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3,192,040

FREE MACHINING ALLOY

Kermit J. Goda, Jr., Leesport, and John J. Gross, Reading, Pa., assignors to The Carpenter Steel Company, Reading, Pa., a corporation of New Jersey
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This application is a continuation-in-part of application Serial No. 80,023, filed January 3, 1961, now abandoned.

This invention relates to steel alloys and more particularly is concerned with the provision of stainless steel alloys having improved machinability.

Machinability may be defined as that property of an alloy which governs the performance of the alloy machining processes and denotes the success with which a material may be machined. Metal machinability is a complex and not fully understood property. However, the manifestations thereof are readily recognized by a skilled artisan from the manner in which the alloy is machined by cutting tools in such operations as turning, milling, broaching, threading, reaming, sawing or grinding. Free machining alloys are characterized, among other things, by the relatively lower degree of friction or gumminess and hence freer cutting action by the tool; by the small chips removed from the work, and the manner by which the chips fall free from and do not adhere to the tool. Of the many factors which affect machinability, the composition of the alloy appears to be the most significant because of its effect upon the structure, processing, and mechanical properties of the alloy.

Metallurgists have long sought to improve machinability of alloys by modifying their composition or form. For example, for the purpose of improving machinability, varying amounts of one or more of such elements as carbon, phosphorus, sulfur, lead, selenium, tellurium, arsenic, zirconium and bismuth have been included in alloys. Sulfur, selenium, tellurium and others of these elements are believed to affect machinability when present in the form of a sulfide, selenide or telluride, respectively, and for this reason one or more of the elements aluminum, chromium, manganese and molybdenum may be included to form such compounds.

The free machining additives hitherto used have had relatively limited usefulness for various reasons. Those compositions in which one or more of the foregoing additives have been utilized with success to provide improved machinability, often had a deleterious effect upon other desired properties. For example, in the case of stainless steel, such as that commonly designated as 18-8 stainless, the addition of about 0.3% sulfur results in a marked reduction in the corrosion resistance of the composition in a medium such as 5% sulfuric acid although a substantial improvement in free machinability is achieved.

The present invention stems from our discovery that boron mononitride (BN) dispersed in the matrix of 18-8 stainless steel, an alloy which is machinable only with difficulty, markedly improves its machinability. This improved free machinability is obtained without the objectionable loss in corrosion resistance normally associated with the addition of such elements as sulfur to 18-8 stainless steel to render the same free machining. On the other hand, when corrosion resistance is of secondary importance to free machinability, boron mononitride in addition to one or more of the aforementioned free machining additives may be used to provide greatly enhanced free machinability.

The foregoing as well as additional advantages of the present invention are achieved by providing a stainless steel alloy which, in its broader aspect, comprises in the

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approximate amounts indicated (here and throughout this application all concentration percentages are given as percent by weight unless otherwise indicated):

	Percent
5 Carbon -----	Up to .2
Manganese -----	Up to 8
Silicon -----	Up to 2
Chromium -----	16-21
Nickel -----	5-12
10 Boron mononitride -----	.05-1

Varying amounts of other elements such as columbium, titanium, molybdenum, copper, phosphorus, sulfur, selenium, may also be included. For example, one or more of up to about .5% phosphorus, up to about .5% sulfur, up to about .5% selenium, up to about 3.5% molybdenum and up to about 3.5% copper, may be added as desired. Titanium may be included in an amount from 8 times the carbon content up to about 1% and columbium may be included in an amount from 10 times the carbon content up to about 1% to stabilize the alloy against carbide precipitation. Thus, the remainder of our alloy is substantially iron but here and elsewhere in this application it is intended not to exclude the presence of such additional elements as well as others in amounts ranging from several thousandths of one percent up to about 3.5% which may be included in keeping with good metallurgical practice or which enhances other desired properties of our alloy.

In our alloy, boron mononitride below about 0.05% is not present in sufficient quantity to provide the desired degree of free machinability in our alloy. On the other hand, the capability of our steel to retain the nitrogen necessary to combine with boron to form boron mononitride necessitates the use of special techniques, as will be more fully pointed out hereinafter, when upwards of about .3% BN is desired and above 1% BN, it may be extremely difficult, if not impossible, to make sound steel in commercial quantities even when presently known special techniques are utilized.

