

1

3,799,765

FREE-MACHINING STAINLESS STEEL

William C. Clarke, Jr., Baltimore, Md., assignor to Armco Steel Corporation, Middletown, Ohio
No Drawing. Filed Feb. 29, 1972, Ser. No. 230,526
Int. Cl. C22c 39/14
U.S. Cl. 75-126 C

7 Claims

ABSTRACT OF THE DISCLOSURE

Straight-chromium stainless steel is characterized by a combination of ready machinability and good corrosion-resistance. In addition to chromium of about 11.5% to 18%, the steel contains critical amounts of the three ingredients phosphorus, sulphur and zirconium, namely, about 0.04% to 0.12% phosphorus, about 0.20% to 0.50% sulphur and about 0.10% to 0.40% zirconium. Conveniently, the steel is melted in the electric arc furnace, and for best results, teeming is effected in a protective atmosphere.

As a matter of introduction, my invention is concerned with the straight-chromium stainless steels, more especially the American Iron and Steel Institute 400 series. Particular mention is made of the 416 and 430F. These contain chromium in amounts ranging from some 12% to 14% for the Type 416 and some 16% to 18% for the Type 430F.

One of the objects of my invention is the provision of a straight-chromium stainless steel which is characterized by a combination of good corrosion-resistance and good machinability with higher cutting rates and lower tool forces than heretofore.

Another is the provision of such a steel which is readily and economically melted, using known furnacing and melting equipment and which lends itself to an ease of working in the hot-mill and cold-mill as by rolling, drawing and forging, and which in the form of bar, rod and wire is suited to a variety of machining operations, such as cutting, sawing, turning, threading and the like as in the production of a host of products of ultimate practical use where common corrosion conditions are encountered.

A further object is the provision of a method for producing the zirconium-containing stainless steel of my invention in simple, efficient manner to give a steel of high quality and free of surface blemishes or discoloration.

Other objects of my invention in part will become apparent during the course of the description which follows and in part will be more especially pointed to.

My invention then resides in the combination of elements, in the relation between the same and in the sequence of operational steps employed, all as described herein, the scope of the application of which is set out in the claims at the end of this specification.

BACKGROUND OF THE INVENTION

In order to gain a better understanding of certain features of my invention, it may be well to note at this point that stainless steels are well established in the art, particularly because of their resistance to corrosion, their strength and in many cases their attractive appearance. For example, there is the AISI Type 410 containing carbon in the amount of 0.15% as a maximum, manganese 1.00% max., phosphorus 0.04% max., sulphur 0.030% max., silicon 1.00% max., chromium in the amount of 11.5% to 13.5% and remainder iron. This is a general purpose steel which is hardenable by heat-treatment. It is employed where either corrosion-resisting or heat-resisting properties are required. It is suited to the production of coal screens, machine parts, valve trim and low-priced cutlery.

2

A general purpose stainless steel which is non-hardenable by heat-treatment is the AISI Type 430. This steel contains carbon 0.12% maximum, manganese 1.25% max., phosphorus 0.040% max., sulphur 0.030% max., silicon 1.00% max., chromium in the amount of 16% to 18% and remainder iron. It is employed in the form of decorative trim, automobile trim, annealing baskets and nitric acid tanks.

Among the most popular of the straight - chromium grades are those which lend themselves to a variety of machining operations. Some of these grades are hardenable by heat-treatment and others are considered to be non-hardenable. Of the former, particular mention is made of the American Iron and Steel Institute, Type 416, comprising carbon up to 0.15% as a maximum, manganese 1.25% max., phosphorus 0.060% max., sulphur 0.15% minimum, silicon 1.00% max., chromium 12% to 14% and remainder iron. This steel is a free-machining grade and is particularly suited to the production of bolts, nuts, screws, carburetor parts, fishing reels, golf club heads, instruments parts, screw machine parts, valve trim and the like. Of the latter that is the non-hardenable free-machining steel, there is AISI Type 430F. This steel is especially suited to the production of screw machine parts, screws and other fasteners. It comprises carbon in the amount of 0.12% as a maximum, manganese 1.25% max., phosphorus 0.060% max., chromium 16% to 18% and silicon 1.00% max., chromium 16% to 18% and remainder iron.

A companion steel, AISI Type 430FSe is similar in composition to the 430F except the sulphur content is set at 0.060% maximum and there is employed selenium in the amount of at least 0.15% as a minimum. This steel too is of a free-machining grade and as such is suited to the production of a variety of machined articles and parts. The machined products present a finish of fine quality.

