Patented Jan. 6, 1953 2,624,670

UNITED STATES PATENT OFFICE

2,624,670

CHROMIUM STEELS

William O. Binder and Roger A. Perkins, Niagara Falls, N. Y., assignors to Union Carbide and Carbon Corporation, a corporation of New York

No Drawing. Application August 15, 1952, Serial No. 304,638

2 Claims. (Cl. 75—125)

This invention relates to hot-workable chromium steels and articles made therefrom, and has for its principal object the provision of steels containing 20% to 23% chromium which have resistance to corrosion in oxidizing or reducing acid conditions comparable to that of austenitic chromium steels, good impact strength at room temperature, and decreased sensitivity to elevated temperatures and conditions of heat-treatment.

High-chromium steels exhibit good resistance to many corrosive media and, hence, have attractive possibilities for industrial use. However, steels for corrosion service not only must be resistant to a wide variety of corrosive media, but also must exhibit good toughness and must maintain these properties after exposure to broad, elevated temperature ranges. The latter needs are not filled with the conventional ferritic chromium steels because they tend to be notch sensitive at room temperature and exhibit reduced properties on exposure to certain elevated temperature ranges. This is especially true when the chromium content exceeds 18%. On the other hand, although the austenitic chromium alloy steels have good impact properties, they are difficult to hot-work because of their great strength and relatively low hot-ductility at elevated temperatures. Further, they contain larger quantities of strategic alloying metals and, hence, are more expensive to make. Tough, substantially ferritic, high-chromium steel has long been a goal sought by metallurgists.

Although some expedients for providing tough ferritic chromium steels have been developed, they have not been adopted commercially to any great extent because of certain economic and inherent technical difficulties. One attack on the problem has been directed toward the control of carbon and nitrogen. The carbon and nitrogen contents of the steels are lowered below certain values which are a function of the chromium content of the steels. For instance, the maximum tolerance for carbon plus nitrogen in 25% chromium steels is about 0.035% to achieve toughness in this way. Although the desired result can be obtained in the laboratory, industry is not yet ready to adopt, on a large scale, the vacuum or inert atmosphere melting techniques required to lower the nitrogen content of the steel below the critical level.

Another expedient is presented in U. S. Serial No. 206,909, filed January 19, 1951, by W. Crafts, wherein it is proposed to add aluminum to high-chromium steels to counteract the effect of nitrogen and increase the impact strength of the steel, and in the application of W. O. Binder, U. S. Serial No. 206,905, filed January 19, 1951, it is

proposed that a small portion of nickel be added to the steel in addition to aluminum. While the steels produced in accordance with these expedients have improved toughness, under some conditions they suffer from certain disadvantages, i. e., hot-cracking on welding and segregated oxide inclusions which not only imparts poor surface qualities but also increases susceptibility to pitting. Further, the impact strength of the aluminum-containing steels is affected by section size and rolling practice, and the corrosion resistance and impact properties of these steels are undesirably sensitive to the conditions of heat-treatment and to elevated temperature exposure.

It is the main object of the present invention to provide a high-chromium steel having good impact strength at room temperature, useful resistance to both oxidizing and reducing acid corrosion, and decreased sensitivity to elevated temperatures and conditions of heat-treatment.

In accordance with the invention, 20% to 23% chromium steel, having a room temperature Izod impact strength averaging at least 50 ft.-lb., having corrosion resistance comparable to that of austenitic chromium-nickel steel, and having decreased temperature sensitivity is produced by the introduction of nickel, manganese, copper, and molybdenum, and by maintaining a proper balance between the chromium content, alloying constituents, and impurities. The invention is a steel consisting of 20% to 23% chromium; 1% to 3% nickel; 2.5% to 4.5% manganese; the sum of said nickel and manganese being less than 6%; 0.2% to 1.0% copper; 0.2% to 0.8% molybdenum; up to 1% silicon; 0.02% to 0.05% carbon; 0.02% to 0.20% nitrogen; the sum of carbon and nitrogen contents being greater than 0.05%; the remainder iron and incidental impurities. Conventional impurities such as phosphorus and sulphur may be present but should be held quite low.