The dispersion of boron mononitride may be formed in our composition by adding the required amounts of boron and nitrogen uncombined as boron mononitride employing conventional techniques for melting and casting an ingot having a desired analysis. When the boron and nitrogen are added separately, that is, uncombined as boron mononitride, the ingot in its as-cast condition contains no more than an ineffective amount of boron mononitride, that is, less than .05%. Apparently, the boron mononitride reaction, if it takes place at all, does so only slowly at the elevated melting temperatures and it is necessary to hold the cast ingot at temperatures from about 1700° F. to 2300° F. for from about 1 to 24 hours, the longer times being required at the lower temperatures in order to ensure formation of the desired amounts of boron mononitride. While the ingot may be heat treated to cause the desired formation of boron mononitride, the heat treatment may be conveniently incorporated in the heating cycles incidental to hot working. When the boron mononitride is formed by heat treating the as-cast ingot, the boron mononitride is apparent in photomicrographs as generally black, spheroidal particles distributed throughout the matrix. After the metal has been hot worked the boron mononitride appears as black, elongated, angular particles which are also plainly visible in photomicrographs. It is to be noted that the boron mononitride does not appear as a grain boundary phenomenon in the hot worked material but is distributed throughout the matrix.

Usually there is no difficulty encountered in incorporating and retaining boron in the melt. On the other hand, during normal melting in air, no more than about .3% nitrogen can be retained in solution during melting

and solidification of the ingots. When the amount of nitrogen retained in solid solution falls short of the theoretical saturation concentration of nitrogen in the melt, the amount of retained nitrogen may be increased by carrying out the melting and casting of the constituents under a nitrogen atmosphere as brought out, for example, in U.S. Patent No. 2,865,736. By means of the process set forth in that patent, the usually attained nitrogen content of less than about .3% may be increased to about .5% to .7% or more.

In accordance with a further feature of the present invention, the boron mononitride, instead of being formed in situ, may be added in the form of the solid boron mononitride compound. This may be accomplished by adding solid boron nitride, as, for example, a powder, to the furnace during melting, by seeding the teeming stream or by putting the boron nitride on the bottom of the ingot mold before teeming.

The properties of boron mononitride make it possible to add the solid boron mononitride to the molten metal without breakdown of the compound into its separate constituents. This is advantageous in attaining the dispersion of boron mononitride in analyses whose properties are sensitive to and are impaired by the presence of borides and nitrides which may be formed by the boron and nitrogen remaining when the boron mononitride reaction by which the compound is formed in situ in the heated solid metal is not carried to completion or when strong boride or nitride formers are present in the analysis.

The boron mononitride dispersed in the matrix of our alloy is a soft compound having a layered crystal structure. When an etched or unetched specimen of the alloy is examined under a microscope, the boron mononitride is readily detected because of its black color. On the other hand, boron uncombined with nitrogen, that is combined with other elements as borides, shows up as an extremely light colored inclusion, which characteristically is hard and brittle.

Boron mononitride is highly insoluble in an acid medium such as a hot aqueous solution of sulfuric acid having a 30% by weight concentration of sulfuric acid. Thus, the amount of boron mononitride present may be found quantitatively by determining the amount of boron and nitrogen which is insoluble in the sulfuric acid. The boron mononitride may also be extracted from the alloy by conventional electrochemical processing.

The present invention provides especially beneficial results in connection with austenitic stainless steels which include the family broadly designated as 18-8 stainless in the industry and which in accordance with the present invention comprises in the approximate amounts indicated:

Table I

	General Range, percent	Preferred Range, percent
Carbon.....	Up to .15.	Up to .07.
Manganese.....	Up to 2.	Up to 2.
Silicon.....	Up to 1.	Up to 1.
Phosphorus.....	Up to .05.	Up to .05.
Sulfur.....	Up to .05.	Up to .05.
Chromium.....	17-19.	18-19.
Nickel.....	5-10.	6-8.
Molybdenum.....	Up to 1.5.	Up to 1.
Copper.....	Up to 1.5.	Up to 1.
Boron Mononitride.....	.05-.35.	.1-.25.

The remainder substantially iron except for incidental impurities but as pointed out hereinabove, it is not intended to exclude the presence of additional elements in amounts ranging from several thousandths of one percent up to several percent which may be included in keeping with good metallurgical practice or which enhances other desired properties without an undesired effect upon the advantageous properties of our alloy.

The following examples are given in Table II as illus-

trative of our invention and not by way of limitation. In the boron and nitrogen columns the amounts of boron and nitrogen present but not combined as boron mononitride are indicated as soluble (Sol.) boron and nitrogen, respectively, while the boron and nitrogen combined as boron mononitride are indicated as insoluble (Insol.). This notation refers to the aforementioned method for determining the amount of boron mononitride present in which sulfuric acid is utilized to solubilize the uncombined boron and nitrogen. In the columns under the subheading "total" the total boron and nitrogen, both the soluble and insoluble, is given.

