	—	0.15% minimum
Silicon	—	1.00% maximum
Chromium	—	17% to 19%
Nickel	—	8% to 10%
Molybdenum	—	0.6% maximum
Iron	—	remainder

The corrosion resistance of Type 303 is usually adequate in mildly corrosive environments. However, in environments containing dilute citric, acetic, phosphoric and/or carbonic acids, it has been found that the manganese sulfide particles of the steel are vigorously attacked and dissolved by these acids, and that as a result of this sulfide dissolution, pitting or localized corrosion of the steel matrix adjacent the manganese sulfide particles is initiated, thereby effecting the release of both sulfide and iron into solutions in contact therewith. It is evident that such contamination could not be tolerated in beverage and food products such as fruit-flavored soft drink syrups.

AISI Type 304 is a widely-accepted austenitic stainless steel which possesses adequate corrosion resistance under a wide variety of conditions, including environments containing citric, acetic, phosphoric and/or carbonic acids. However, Type 304 has poor machinability.

It is thus apparent that Type 303 stainless steel possesses good machinability but has poor resistance against localized and general corrosion in environments containing dilute citric, acetic, phosphoric and/or carbonic acids, while Type 304 possesses sufficient corrosion resistance in such environments but has poor machining characteristics. Since fittings such as valves, connectors, and the like used in the beverage and food industry would be prohibitive in cost if not made from stainless steels possessing good machinability, it is evident that there is a definite need for a stainless steel which provides the combination of good machining characteristics and resistance to attack in environments containing dilute citric, acetic, phosphoric and/or carbonic acids.

In an attempt to maintain good machinability without sacrificing corrosion resistance, the prior art has suggested the substitution of chromium sulfides in place of manganese sulfides in ferritic stainless steels, by reducing the manganese content of the steel. It has been reported that a dispersion of chromium-rich sulfides throughout the steel resulted in adequate machining characteristics, although inferior to manganese sulfide in this respect. An article by H. W. Garvin and R. M. Larrimore, Jr. in "Mechanical Working of Steel II," Volume 26, pages 133–144 (1965), reported that the addition of sulfur to a ferritic 17% chromium stainless steel resulted in the formation predominantly of chromium sulfide when the manganese content was below about 0.40% by weight.

The substitution of chromium sulfide in place of manganese sulfides has thus been suggested in ferritic sulfur-treated stainless steels, and the prior art has indicated that adequate machining characteristics are retained in such steels. However, to the best of applicant's knowledge the substitution of chromium sulfide in place of manganese sulfide in an austenitic sulfur-treated stainless steel such as AISI Type 303 has not previously been suggested or considered by the prior art.

SUMMARY

It is a principal object of the present invention to provide an austenitic stainless steel having in combination excellent machining characteristics, and excellent resistance to corrosion in environments containing dilute citric, acetic, phosphoric and/or carbonic acids.

The present invention constitutes a discovery that an austenitic stainless steel, containing sulfur in an amount sufficient to combine with chromium can be made corrosion resistant in acid environments of the above-mentioned type provided a critically low manganese content is observed, and further that a critically low carbon content unexpectedly results in excellent machinability. A maximum of 0.035% carbon and a maximum of 0.5% manganese must be observed, with the manganese to sulfur ratio being maintained at less than 2:1.

In its broad composition range, the steel of this invention consists essentially of the following elements, by weight percent:

carbon	—	up to 0.035%
chromium	—	about 17% to about 19%
nickel	—	about 8% to about 10%
manganese	—	up to 0.5%
sulfur	—	about 0.25% to about 0.6%
silicon	—	up to about 1%
phosphorus	—	up to about 0.20%
molybdenum	—	up to about 0.6%
iron	—	remainder, except for incidental impurities

In the above composition range, the manganese to sulfur ratio is maintained at less than 2:1 by weight. Sulfur is thus predominantly in the form of chromium sulfide.

Carbon is present and ordinarily will amount to about 0.01%. However, a maximum of 0.035% carbon has been found to be necessary in order to obtain machining characteristics superior to those of Type 303. More specifically, a carbon content of 0.035% or less attains an average of at least about 170 surface feet per minute (SFM) for a 5-hour cutting tool life by the test hereinafter described.

At least about 17% chromium is required for general corrosion resistance. More than about 19% chromium provides little additional benefit from the standpoint of corrosion resistance and would upset the austenitic balance of the steel.

At least 8% nickel is required for general corrosion resistance and for insuring an austenitic structure. More than about 10% nickel confers little additional corrosion resistance and unduly increases the cost of the alloy.

