(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 265 062**
A2

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **87307995.8**

(51) Int. Cl.[4]: **C22C 38/40**

(22) Date of filing: **10.09.87**

(30) Priority: **19.09.86 US 910239**

(43) Date of publication of application:
27.04.88 Bulletin 88/17

(84) Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

(71) Applicant: **CRUCIBLE MATERIALS CORPORATION**
P.O. Box 88 Parkway West & Route 60
Pittsburgh Pennsylvania 15230(US)

(72) Inventor: **Haswell Jr., Walter T.**
4340 Barker Hill Road
Jamesville New York 13078(US)
Inventor: **Pinnow, Kenneth E.**
131 Drood Lane
Pittsburgh, PA 15237(US)
Inventor: **Eckenrod, John J.**
126 S. Jamestown Road
Coraopolis, PA 15108(US)
Inventor: **Rhodes, Geoffrey O.**
219 Cannon Hill Road
Saxonburg, PA 16056(US)

(74) Representative: **Sheader, Brian N. et al**
ERIC POTTER & CLARKSON 27 South Street
Reading Berkshire, RG1 4QU(GB)

(54) **Low carbon plus nitrogen, free-machining austenitic stainless steel.**

(57) A low carbon plus nitrogen, free-machining, austenitic stainless steel having improved machinability and excellent corrosion resistance. The steel composition in weight percent is essentially carbon plus nitrogen up to about 0.06, chromium 16 to 20, nickel 6 to 14, manganese up to 0.60, sulfur 0.15 to 0.50, silicon up to about 1, phosphorus up to about 0.20, molybdenum up to about 1 and balance iron.

EP 0 265 062 A2

LOW CARBON NITROGEN FREE-MACHINING AUSTENITIC STAINLESS STEEL

This invention relates to low carbon plus nitrogen free-machining austenitic stainless steel.

Conventional resulfurized free-machining austenitic stainless steels such as AISI Type 303 generally do not have sufficient corrosion resistance to allow them to be used in applications for acid soft drink or beverage syrups without significantly affecting the flavour of these products. The problem largely relates to the fact that the manganese or manganese-rich sulfides present in Type 303 are readily attacked in acid soft drink or beverage syrups. As a result of this attack, the local environment is so changed that the stainless steel adjacent to the manganese or manganese-rich sulfides corrodes, thereby releasing both sulfide and metal ions into the syrups and causing odour or taste problems. Passivating free-machining austenitic stainless steels such as AISI Type 303 in nitric acid solutions can minimize this difficulty by removing most of the manganese or manganese-rich sulfides from the surfaces of the articles machined from these steels before they are placed in service. However, the general corrosion resistance of the stainless steel matrix of AISI Type 303 is often insufficient, even in the absence of substantial sulfide dissolution, to avoid changes in the quality or taste of the beverage syrups. Thus, to improve the corrosion resistance of free-machining austenitic stainless steels in acid beverage syrups, the use of a more corrosion resistant free-machining additive along with improvements in the general corrosion resistance of the steel matrix in acid beverage syrups are necessary.

In this respect, U.S. Patent 3,902,398 discloses that the corrosion resistance of resulfurized free-machining austenitic stainless steels can be significantly improved in acid beverage syrups by restricting their manganese content to a maximum of about 0.50% and by controlling the manganese to sulfur ratio such that chromium or chromium-rich sulfides are formed instead of manganese or manganese-rich sulfides. Chromium sulfides are more corrosion resistant than are manganese or manganese-rich sulfides in acid beverage syprups, and improve machinability bvut not nearly to the same extent as manganese or manganese-rich sulfides. As also disclosed in U.S. Patnt 3,902,398, the loss in machinability related to the replacement of manganese or manganese-rich sulfides by chromium sulfides can be partly offset by lowering the carbon content of such steels to below about 0.035%.

It s an object of the present invention to provide a chromium-nickel, free-machining austenitic stainless steel having improved machinability and high resistance to corrosion, especially in acid soft drink or beverage syrups.