In Table II, the machinability of specimens of the alloys is indicated under the column heading "Mach." as the average depth of penetration, in inches, into the specimens attained under carefully controlled conditions. While there is no universally accepted standard for measuring machinability, the free machining values were obtained by measuring the depth of penetration into the specimens by a quarter inch drill in a time interval of 15 seconds with the drill rotating at about 670 r.p.m. under constant torque. Before the start of each drilling operation, the drill mounted in a conventional drill press was brought against the surface of the specimen where it was maintained by a constant weight of 100 pounds. The depth of penetration was measured with a micrometer and the values given in the table are the average depth in inches of seven drilled holes. Thus, the figures listed under machinability provide an accurate indication of the relative free machinability of the various alloys tested.

Examples 1-13, set forth in Table II, were prepared utilizing the techniques of conventional metallurgical practices. Boron and nitrogen were introduced into the melt by adding a master ferrous alloy containing boron, such as ferrobore (FeB), and one containing nitrogen, such as nitrated ferrochromium (N_2FeCr). Melting and casting of the various analyses as ingots were carried out in keeping with conventional practices.

The analytic methods utilized were capable of detecting as little as .001% boron mononitride and yet the presence of boron mononitride could not be detected in the as-cast ingots. We found that it is necessary to maintain our alloy at an elevated temperature in order for the boron and nitrogen to interact to form boron mononitride. It may be well to note here that an important advantage of the present invention resides in the fact that a treating temperature may be selected from the range of about 1700° to 2300° F. and a duration which is best suited for the particular analysis being processed. In practice, it has been found that heat treating for a period of up to about 8 hours at a temperature of about 2100° to 2300° F. is preferred for providing maximum amounts of boron mononitride.

After being melted and cast, the ingot was hot worked, annealed and then machined to provide specimens suitable for testing. All but Examples 1 and 2 of Table II were heated for from 8 to 10 hours at about 2200° to 2250° F. incidental to hot working. The ingots from which the specimens of Examples 1 and 2 were obtained were somewhat smaller in size and hot rolling together with the heating cycle of about 4 hours at about 2200° to 2250° F. incident thereto was omitted. Thus, Examples 1 and 2 were maintained at about 2200° to 2250° F. for only about 4 to 6 hours.

Examples 1-4 demonstrate the beneficial effect of increasing amounts of boron mononitride upon free machinability. With as little as .05% boron mononitride, as in the case of Example 1, the machinability is significantly improved over that of Example 6 which is a typical analysis of A.I.S.I. Type No. 304, the latter having a machinability of .053 and being generally recognized in the industry as being difficult to machine.

On comparing Example 5 with Example 3, it is apparent that, apart from the amount of boron mononitride present,

the two analyses are the same for practical purposes. The superior free machinability of Example 3 results from the fact that this alloy contains a much smaller quantity of metal borides than is contained in the alloy of Example 5.

Theoretically the formation of boron mononitride is favored by bringing boron and nitrogen together in proportions corresponding to their stoichiometric amounts, that is when the ratio of the percentage concentration of nitrogen to that of boron is 1.273.

In practice it has been found that when the larger concentrations of boron and nitrogen are added separately in the melt, best results are achieved when the ratio of the nitrogen and boron additions ranges from about 1.5 to 2.5 or above. The extent to which the larger excess amounts of nitrogen may be tolerated will vary depending upon the particular analysis in question as is well known in the art. For example, in an alloy such as Example 6, an excess amount of nitrogen uncombined with the boron greater than about .3% affects the work hardening of the material. When the smaller amounts of boron are utilized to form the desired boron mononitride in situ in the alloy, the larger proportions of nitrogen relative to the boron concentration are added as is illustrated by Example 1. There the ratio of nitrogen and boron concentrations is about 5.9 but the soluble nitrogen content of .19% is well within the tolerable limits for the composition. At the present time, it is believed that the greater proportions of nitrogen relative to the boron concentrations are required with the smaller boron concentrations because of the conditions under which the nitrogen and boron interact in the alloy. It appears that because of the relatively lower mobility of the boron atoms in the alloy resulting partly from their larger size, a greater excess of the nitrogen atoms favors the carrying out of the desired boron mononitride reaction.