A maximum of 0.50% manganese must be observed in order to insure that sulfur is predominantly in the form of chromium sulfide. Although a small amount of manganese sulfide may be present in the steel at the maximum content of 0.5% manganese, the amount so combined is too small to affect adversely the corrosion resistance in environments containing dilute citric, acetic, phosphoric and/or carbonic acids.

At least 0.25% by weight sulfur must be present in order to combine with chromium and impart the desired free-machining characteristics. More than about 0.60% sulfur provides little additional benefit in machinability and adversely affects the hot and cold working of the steel.

Molybdenum is not necessary in the steel of the invention and ordinarily will not exceed residual amounts. Up to 0.6% molybdenum may be present, but molybdenum in excess of this amount should be avoided in order to minimize cost.

Silicon and phosphorus, which are normally present as impurities, may be tolerated in amounts up to about 1% and about 0.20%, respectively, without adverse effect on the properties of the steel. The remainder is substantially iron, except for incidental impurities usually associated with the production of stainless steel.

While the composition range of the steel of the invention falls within the broad melting specifications of AISI Type 303, the critically low carbon and manganese contents of the present alloy surprisingly result in excellent resistance against corrosion in environments containing dilute citric, acetic, phosphoric and/or carbonic acids, and in excellent machining characteristics which are superior to those of AISI Type 303. It should be noted that AISI Type 303 stainless steel sold commercially in this country contains from about 0.06 to about 0.1% carbon and from about 1.25 to about 1.5% manganese.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Within the above broad composition range, carbon is preferably restricted to a maximum of about 0.03% by weight, with the ranges of other elements remaining the same. Similarly, manganese is preferably restricted to a maximum of about 0.4% by weight, with the ranges of other elements remaining the same. Sulfur is preferably present in amounts of about 0.4 to about 0.5%, with the ranges of other elements remaining the same. Optimum properties are obtained when the preferred limits of carbon, manganese and sulfur are observed in combination, with a maximum manganese to sulfur weight ratio of 1:1.

A more preferred composition range for the steel of the invention thus is as follows, all percentages being by weight:

carbon	—	up to about 0.03%
chromium	—	about 17% to about 19%
nickel	—	about 8% to about 10%
manganese	—	up to about 0.4%
sulfur	—	about 0.4% to about 0.5%
silicon	—	up to about 1%
phosphorus	—	up to about 0.20%
molybdenum	—	up to about 0.6%
iron	—	remainder, except for incidental impurities

The compositions of a steel in accordance with the present invention is set forth below in Table I together with that of a low carbon AISI Type 303 steel. Corrosion resistance tests in beverage syrups were conducted on these two steels and are summarized in Table II below.

An empirical test for corrosion resistance was devised and carried out with the steel of the present invention and with the AISI Type 303 steel having the compositions set forth in Table I. The test environments were syrups of soft drinks sold under the registered trademarks COCA-COLA and FRESCA, respectively. Corrosion resistance was determined by the amount of iron picked up in the syrups after immersion of a sample in syrup (proportioned so as to provide 1 cubic inch of syrup per 20 square inches of sample) for 96 hours at room temperature. Full-strength syrups were used as test solutions. Diluted values were calculated by dividing iron pick-up by 6.5.

As indicated in Table II the steels were tested in the as-machined condition, and with two different surface passivating treatments. Such passivating treatments are well-known in the art and are commonly used to clean machined stainless steel parts generally and to remove iron particles which may be embedded in the surface of the part as a result of machining.

TABLE I

Type Of Steel	COMPOSITIONS IN WEIGHT PERCENT C	Cr	Ni	Mn	S	Si	P	Mo
Present Invention	.031	17.59	9.37	.40	.34	.61	.020	.28
Low Carbon AISI 303	.031	18.0	9.30	1.34	.33	.64	.022	.26

TABLE II

CORROSION TESTS IN BEVERAGE SYRUPS
IMMERSION IN SYRUP 96 HOURS AT ROOM TEMPERATURE

Condition	Type of Steel	Test Syrup FRESCA Fe in ppm (Average of 2 Samples) Diluted Syrup	Test Syrup FRESCA Fe in ppm (Average of 2 Samples) Full-Strength Syrup	Test Syrup COCA-COLA Fe in ppm (Average of 2 Samples) Diluted Syrup	Test Syrup COCA-COLA Fe in ppm (Average of 2 Samples) Full-Strength Syrup
As-machined	Present Invention	3.3	21.4	2.5	16.2
	AISI 303	3.2	20.8	2.6	16.9
20% HNO_3–5% $Na_2Cr_2O_7$	Present Invention	0.90	5.85	0.60	3.90
+6% HCl+20% HNO_3–5% $Na_2Cr_2O_7$	AISI 303	1.1	7.15	1.6	10.4
10% HNO_3–3% HF+20% HNO–5% $Na_2Cr_2O_7$	Present Invention	0.58	3.77	0.19	1.23
	AISI 303	0.90	5.85	0.86	5.58