The steel of the invention has an average Izod impact strength in the annealed condition of at least 50 ft.-lb. at room temperature, has a corrosion rate not exceeding 0.2 inch penetration per month in non-aerated 10% sulphuric acid at 70° C., and has the ability to retain these properties after exposure to temperatures from 700° C. to 1100° C. or on slow cooling from these temperatures. It possesses these properties despite the fact that it contains carbon and nitrogen in total amounts heretofore found detrimental to the toughness of ferritic 20% to 30% chromium steels.

The impact strength of several typical examples of the steel of the invention after annealing in the four different procedures indicated is set forth in Table I.

Table I

Composition percent							Izod impact strength at 25° C. foot-pounds			
Cr	Ni*	Mn	Cu*	Mo*	C	N	1	2	3	4
21.34	1.75	2.35	0.5	0.5	0.027	0.046	109	59	72	26
21.75	1.75	2.80	.5	.5	.028	.048	113	69	86	17
21.91	1.75	2.63	.5	.5	.034	.052	107	45	90	21
20.10	1.75	3.56	.5	.5	.032	.058	120+	112	62	49
20.98	1.75	3.40	.5	.5	.028	.060	120+	54	100	52
21.99	1.75	3.56	.5	.5	.033	.049	116	59	90	32
22.85	1.75	3.54	.5	.5	.033	.053	104	45	93	15
21.13	1.75	3.63	.5	.5	.038	.136	120+	120+	120+	99

*Percent added.
1. Annealed by heating 3 hours at 900° C. and water-quenching.
2. Annealed by heating ½ hour to 1 hour at 1100° C. and water-quenching.
3. Annealed by heating 3 hours at 900° C. and 1 hour at 750° C. and water-quenching.
4. Annealed by heating 3 hours at 900° C. and furnace-cooled.

The resistance of the steels of Table I to corrosion in non-aerated dilute sulphuric acid is recited in Table II.

Table II

Composition percent							Inch penetration per month in non-aerated 10% sulphuric acid at 70° C.			
Cr	Ni*	Mn	Cu*	Mo*	C	N	1	2	3	4
21.34	1.75	2.35	0.5	0.5	0.027	0.046	0.014	0.31	0.031	0.33
21.75	1.75	2.80	.5	.5	.028	.048	.020	.21	.025	.026
21.91	1.75	2.63	.5	.5	.034	.052	.015	.11	.023	.022
20.10	1.75	3.56	.5	.5	.032	.058	.118	.012	.738	.915
20.98	1.75	3.40	.5	.5	.028	.060	.018	.009	.015	.310
21.99	1.75	3.56	.5	.5	.033	.049	.011	.018	.026	.018
22.85	1.75	3.54	.5	.5	.033	.053	.014	.038	.024	.022
21.13	1.75	3.63	.5	.5	.038	.136	.007	.011	.017	.024

*Percent added.
1. Annealed by heating 3 hours at 900° C. and water-quenching.
2. Annealed by heating ½ hour to 1 hour at 1100° C. and water-quenching.
3. Annealed by heating 3 hours at 900° C. and 1 hour at 750° C. and water-quenching.
4. Annealed by heating 3 hours at 900° C. and furnace-cooled.

As can be seen from the data of Tables I and II, the steel of the present invention not only has unusually high impact strength but also possesses useful resistance to corrosion in dilute non-aerated sulphuric acid. Ferritic 18% chromium steels generally exhibit a corrosion rate of 1.5 to 2.5 inch penetration per month in non-aerated 10% sulphuric acid at 70° C., about ten to one hundred times the rate of the steel of the invention. Furthermore the excellent properties of the steel of this invention are attained over a wide range of heat-treatment, whereas the conventional ferritic chromium steels are far more sensitive to the conditions of heat-treatment.