Another object of this invention is to provide machined chromium-nickel austenitic stainless steel fittings and articles with improved machinability and high corrosion resistance, especially in acid soft drink and beverage syrups.

In accordance with this invention, it has been discovered that the machinability of chromium-nickel austenitic stainless steels containing chromium or chromium-rich sulfides and with low-manganese up to 0.60% can be greatly improved by reducing their carbon plus nitrogen contents below conventional levels. In this regard, total carbon plus nitrogen in combination at low levels in accordance with the invention is more effective than either low carbon or nitrogen alone. In addition, it has been discovered that the addition of copper to these steels in controlled amounts not only improves machinability, but more importantly significantly improves their corrosion resistance, particularly in the passivated condition, in acid soft drink syrups. The improvements in machinablity achieved by reducing carbon plus nitrogen content are obtained both at residual and elevated copper contents. However, the greatest improvements in machinability as well as in the resistance to corrosion in acid soft drinks are obtained with the copper bearing steels of this invention.

The steels of this invention have particular advantage in the application of fittings and articles used for handling and dispensing acid soft drink syrups. With these steels, the decrease in machinability normally associated with the replacement of manganese or manganese-rich sulfides by chromium or chromium-rich sulfides is offset by the lower than conventional carbon plus nitrogen contents and by the addition of copper. Further, the copper bearing steels of this invention exhibit much better corrosion resistance in acid soft drink syrups, which is an additional advantage over prior art steels used in these applications.

In their broad composition range, the steels and machined fittings and articles of this invention consist essentially of the following elements, by weight percent:

carbon plus nirogen - up to 0.06%
chromium - 16 to 20%
nickel - 6 to 14%
manganese - up to 0.60%
sulfur - 0.15 to 0.50%

phosphorus - 0 to 0.20%
silicon - 0 to 1%
molybdenum - 0 to 1%
copper - 0 to 3.00%
boron - 0 to 0.01%
iron - balance, except for incidental impurities

Carbon and nitrogen are normally present in the steels of this invention, but to obtain the desired improvements in machinability, it is essential in the steels of this invention to control the total carbon plus nitrogen levels below 0.06% and preferably below about 0.05 or 0.04%.

In general, 16 to 20% chormium and preferably 17 to 19% chromium is required in the steels of this invention to obtain the required degree of corrosion resistance in acid soft drink syrups and to adjust for the amount of chromium involved in the formation of chromium or chromium-rich sulfides.

6 to 14% and preferably 8 to 11% nickel are required in the steels of this invention to obtain an austenitic microstructure and to minimize austenite transformation during processing operations at ambient temperature.

A maximum of 0.60% manganese is required to minimize the formation of manganese or manganese-rich sulfides which are known to have an adverse effect on corrosion resistance in acid soft drink syrups and still permit the use of low cost scrap revert melting practices. In applications where maximum resistance to corrosion in acid soft drinks is required, the manganese content must be controlled below about 0.50 and the maximum manganese to sulfur ratio is 1 to 1.

A minimum of 0.15 and a maximum of 0.50% of sulfur are needed in the steels of this invention to obtain the desired degree of machinability.

Copper in amounts of about 0.75 to 3.00 and preferably in the amounts of 1.00 to 2.50 is very useful for increasing the stability of the austenite, for improving the machinability, and particularly for increasing the corrosion resistance of the steels of this invention in acid soft drink syrups.

Molybdenum is not necessary in the steels of this invention, but may be used in amounts up to about 1 percent for improving general corrosion resistance.

Silicon and phosphorus, may be present in amounts up to 1% and 0.20%, respectively, in the steels of this invention. The remainder of the composition is essentially iron, except for incidental impurities usually associated with the production of stainless steels and except for up to 0.01% boron which may be added to improve hot workability.