It should also be noted that, to the extent that the boron mononitride reaction is not carried to completion, there is a residue of boron uncombined as boron mononitride which forms metal borides in our alloy. The formation of an excess of metal borides in any significant amount in our alloy is undesired because of such ill-effects which may result therefrom as embrittlement and poor machinability, as well as impaired ductility, impact strength and cold workability.

Referring once again to Table II, the alloy of Example 7 contains .26% nitrogen but only .004% boron in the form of metal borides, but no boron mononitride was detected. With such an increased concentration of nitrogen as compared to the alloy of Example 6, the machinability is not improved. Similarly, the alloy of Example 8, containing .18% boron in the form of metal borides and only such a small amount of nitrogen as .04%, demonstrated for all practical purposes no significant change in machinability.

Table II¹

Ex. No.	C	Mn	Si	P	S	Cr	Ni	Mo	B			N ₂			BN	Mach.
									Sol.	Insol.	Total	Sol.	Insol.	Total		
1-----	.063	.80	.43	.015	.012	17.83	9.39	.07	.02	.02	.04	.19	.04	.23	.05	.140
2-----	.056	.75	.41	.014	.014	17.81	9.34	.08	.03	.03	.06	.16	.06	.22	.07	.205
3-----	.036	.85	.52	.16	.007	17.10	9.58	.11	.06	.04	.10	.10	.06	.16	.09	.230
4-----	.040	.82	.53	.014	.024	18.13	9.71	.08	.04	.11	.15	.14	.15	.29	.25	.285
5-----	.034	.85	.49	.015	.007	17.50	9.33	.11	.12	.07	.19	.12	.14	.26	.16	.215
6-----	.068	.95	.67	.024	.166	18.61	10.23	.20	-----	-----	-----	-----	-----	-----	-----	.053
7-----	.033	.88	.54	.014	.015	18.16	9.69	.08	.004	-----	.004	.26	-----	.26	-----	.040
8-----	.028	.86	.53	.015	.016	18.04	9.68	.08	.18	-----	.18	.04	-----	.04	-----	.085
9-----	.032	.77	.48	.016	.011	17.74	9.45	.10	.05	<.001	.05	.08	<.001	.08	-----	.055
10-----	.028	.75	.45	.014	.336	17.60	9.34	.11	-----	-----	-----	-----	-----	-----	-----	.283
11-----	.035	.88	.57	.013	.194	18.16	9.70	.08	.04	.09	.13	.14	.14	.28	.21	.385
12-----	.046	.86	.59	.012	.20	18.25	9.65	.09	.06	.10	.16	.13	.17	.30	.23	.340
13-----	.041	.88	.70	.020	.30	19.00	7.20	.48	.025	.055	.08	.14	.07	.21	.13	.371

¹ Remainder substantially iron.

The alloy of Example 9, contains .05% soluble boron and .08% soluble nitrogen. Less than .001% of insoluble boron or nitrogen was found in this composition, and

no boron nitride could be detected. Referring to Example 1, with only .04% total boron the larger proportion of nitrogen of .23% gave a boron nitride concentration of .05% in contrast to the ineffectiveness of .08% nitrogen with .05% boron to form boron nitride in Example 9. Thus, with both boron and nitrogen present but with essentially all of the boron present as metal borides and with no boron nitride present, there is no favorable effect upon the machinability of the composition.

It is a further feature of the present invention that advantage may be taken of the beneficial effect of boron mononitride upon the free machinability of an alloy without impairing its other properties by including boron mononitride in the alloy along with other free machining additives hitherto utilized. For example, the alloy of Example 10 will be recognized by those skilled in the art as A.I.S.I. Type No. 303. This alloy contains a significant amount of sulfur added for the purpose of improving the free machinability of the alloy as compared, for example, to that of A.I.S.I. Type No. 304, Example 6. While the sulfur content of the alloys of Examples 11 and 12 is less than that of Example 10, the boron mononitride present as indicated provides a unique improvement in free machinability.

Example 13 is illustrative of the preferred balance of the elements in our alloy. Here, the nickel content is reduced while the chromium content is increased as compared to the remaining examples to facilitate hot working.