Although the steel of the invention is, as indicated, amenable to heat-treatment over a relatively wide temperature range, the optimum combination of impact strength and corrosion resistance is attained by heating the steel in the range 800° C. to 1100° C. for a sufficiently long time to form a substantial proportion of austenite containing most of the carbides and nitrides in solid solution, the proportion of austenite generally being less than 50%. A preferred time for this purpose is 3 to 6 hours. Following the heating for solubility and homogeneity, the steel should be cooled rapidly using air, oil, or water as the quenching medium. In the annealed condition, the steel is partially austenitic and is formable, machineable, weldable, and suitable for manufacture into corrosion-resistant articles and numerous other products subjected to high stresses in service.

The composition limits of the steel of the present invention are critical, and a precise chemical balance must be maintained to obtain the desired properties. For instance, to attain the desired corrosion resistance, the chromium content must be at least 20%, but if chromium exceeds 23%, the steel becomes excessively notch sensitive. In Table III are shown impact and corrosion data which establish these conclusions. The data were obtained on steels containing about 1.8% nickel; 3.5% manganese; 0.5% molybdenum; 0.5% copper; 0.4% silicon; 0.03% carbon; 0.06% nitrogen; the percentages of chromium shown in the table; remainder iron. The specimens were tested after having been annealed by heating three hours at 900° C. and cooled in the furnace, furnace cooling generally being detrimental for high-chromium steels.

Table III

Chromium percent	Average Izod impact strength at 25° C. foot-pounds	Inch penetration per month in non-aerated 10% sulphuric acid at 70° C.
20.10	49	0.915
20.98	52	.310
21.99	32	.018
22.85	15	.022

Similar tests demonstrate the criticality of the nickel content of the steel of the invention. In these tests specimens of steels containing about 21% chromium; 3.5% manganese; 0.5% molybdenum; 0.5% copper; 0.4% silicon; 0.03% carbon; 0.06% nitrogen; the different proportions of nickel indicated in Table IV; and the remainer iron, were annealed by heating at 900° C. for three hours (six hours in the case of the nickel-free steel) followed by water-quenching and subjected to the impact and corrosion tests reported in the table. It will be seen that nickel provides great improvement in impact strength and corrosion resistance. However, if more than 3% nickel is added to these steels they become more austenitic and partake of the disadvantages of austenitic steels.

Table IV

Nickel percent	Average Izod impact values at 25° C. foot-pounds	Inch penetration per month in non-aerated 10% sulphuric acid at 70° C.
Nil	9	2.44.
1.54	115	0.033.
1.86	117	0.023.
1.93	120+	Not tested.

The proportion of manganese in the steel of the invention, too, is critical. Manganese within the ranges indicated imparts toughness and decreases the sensitivity of the steel to exposure to elevated temperatures. Demonstrating this are the data of Table V below which were obtained by testing specimens of steels containing about 21% chromium; 1.8% nickel; 0.5% molybdenum; 0.5% copper; 0.4% silicon; 0.03% carbon; 0.06% nitrogen; 0.7% or 3.5% manganese as indicated in the table; remainder iron. The specimens were tested after having been annealed by heating for three hours at 900° C. and water-quenched and then subjected to the indicated heat-treatments.

Table V

Condition of metal	Average Izod impact values at 25° C. foot-pounds		Inch penetration per month in non-aerated 10% sulphuric acid at 70° C.	
	0.7% Mn Alloy	3.5% Mn Alloy	0.7% Mn Alloy	3.5% Mn Alloy
Heated 1 hr. at 600° C. and water-quenched	20	112	1.64	0.59
Heated 1 hr. at 700° C. and water-quenched	23	106	1.33	.026
Heated 1 hr. at 800° C. and water-quenched	15	120+	.07	.016
Heated 1 hr. at 900° C. and water-quenched	46	120+	.029	.018
Heated 1 hr. at 1,000° C. and water-quenched	95	120+	.017	.008
Heated 1 hr. at 1,100° C. and water-quenched	40	106	.57	.013
Heated 1 hr. at 1,200° C. and water-quenched	--------	--------	.90	.43

Decreased temperature sensitivity of the steel of this invention is illustrated by the retention of good impact strength and excellent corrosion resistance after exposure to this broad range of high temperatures. Similar tests have shown that a minimum of 2.5% manganese is required for best performance under a wide variety of conditions of heat-treatment. Also, it has been found that if the sum of the manganese and nickel contents is greater than 6.0%, the alloy becomes more susceptible to intergranular corrosion, and it is for this reason that the manganese content should not exceed 4.5% and that the sum of the manganese and nickel must be maintained below 6.0% in the steel of the present invention.