SPECIFIC EXAMPLES

To demonstrate the invention and specifically the heretofore undisclosed effects of low carbon plus nitrogen and copper in accordance with the invention on machinability and corrosion resistance, fourteen 50-pound (22.68kg) laboratory heats were vacuum induction melted and cast into ingots. The ingots were heated to 2200°F (1204°C) and hot forged to 1-1/4-inch (31.75mm) octagonal shaped bars and air cooled. The bars in turn were annealed by heating to 1950°F (1065°C), holding at 1950°F (1065°C) for one hour, and then water quenching. Samples from these bars were machined to one inch (25.4mm) square by four inch (101.6mm) long specimens for drill machinability testing.

TABLE I--Chemical Composition and Drill Machinability Rating (DMR) of Laboratory Heats

Weight Percent (balance iron)

Heat Number	C	Mn	P	S	Si	Ni	Cr	Mo	Cu	N	C+N	DMR
V489	0.018	0.33	0.029	0.41	0.55	10.31	17.96	0.35	0.29	0.007	0.025	108
V505	0.013	0.30	0.034	0.41	0.54	10.34	18.20	0.35	0.29	0.024	0.037	106
V560	0.026	0.34	0.030	0.38	0.55	10.41	18.35	0.35	0.28	0.20	0.046	106
V603	0.048	0.33	0.028	0.41	0.52	10.39	18.20	0.35	0.29	0.005	0.053	105
V603A	0.064	0.34	0.029	0.41	0.52	10.42	18.42	0.35	0.28	0.010	0.074	104
V506	0.020	0.30	0.033	0.39	0.55	10.37	18.28	0.35	0.28	0.059	0.079	100
V541	0.015	0.35	0.029	0.39	0.55	10.13	18.25	0.35	0.28	0.091	0.106	98
V563	0.017	0.35	0.030	0.39	0.54	10.39	18.20	0.35	0.75	0.016	0.033	104
V508	0.020	0.33	0.032	0.39	0.55	9.31	18.28	0.35	1.24	0.029	0.049	112
V507	0.021	0.32	0.031	0.39	0.55	10.48	18.13	0.35	1.26	0.023	0.044	109
V564	0.018	0.36	0.030	0.40	0.53	10.29	18.42	0.34	1.79	0.021	0.039	109
V567	0.020	0.59	0.035	0.42	0.56	10.84	18.08	0.35	2.24	0.012	0.032	114
V568	0.021	0.57	0.035	0.41	0.56	10.64	18.04	0.73	2.25	0.023	0.044	113
V565	0.021	0.34	0.029	0.36	0.53	10.35	18.03	0.34	2.29	0.025	0.046	112

0 265 062

Table I lists the resulting chemical compositions of the laboratory heats. Other than variations in carbon, nitrogen, manganese, molybdenum and copper, all the alloys are essentially 0.40 percent sulfur, 18 percent chromium, 10 percent nickel, free-machining austenitic stainless steels.

The machinability of the experimental alloys of Table I was evaluated using the aforementioned test specimens and a drill machinability test. In the drill machinability test, the total time taken to drill a specified number of holes to a specified depth in the material to be evaluated is compared to the total time to drill the same number of holes to the same depth in a material having known, established machining characteristics. The ratio between the time taken to drill the established material and the time taken to drill the test material multiplied by 100 provides a drill machinability rating (DMR) for the test material. Specific conditions used for these tests were as follows:

Drills - 1/4 inch (6.35mm) diameter high speed steel jobber bits·
Drill Speed - 405 revolutions per minute
Load on Drill - 14.2 pounds (6.44 kg)
Break-in Hole Depth - 0.1 inch (2.54mm)
Timed Hole Depth - 0.3 inch (7.62mm)

$$\text{Drill Machinability Rating (DMR)} = \frac{\text{Time to drill established steel}}{\text{Time to drill test steel}} \times 100$$

Heat number V506 containing 0.079 percent carbon plus nitrogen, about the concentrations of these elements in a typical steel of this type, was assigned a DMR of 100. Thus, steels having DMR values of greater than 100 have better drill machinability than conventional, typical steels of this type; and values less than 100, poorer drill machinability. Also, increasing DMR values indicate improved drill machinability.