While the straight-chromium grades such as the AISI Types 410 and 430 are viewed as having good resistance to a wide variety of corrosive media, they do not lend themselves to anything more than the most limited machining operations, such as cutting and sawing. And while the types, notably AISI Type 416, 430F and 430FSe, do indeed possess good machining characteristics, the corrosion resisting qualities significantly suffer. Although other straight chromium grades of stainless steel containing sulphur, and indeed also containing zirconium, are known in the art, as described and claimed in the Palmer U.S. Pat. 1,835,960 of Dec. 8, 1931, these too evidence a loss of corrosion resistance with the gain in machinability. A further straight-chromium stainless steel in which any one or more of phosphorus, sulphur and selenium is employed and in which zirconium and molybdenum are viewed as equivalent additions, forms the subject of Nishikiori U.S. Pat. 2,897,078 of July 28, 1959. But in the steel of that patent, both copper and aluminum are necessary and essential ingredients. The steel of this patent, as well as that of the Palmer patent, lacks the combination of corrosion-resistance and free-machinability which characterizes the steel of my invention.

Accordingly, then, one of the objects of my invention is the provision of a stainless steel which, while comparatively inexpensive and of ready production, enjoys good machinability along with good resistance to corrosion, which steel works well in the mill, lends itself to variety of fabricating and machining operations, particularly cutting, threading, tapping, drilling, and the like with minimum tool forces, maximum tool life and yet presents a high quality surface finish. Another is the provision of a simple, direct and economical method for assuring efficient and reliable production of the steel of high surface quality together with a desired combination of machinability and good corrosion-resistance.

BRIEF SUMMARY OF THE INVENTION

Turning now more particularly to the practice of my invention, my steel essentially consists of about 11.5% to about 18% chromium, about 0.07%, or even 0.04%, up to about 0.12% phosphorus, about 0.20% to about 0.50% sulphur, about 0.10% to about 0.40% zirconium, up to about 1.12% selenium, not over about 0.15%, and preferably not over about 0.07% carbon, and remainder substantially all iron. Manganese and silicon, of course, are commonly present, the manganese being up to about 1.25%, preferably about 0.10% to about 1%, and the silicon in amounts up to about 1%.

The steel of my invention conveniently is melted in the electric arc furnace. Where desired, however, other melting techniques, such as partial pressure processes or even vacuum furnaces, can be used, but these at somewhat higher cost. The steel as melted contains the desired amounts of chromium, carbon, manganese, silicon, phosphorus and sulphur, along with selenium where employed. With metal made to desired specification, the furnace is tapped into a suitable ladle for teeming. It is at this point that the zirconium addition is made. And best results are had here by adding the zirconium to the ladle in the form of ferro-zirconium. Immediately prior to making the zirconium addition, I add to the metal aluminum scrap, pig or pellets in order to effect deoxidation and, at the same time, rid the metal of oxygen. Contamination of the zirconium addition in the ladle is thus avoided.

In teeming the metal, I first flush the ingot molds employed with argon or other heavy inert gas. This serves to float out the normal atmosphere of the mold. And for best results, I also provide a protective envelope of argon or the like about the steam of metal flowing from the ladle into the mold. This is achieved by way of a collar spaced around the nozzle of the ladle, the collar being provided with suitable orifices leading toward the nozzle and providing a flow of gas enveloping and surrounding the stream of molten steel. The teemed metal thus is effectively prevented from oxidation throughout the teeming operation, protection being had for the naked stream and for the metal rising in the mold.

The zirconium-containing steel of my invention, which essentially contains the two further ingredients phosphorus and sulphur, is strong, resistant to corrosion, and at the same time, is characterized by good machinability. The steel especially may be viewed as one of good machinability, lending itself to cutting, turning, tapping, threading and the like, as in the production of a host of articles and parts of ultimate use, and yet with good retained resistance to corrosion, a resistance of corrosion characterizing the known and used AISI stainless steels of the 400 series.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

While the steel of my invention in broad aspect essentially consists of about 11.5% to about 18% chromium, about 0.04% to about 0.12% phosphorus, about 0.20% to about 0.50% sulphur, about 0.10% to about 0.40% zirconium, with or without selenium in amounts up to about 0.12%, and remainder substantially iron, there are several steels of more specific composition in which there are enjoyed a best combination of properties. One such steel essentially consists of about 11.5% to about 18% chromium, about 0.07 or 0.08% to about 0.12% phosphorus, about 0.35% to about 0.40% sulphur, about 0.20% to about 0.25% zirconium, with carbon not over about 0.07% and remainder substantially all iron. Manganese may be present in amounts up to about 1.25% and silicon present in amounts up to about 1%. This steel is non-hardenable by heat-treatment and enjoys an excellent combination of free-machinability along with resistance to corrosion.