The test results of Table II show that the steel of the present invention exhibits resistance to attack by beverage syrups superior to that of AISI Type 303 steel. The relatively high values reported for the as-machined condition result from iron particles embedded in the surface as a result of machining and can be disregarded. Table II further demonstrates that optimum corrosion resistance in the steel of the invention is achieved after a surface treatment which involves a short exposure to dilute nitric and hydroflouric acids followed by passivation treatment in 20% nitric acid containing sodium dichromate. The iron pick-up of the steel of the invention in this condition in COCA-COLA test syrup was exceptionally low.

It is therefore apparent that low manganese is essential in obtaining the excellent corrosion resistance of the steel of the invention.

Machinability tests have shown that the steel of the invention exhibits machining characteristics superior to those of regular AISI Type 303, i.e., with a carbon content of 0.06 to 0.1% and a manganese content of 1.25 to 1.5%. Tests were conducted by making successive 1/16 inch transverse cuts on approximately 1 inch diameter bar (outside to center) with a constant feed of 0.0025 inch per revolution using high speed tooling and sulfur-based oil. The highest surface feet per minute (SFM) for a 5-hour cutting tool life was taken as the machinability index of the alloy. The results, reported as an average of at least 5 samples of Type 303 from different sources with carbon contents ranging from 0.06 to 0.1%, and the steel of the invention of Table I, were as follows:

	5-hour form tool life SFM
AISI 303 (0.06%–0.1% C)	150
Present Invention (composition of Table I)	177

The steel of the invention may be melted, cast, hot reduced and cold reduced to plate, sheet, strip, bar and rod by conventional steel making procedures. The hot working characteristics, cold forming qualities and mechanical properties are equivalent to those of regular AISI Type 303. The steel of the invention, after conventional processing into plate, sheet, strip, bar or rod form, is then readily fabricated on conventional machines into parts and fittings, such as valves, tubing, containers and the like, after which the surfaces of the machined fittings are subjected to passivating treatments of the type disclosed above or other types conventional in the art. The steel can be subjected to annealing treatments of the type generally applied during hot and cold reduction without adverse effect. Good welding characteristics are exhibited by the steel of the invention both in the hot reduced and cold reduced and annealed conditions.

It is known in the art that the size, distribution and composition of sulfide inclusions are important in determining the machinability of free-machining steels. More specifically, machinability increases with increasing sulfur content, increasing sulfide size and decreasing length to width ratio of the sulfide inclusions. However, high sulfur contents in excess of about 0.65% result in inferior hot workability and decrease in transverse strength and toughness. Although forming no part of the present invention, such conventional prior art techniques in obtaining optimum size and distribution of sulfide inclusions are preferably followed in order to achieve optimum machining characteristics.

The invention has been disclosed by way of preferred exemplary embodiments, but it will be apparent that modifications may be made without departing from the scope of the invention. Hence no limitations are to be inferred except insofar as specifically set forth in the claims which follow.

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

1. An austenitic, free-machining stainless steel having excellent resistance to corrosion in environments chosen from the group consisting of citric, acetic, phosphoric, carbonic acids and mixtures thereof, and excellent machinability, said steel consisting essentially of, by weight percent, up to 0.035% carbon, from about 17 to about 19% chromium, from about 8 to about 10% nickel, up to 0.5% manganese, from about 0.25 to about 0.6% sulfur, up to about 1% silicon, up to about 0.20% phosphorus, up to about 0.6% molybdenum, and remainder iron except for incidental impurities, the manganese to sulfur weight ratio being less than about 2:1, whereby sulfur is predominantly in the form of chromium sulfide.

2. The steel claimed in claim **1**, containing a maximum of about 0.03% carbon, a maximum of about 0.4% manganese, and from about 0.4 to about 0.5% sulfur.

3. The steel claimed in claim **1**, wherein the maximum carbon content is about 0.03%.

4. The steel claimed in claim **1**, wherein the maximum manganese content is about 0.4%, and wherein the maximum manganese to sulfur weight ratio is 1:1.

5. The steel claimed in claim **1**, wherein sulfur is from about 0.4 to about 0.5%, and wherein the maximum manganese to sulfur weight ratio is 1:1.

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