Table I presents the results of one drill machinability testing of the laboratory steels. Allowing for some experimental scatter in the data and considering the steels containing about 0.30 percent copper and 0.025 to 0.106 percent carbon plus nitrogen, i.e., heat number V489, V505, V560, V603, V603A, V506, and V541, it is clearly evident that lowering the total combination of carbon plus nitrogen content of the steel results in improved drill machinability. Steels within the scope of the invention, i.e., heat number V489, V505, V560, and V603, all display improved machinability compared to heat number V506.

The data in Table I also show that heat numbers V560 and V603, which have similar carbon plus nitrogen contents of about 0.05%, have similar drill machinability despite the fact that the carbon contents of the heats are respectively below and above the critical value of 0.035% specified in U.S. Patent 3,902,398 for stainless steels of this type. A like result is obtained when comparing the drill machinability of heats V506 and V603A, which have similar carbon plus nitrogen contents of about 0.075% and carbon contents respectively below and above the critical value of 0.035% specified in the above patent. Thus, carbon plus nitrogen content is more critical than carbon content in regard to the machinability of the low manganese austenitic stainless steels of this invention.

At an equivalent carbon plus nitrogen content, adding at least 1.24 percent copper to the invention steels results in still further improvements in machinability as illustrated by heat numbers V508, V507, V564, V567, and V565. A molybdenum addition to heat number V568 appears to have essentially no effect on drill machinability when compared to heat number V567 containing a similar amount of copper but less molybdenum and slightly less carbon plus nitrogen.

An empirical test in a commercial acid soft drinks syrup sold under the registered trade name SPRITE was conducted to compare the corrosion resistance of heat numbers V505, V506, V562, V507, V508, V564, and V565 with those disclosed in U.S. Patent 3,902,348, and AISI Type 303 stainless. In this test, six-inch (152.4mm) lengths of the bars produced from these stainless steels and the AISI Type 303 were milled to the bar centres in order to obtain chips that were representative of the entire bar cross section. Ten grams of both as-machined and passivated (50% nitric acid plus 2% sodium dichromate) chips were then immersed in 50 milliliters (ml) of SPRITE syrup (pH-3) for five days. During this period of exposure, hydrogen sulfide (H2S) gas generation was monitored with moistened lead acetate test paper. The colour changes in the lead acetate paper, if any, were recorded and rated visually in regard to the degree of H S evolution according to the following system: 0 - None, 1 - very light, 2 - light, 3 - moderate, 4 - heavy, 5 - very heavy. Also, at the end of the five day test period, the syrups were separated from the chips and diluted to 200 ml with deionized water. The dilute syrups were then analyzed for iron, manganese, nickel, chromium and copper ions. The results of all the soft drink syrup tests are given in Table II.

TABLE II--Hydrogen Sulfide Generation and SPRITE Syrup Analysis Test Results on Machined Chips

Heat Number	Composition					Average Lead Acetate Test Paper Rating[a]		SPRITE Syrup Analysis Total Metal Ions Fe, Mn, Ni, Cr. Cu - ppm[b]	
	C+N	Mn	S	Ni	Cu	As-Machined	Passivated[b]	As-Machined	Passivated
V505	0.037	0.30	0.41	10.34	0.29	0.1	0.2	78	57
V506	0.079	0.30	0.39	10.37	0.29	0.3	0.2	74	57
V562	0.033	0.35	0.39	10.39	0.75	0.2	0.4	71	58
V507	0.044	0.32	0.39	10.48	1.26	0	0	63	49
V508	0.049	0.33	0.39	9.31	1.24	0	0	63	45
V564	0.039	0.36	0.40	10.29	1.79	0	0	65	47
V565	0.046	0.34	0.36	10.35	2.29	0	0	70	36
A-15596	0.081	1.70	0.32	8.85	0.21	(c) 5	2.1	330	120

(a) Lead Acetate Test Paper Ratings = 0 - None, 1 - Very Light, 2 - Light, 3 - Moderate, 4 - Heavy, 5 - Very Heavy

(b) Passivated (treated) in a solution of 20% nitric acid and 2% sodium dichromate for 30 minutes at 150°F (65.5°C)

(c) Commercial AISI Type 303 stainless.