Another steel according to my invention essentially consists of about 12% to about 14% chromium, about 0.07%

to about 0.12% phosphorus, about 0.20% to about 0.50% sulphur, about 0.10% to about 0.40% zirconium, not over about 0.15% and for best results not over about 0.07% carbon and remainder substantially all iron. Again, manganese here may be present in amounts up to about 1.25% and silicon in amounts up to about 1%. While the steel of the higher permissible carbon content is hardenable by heat-treatment and is characterized by a combination of good machinability and good resistance to corrosion, the steel of the lower carbon content remains substantially unhardenable by heat-treatment while retaining the good combination of machinability and corrosion resistance.

A further steel essentially consists of about 14% to about 18% chromium, about 0.07% to about 0.12% phosphorus, about 0.20% to about 0.50% sulphur, about 0.10% to about 0.40% zirconium with carbon not exceeding about 0.07% and remainder substantially all iron. Manganese and silicon both may be present, each in amounts up to about 1%. This steel, while enjoying good free-machinability, is characterized by somewhat better corrosion resistance than the steel of the 12% to 14% chromium content.

A steel enjoying somewhat better corrosion resistance along with good free-machinability essentially consists of about 16% to 18% chromium, up to about 1% manganese, up to about 1% silicon, about 0.07% to about 0.12% phosphorus, about 0.20% to about 0.50% sulphur, about 0.10% to about 0.40% zirconium, carbon not exceeding about 0.07% and remainder substantially all iron.

In the steel of my invention, both the broad composition as well as specific composition, there is had a good combination of the two properties, resistance to corrosion and free-machinability. The steel lends itself to cutting, sawing, turning, threading, tapping and the like. Cutting tool life is at a maximum. Tool forces, that is the cutting force encountered, are at a minimum. And the metal is seen to have a clean, bright finish free of blemishes, which well resists attack by the atmosphere and by the acids, bases and salts commonly encountered in use.

In the steel of my invention, the amounts of the three ingredients phosphorus, sulphur and zirconium are in every sense critical. First, there is the matter of the zirconium content. This I find is required in the amount of at least about 0.10% or even 0.15% and for best results, at least about 0.20%. The zirconium content, however, should not exceed about 0.40%, particularly with air melting and/or teeming, for otherwise a streaked surface results. I find that where the molten metal is permitted to come in contact with the air, objectionable stringers are formed, these being composed of zirconium oxides and/or zirconium nitrides. These oxides not only mar the surface of the converted steel products but, in addition, cause a loss in machinability and tool life. To achieve a best surface, the metal is teemed in a protective atmosphere so as to preclude a pick-up of oxygen or nitrogen from the air. Where air melting nevertheless is employed, the zirconium content should not exceed about 0.25%. In general, the zirconium content amounts to from 0.15% to about 0.30% and teeming is had in a protective atmosphere of argon.

The sulphur content of my steel is at least in the amount of about 0.20% in order to achieve good machinability; even better properties are had with sulphur in the amount of at least 0.35%. The sulphur content, however, should not exceed about 0.50%, for otherwise the hot-workability of the metal is inclined to suffer. For best results the sulphur content amounts to some 0.35% to 0.50%. I feel that the zirconium and sulphur present form a zirconium sulphide which is dispersed throughout the metal in the form of big, fat discontinuities which in a measure lubricate the cutting tool in a machining operation.

The ingredient phosphorus is employed in the amount of at least about 0.04% and for best results at least about 0.07% or 0.08% on up to about 0.12%. Phosphorus in amounts less than 0.07% and certainly in the amount less than 0.04% are inadequate. In my view, at least 0.07% phosphorus and certainly at least 0.04% is required in order to effect proper segregation and growth of the zirconium sulphides present, the zirconium sulphides appearing as big, fat bodies which are readily seen under the microscope. The zirconium sulphides particularly contribute to the free-machining qualities of the metal. Without the critical phosphorus content, I find that the zirconium sulphides are of inconsequential size and contribute little to machinability.

Any selenium employed in my steel is in amounts up to about 0.12%. Selenium, too, aids in the growth of the larger sulphides, notably zirconium sulphides and manganese sulphides, as well as to further improve machinability. Moreover, with the selenium addition, there is had some slight improvement in the surface appearance of the machined metal.

The chromium content of my steel is in the amount of at least about 11.5% for with a lesser chromium content, there is inadequate corrosion resistance. The chromium content, however, should not exceed about 18% for otherwise the metal becomes unnecessarily costly. Moreover, machinability begins to suffer with the higher chromium content.