The combination of copper and molybdenum in the range 0.2% to 0.8% each exerts a strong influence on sensitivity to conditions of heat-treatment and is similar to manganese in this respect; in addition, these elements improve the resistance of the steel to corrosion by reducing acids and to pitting. If the molybdenum content is greater than about 0.8%, however, the steel becomes more susceptible to embrittlement on exposure to temperatures below 800° C.

Carbon and nitrogen also have a marked effect on both the corrosion resistance and impact strength. With carbon contents greater than 0.05%, the steel exhibits reduced properties after exposure to temperatures below 800° C., and is more susceptible to intergranular corrosion after exposure to temperatures of 1100° C. or above. To insure high impact strength and excellent corrosion resistance under a wide variety of conditions of heat-treatment, the steel of this invention should not contain over 0.05% carbon and the nitrogen content should be in excess of 0.08%.

The residual silicon content should not exceed 1.0% as it imparts brittleness.

The steel of this invention may be made in Heroult-type furnaces by conventional electric arc furnace practices having general applicability to the production of stainless steels, as nitrogen does not have to be excluded from the furnace atmosphere and conventional low-carbon raw materials are employable. It can be made by induction-furnace melting practices if due regard is given to the carbon content of the raw materials, as the carbon content of the steel must not exceed 0.05%. The steel ingot form is hot-workable at a metal temperature of about 1100–1175° C., and the comparative ease of working at this temperature contributes to simplicity in achieving desired products by hot-working.

The steel of this invention, by virtue of its chemical composition, possesses good mechanical properties and corrosion resistance after a relatively simple annealing treatment. It may be heated in the range of 700° C. to 1100° C. without detriment to impact strength and corrosion resistance, but is subject to loss of toughness on prolonged exposure below these temperatures and becomes susceptible to intergranular corrosion after exposure to temperatures above this range. The loss of toughness and corrosion resistance can be restored by annealing in the range of 800° C. to 1100° C. It may be fabricated readily into products suitable for service requiring toughness and resistance to corrosion. The steel has a high yield strength, tensile ductility, and reduction of area indicating its suitability for structural service where high stresses are involved. The relative ease of melting and hot-working the steel and the fact that it can be made by conventional commercial melting practices render it economical to produce. Further, it has the advantage of requiring much smaller quantities of strategic alloying metals than the standard austenitic grades of stainless steel.

What is claimed is:

1. Steel consisting of 20% to 23% chromium; 1% to 3% nickel; 2.5% to 4.5% manganese; the sum of nickel and manganese being less than 6%; 0.2% to 1.0% copper; 0.2% to 0.8% molybdenum; up to 1% silicon; 0.02% to 0.05% carbon; 0.02% to 0.20% nitrogen; the sum of the carbon and nitrogen contents being greater than 0.05%; the remainder iron and incidental impurities; said steel having, in the annealed condition, an average Izod impact strength of at least 50 foot-pounds at room temperature.

2. Steel consisting of 20% to 23% chromium; 1.5% to 2.0% nickel; 2.5% to 4.5% manganese; the sum of nickel and manganese being less than 6%; 0.4% to 0.6% molybdenum; 0.4% to 0.8% copper; 0.3% to 0.6% silicon; 0.02% to 0.04% carbon; 0.08% to 0.15% nitrogen; the remainder, iron and incidental impurities; said steel having in the annealed condition an average Izod impact strength of at least 50 foot-pounds at room temperature.

WILLIAM O. BINDER.
ROGER A. PERKINS.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,120,554	Franks	June 14, 1938

FOREIGN PATENTS

Number	Country	Date
803,361	France	Sept. 29, 1936