0 265 062

The results of the lead acetate paper monitoring of H S generation and of the syrup analyses indicate that increasing the copper content of the low manganese-chromium-nickel, free-machining stainless steels of this invention to above about 0.75% and particularly from 1.26 to 2.29% significantly improves their resistance to corrosion in SPRITE soft drink syrup, especially in the passivated condition. This effect of copper is most clearly evidenced by heat numbers V507, V564, and V565 which contain 1.26, 1.79, and 2.29% copper, respectively, and which show essentially no H S evolution during testing and significantly less contamination of the SPRITE soft drink syrup than do similar steels with residual copper, such as Heat V506, and much less than AISI Type 303, as represented by heat number A-15596. Thus, the low carbon plus nitrogen, low manganese, copper bearing austenitic stainless steels of this invention exhibit much better resistance to corrosion in acid soft drink syrups than do prior art steels of this general type.

Claims

1. A low carbon plus nitrogen, free-machining, austenitic stainless steel having improved machinability and excellent resistance to corrosion in acid soft drink syrups, especially in the passivated condition, characterised by said steel consisting of, by weight percent

carbon plus nitrogen up to 0.06
chromium 16 to 20
nickel 6 to 14
manganese up to 0.60
sulfur 0.15 to 0.50
silicon 0 to about 1
phosphorus 0 to about 0.20
molybdenum 0 to about 1.0
copper 0 to 3.00
boron 0 to 0.01
and remainder iron except for incidental impurities.

2. A steel according to claim 1, having carbon plus nitrogen up to about 0.05.

3. A steel according to claim 1 or 2, having carbon plus nitrogen up to about 0.04.

4. A steel according to claim 1, 2 or 3 having 0.78 to 3.00 copper.

5. A steel according to claim 1, 2 or 3 having 1.00 to 2.50 copper.

6. A steel according to any one of the preceding claims, having 17 to 19 chromium.

7. A steel according to any one of the preceding claims having 8 to 11 nickel.

8. A steel according to any one of the preceding claims having up to 0.50 manganese.

9. A steel according to claim 8, wherein the maximum manganese to sulfur ratio is 1:1.

10. Machined austenitic stainless steel fittings and articles characterized by having improved machinability and resistance to corrosion in acid soft drink syrups, especially in the passivated condition, said fittings and articles characterised in consisting of, by weight percent

carbon plus nitrogen up to 0.06
chromium 16 to 20
nickel 6 to 14
manganese up to 0.60
sulfur 0.15 to 0.50
silicon 0 to about 1
phosphorus 0 to about 0.20
molybdenum 0 to about 1
copper 0 to 3.00
boron 0 to 0.01
and remainder iron except for incidental impurities.

11. The machined austenitic stainless steel fittings and articles of claim 11 having carbon plus nitrogen up to about 0.05.

12. The machined austenitic stainless steel fittings and articles of claim 11 having carbon plus nitrogen up to about 0.04.

13. The machined austenitic stainless steel fittings and articles of any one of claims 10, 11 or 12, having from about 0.75 to 3.00 copper.

14. The machined austenitic stainless steel fittings and articles of any one of claims 10, 11 or 12, having from 1.00 to 2.50 copper.

15. The machined austenitic stainless steel fittings and articles of any one of claims 10 to 14, having 17 to 19 chromium.

16. The machined austenitic stainless steel fittings and articles of any one of claims 10 to 15, having 8 to 11 nickel.

17. The machined austenitic stainless steel fittings and articles of any one of claims 10 to 16, having up to 0.50 manganese.

18. The machined austenitic stainless steel fittings and articles of claim 17, wherein the maximum manganese to sulfur ration is 1:1.