The carbon content usually is not over about 0.15%. For many applications, carbon is employed in amounts not exceeding about 0.07%. With a carbon content exceeding 0.15%, I find a loss in corrosion resistance. Moreover, an excessive carbon content is inclined to the formation of carbides, which segregate toward the surface of the ingot during solidification, in a measure competing with the zirconium sulphides and causing some loss in machinability. For a best combination of properties, then, there is desired a carbon content not exceeding about 0.07%.

Manganese, as noted above, may be employed in amounts up to about 1.25%, preferably in amounts not exceeding about 1%. An excessive manganese content results in a loss of corrosion resistance without any compensating benefits. And silicon is employed in amounts up to about 1%, an excessive silicon content tends to produce glassy silicates in the steel which are known to shorten tool life.

As more particularly illustrative of the steel of my invention, I give below in Tables I(a) and I(b) eight examples, along with nine of the known Types 416 and 430F. The chemical composition of the various samples is given in Table I(a).

TABLE I(a)
Chemical composition of 17 examples of free-machining stainless steels

Heat number	C	Mn	P	S	S	Cr	Ni	Se	Zr
310306.....	.114	.54	.028	.35	.50	12.40	.50	-----	-----
310219.....	.12	.50	.027	.33	.39	12.54	.20	-----	-----
310215.....	.12	.50	.025	.35	.44	12.69	.23	-----	-----
500120.....	.10	.60	.018	.32	.79	13.18	.46	-----	-----
390649.....	.11	.66	.020	.31	.69	13.40	.32	-----	-----
57161.....	.10	.79	.017	.36	.61	12.84	.18	-----	-----
48018.....	.10	.52	.018	.35	.61	13.40	.34	-----	-----
480435.....	.097	.72	.015	.33	.64	12.94	.36	-----	-----
52198.....	.065	.73	.011	.27	.41	16.56	.65	-----	-----
R5942 ¹	.036	.30	.072	.40	.27	16.41	.24	.08	.22
R5869 ¹	.033	.74	.083	.38	.51	13.03	.24	.08	.22
R5871 ¹	.038	.54	.088	.39	.69	13.08	.21	.08	.32
R5842 ¹	.042	.32	.079	.42	.26	12.87	.15	.08	.17
R5839 ¹	.031	.26	.075	.42	.33	12.77	.19	.06	.13
R5435 ¹	.033	.84	.12	.34	.40	13.12	.22	-----	.15
R5844 ¹	.038	.35	.079	.41	.47	13.00	.16	.02	.20
R5841 ¹	.043	.31	.087	.42	.36	12.63	.16	-----	.16

¹ Steels of the invention.

The properties of the steels of Table I(a), that is hardness, tool life and required cutting force, are given in Table I(b). The hardness is given in Brinell. The tool life is given in terms of surface feet per minute for a five-hour life period. And the required cutting force is given in pounds. All samples are in the form of bar

stock and are in the condition following heating at 1200° F. for four hours and air cooling.

TABLE I(b)

Hardness, tool life and required cutting force of the steels of Table I(a)

	Brinell hardness	Tool life	Cutting force in pounds
Heat number:			
310306.....	228	205	327
310219.....	212	210	316
310215.....	207	200	344
500120.....	223	180	340
390649.....	212	210	344
57161.....	235	210	320
48018.....	235	185	345
480435.....	228	210	344
52198.....	163	-----	400
R5942 ¹	156	250	237
R5869 ¹	167	258	243/234
R5871 ¹	167	250	236/235
R5842 ¹	156	275	215/211
R5839 ¹	163	265	225/224
R5434 ¹	183	252	234
R5844 ¹	153	262	224/228
R5841 ¹	159	262	226/224

¹ Steels of the invention.

Careful review of the test results presented above rather forcefully reveals that while the AISI Type 416 stainless steel (carbon 0.15% max., manganese 1.25% max., phosphorus 0.060% max., sulphur 0.15% min., silicon 1.00% max., chromium 12% to 14%, and remainder iron, as noted above) is characterized by a Brinell Hardness of some 207 to 235, the steel according to the present invention (Heat Numbers R5942, R5869, R5871, R5842, R5839, R5435, R5844, and R5841) reveals Brinell Hardness Numbers running from 153 for Heat R5844 to 183 for Heat R5435; much lower hardness is had in the steel of interest.