Table III¹

Ex. No.	Ultimate Tensile Strength	2% Yield Strength	Percent Elong.	Percent R.A.	BHN	5% H ₂ SO ₄ at 80° C.
1-----	92,750	48,250	48.2	51.9	159	Not determined.
2-----	85,500	41,875	48.6	45.7	159	Do.
3-----	80,125	36,250	56.2	65.4	134	138.21 ² mls/yr.
6-----	84,875	38,125	52.8	60.3	140	233.85 ² mls/yr.
8-----	85,000	35,000	60.0	70.0	150	(3).
9-----	85,812	38,625	56.2	72.1	140	159.09 ² mls/yr.
10-----	84,312	34,437	56.2	60.1	141	790.66 ² mls/yr.

¹ All specimens annealed 1950° F. one hour, water quench. Corrosion rates are an average of five 48 hour periods except where noted.

² Average of two tests each consisting of five 48 hour periods.

³ As pointed out hereinabove, Example 6 is a typical analysis of A.I.S.I. type 304, the corrosion rate of which is nominally given as greater than 50 mls/yr. and usually has a corrosion rate ranging from about 100 to 400 mls/yr.

From the test data set forth in Table III, it is apparent that additions of boron mononitride do not have any objectionable effect upon such mechanical properties of our alloy as ultimate tensile strength, yield strength, and ductility. On the other hand, the corrosion resistance to 5% sulfuric acid (at 80° C.) of our alloy without such free machining additives as sulfur is markedly improved over an alloy such as Example 10 which will be recognized as A.I.S.I. type 303 containing sulfur as a free

machining additive. The average rate in mils of thickness lost per year in 5% sulfuric acid at 80° C. was 790.66 mils in the case of a specimen having the analysis of Ex-

ample No. 10, which had a free machinability of .283 inch (Table II). On the other hand, Example 3 is illustrative of the improvement in free machinability attainable in accordance with our invention without the loss in corrosion resistance associated with the use of sulfur. Example 3, containing .09% boron mononitride, had a free machinability of .230 inch and a corrosion rate of 138.21 mils per year in 5% sulfuric acid at 80° C.

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. An austenitic stainless steel alloy characterized in its heat treated condition by good free machinability consisting essentially of up to about .2% carbon, up to about 8% manganese, up to about 2% silicon, from about 16% to 21% chromium, from about 5% to 12% nickel, from about .05% to 1% boron mononitride, said boron mononitride being dispersed throughout the matrix of the alloy, up to about 1% columbium, up to about 1% titanium, up to about 3.5% molybdenum, up to about 3.5% copper, up to about .5% phosphorus, up to about .5% sulfur, up to about .5% selenium, and the remainder consisting essentially of iron.

2. An austenitic stainless steel alloy characterized in its heat treated condition by good free machinability consisting essentially of up to about .15% carbon, up to about 2% manganese, up to about 1% silicon, up to about .5% phosphorus, up to about .5% sulfur, from about 17% to 19% chromium, from about 5% to 10% nickel, up to about 1.5% molybdenum, up to about 1.5% copper, from about .05% to .35% boron mononitride, and the remainder consisting essentially of iron.

3. An austenitic stainless steel alloy characterized in its heat treated condition by good free machinability consisting essentially of up to about .07% carbon, up to about

2% manganese, up to about 1% silicon, up to about .05% phosphorus, up to about .5% sulfur, from about 18% to 19% chromium, from about 6% to 8% nickel, up to about 1% molybdenum, up to about 1% copper, from about .1% to .25% boron mononitride, and the remainder consisting essentially of iron.

4. An austenitic stainless steel alloy characterized in its heat treated condition by good free machinability consisting essentially of up to about .07% carbon, up to about 2% manganese, up to about 1% silicon, up to about .05% phosphorus, up to about .030% sulfur, from about 18% to 19% chromium, from about 6% to 8% nickel, up to about 1% molybdenum, up to about 1% copper, from about .1% to .25% boron mononitride, and the remainder consisting essentially of iron.

5. An austenitic stainless steel heat treated article characterized by good free machinability consisting essentially of up to about .07% carbon, about .88% manganese, about .7% silicon, about .3% sulfur, about 19% chromium, about 7.2% nickel, and about .13% boron mononitride, and the remainder consisting essentially of iron except for incidental impurities.

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DAVID L. RECK, *Primary Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,192,040

June 29, 1965

Kermit J. Goda, Jr., et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 49, strike out "improved"; column 3, line 15, for "nitrite" read -- nitride --; columns 5 and 6, Table II, fifth column, line 3 thereof, for ".16" read -- .016 --; same table, sixth column, line 6 thereof, for ".166" read -- .016 --; column 6, line 3, for ",23%" read -- .23% --.

Signed and sealed this 22nd day of February 1966.

(SEAL)

Attest:

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