The required cutting force for the standard Type 416 is on the order of some 316 pounds as a low (Heat No. 310219) to a high of 345 (Heat No. 48018). Five of the examples are shown to require a cutting force on the order of 340 pounds. As contrasted with the figures given for the standard Type 416, the steel of my invention of like chromium content only requires a cutting force on the order of some 215/211 pounds for the Heat No. R5842 to a high of 243/234 for the Heat No. R5869, figures significantly below that required for the standard Type 416. And of special significance, the tool life enjoyed by the steel of the present interest is on the order of some 250 to 275 surface feet per minute as against a figure of 180 to 210 surface feet per minute for the standard Type 416.

Similar comparative figures are had for the Type 430F examples. While the steel according to my invention (Heat No. R5942) is characterized by a Brinell Hardness of 156, a cutting force of 237 pounds and a tool life figure of 250 surface feet per minute, that of the standard Type 430F (Heat No. 52198) has a Brinell Hardness of 163, and a required cutting force of 400 pounds. No tool life figures are given for the standard steel. But there is no reason to suppose that they would not significantly depart from the figures given for the standard Type 416.

Thus, it will be seen that I provide in my invention a stainless steel of the straight chromium grade in which there are many practical advantages. The steel is characterized by a combination of the two properties, free-machinability and corrosion resistance. It is comparatively inexpensive in production even with the novel technique employed with protective teeming atmosphere and well lends itself to a wide variety of machining operations to achieve a host of articles of ultimate use.

Since many embodiments may be made of my invention and many changes made in the several illustrative embodiments set out above, it is to be understood that all material described herein is to be interpreted as illustrative and not by way of limitation.

What is claimed is:

1. Alloy steel enjoying a combination of free-machinability and corrosion-resistance essentially consisting of about 11.5% to about 18% chromium, up to about 1.25% manganese, up to about 1% silicon, about 0.07% to about 0.12% phosphorus, about 0.20% to about 0.50% sulfur, about 0.10% to about 0.40% zirconium, up to 0.12% selenium, not over about 0.15% carbon and remainder substantially all iron.

2. Alloy steel enjoying a combination of free-machinability and corrosion-resistance essentially consisting of about 11.5% to about 18% chromium, about 0.07% to about 0.12% phosphorus, about 0.35% to about 0.50% sulphur, about 0.15% to about 0.30% zirconium, not over about 0.07% carbon and remainder substantially all iron.

3. Alloy steel enjoying a combination of free-machinability and corrosion-resistance essentially consisting of about 12% up to about 14% chromium, up to about 1.25% manganese, up to about 1% silicon, about 0.07% to about 0.12% phosphorus, about 0.20% to about 0.50% sulphur, about 0.10% to about 0.40% zirconium, not over about 0.15% carbon and remainder substantially all iron.

4. Alloy steel enjoying a combination of free-machinability and corrosion-resistance essentially consisting of about 14% to about 18% chromium, up to about 1% manganese, up to about 1% silicon, about 0.07% to about 0.12% phosphorus, about 0.20% to about 0.50% sulphur, about 0.10% to about 0.40% zirconium, carbon not exceeding about 0.07% and remainder substantially all iron.

5. Alloy steel enjoying a combination of free-machinability and corrosion-resistance essentially consisting of

about 16% to about 18% chromium, up to about 1% manganese, up to about 1% silicon, about 0.07% to about 0.12% phosphorus, about 0.20% to about 0.50% sulphur, about 0.10% to about 0.40% zirconium, carbon not exceeding about 0.07% and remainder substantially all iron.

6. Alloy steel ingot essentially consisting of about 11.5% to about 18% chromium, phosphorus about 0.07% to about 0.12%, sulphur about 0.20% to about 0.50%, zirconium about 0.10% to about 0.40%, carbon not over about 0.15%, and remainder iron, wherein said zirconium is present in the form of comparatively big zirconium sulphides largely segregated within said ingot.

7. Alloy steel bar stock essentially consisting of about 11.5% to about 18% chromium, phosphorus about 0.07% to about 0.12%, sulphur about 0.20% to about 0.40%, zirconium about 0.10% to about 0.40%, and remainder iron, in which zirconium sulphides are present near the surface of said stock.

References Cited

UNITED STATES PATENTS

1,835,960	12/1931	Palmer	75—126 L
1,846,140	2/1932	Palmer	75—126 M
2,052,136	8/1936	Gill	75—126 L
2,121,001	6/1938	Arness	75—125 M
3,000,730	9/1961	Tanczyn	75—126 F
3,615,367	10/1971	Tanczyn	75—126 M

HYLAND BIZOT, Primary Examiner

U.S. Cl. X.R.

75—126 F, 126 R, 126 L, 126 M