Patented July 8, 1952 2,602,737

UNITED STATES PATENT OFFICE

2,602,737

CORROSION RESISTING STEELS

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No Drawing. Application May 10, 1949, Serial No. 92,497

2 Claims. (Cl. 75—128)

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This invention relates to austenitic chromium-nickel steels for use in chemical service in the welded condition, and more particularly to a method for enhancing the resistance of such steels to intergranular corrosion.

Austenitic chromium-nickel steels, for example the 18% chromium-8% nickel and 25% chromium-20% nickel are noted for their excellent resistance to corrosion. However, the precipitation of chromium carbide, which occurs when the steels are heated at temperatures between 400° and 900° C. such as during welding, renders these steels susceptible to grain boundary attack. In this condition, the steels may fail by intergranular corrosion when exposed to relatively weak corrosives.

A number of methods to eliminate the intergranular susceptibility of these steels have been proposed; namely, heat-treating at temperatures above about 1000° C. and cooling rapidly, lowering of carbon content, cold-working the steel and subsequently precipitating the carbides and rendering them harmless by suitable coagulating heat-treatments, adjusting the chromium or nickel contents to form an austenitic structure with some delta ferrite, and introducing such elements as columbium or titanium which preferentially combine with carbon and form more insoluble carbides than chromium.

None of these methods has proved completely satisfactory by reason of such factors as cost, limited practicality, inadequate corrosion resistance, decreased hot-workability, limited weldability and formability, and combinations of these and related factors. For example, to reduce costs there is a great demand for cheaper austenitic chromium-nickel steels than those containing columbium or titanium having good weldability and good resistance to intergranular attack after limited periods of heating in the carbide precipitation temperature range. In the majority of service conditions, in which the austenitic chromium-nickel steels are usable, the steels are not exposed to the detrimental temperature range for prolonged periods of time, hence they do not need the complete immunity to sensitization to intergranular corrosion that more extended heating requires. It has been proposed to use steels containing 0.03% maximum carbon for this purpose because they possess excellent resistance to intergranular attack after limited periods of exposure to temperatures in the sensitizing range, such as those encountered during welding, and they are cheaper than the fully stabilized steels. It is difficult, however, to make these extremely

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low-carbon steels because of carbon pickup during melting and processing which renders them unsuitable for resisting intergranular corrosion after fabrication. There is, accordingly, a great need for steels having an effective degree of intergranular corrosion resistance at carbon levels greater than 0.03% maximum to allow for the above-mentioned manufacturing difficulties.

The object of this invention is to fulfill this need. More specifically, it is the object of the invention to provide a method for improving the resistance to intergranular corrosion of austenitic chromium-nickel steels containing 16% to 25% chromium, 5% to 25% nickel, up to 3% molybdenum, up to 0.2% nitrogen, and up to about 0.06% carbon, under conditions in which the steel is exposed for only limited periods of time at temperatures in the carbide precipitation range.

The invention, by means of which these objectives are achieved, is based on the discovery that the resistance of austenitic chromium-nickel steels, containing 16% to 25% chromium, 5% to 25% nickel, up to 3% molybdenum, up to 0.2% nitrogen, and up to about 0.06% carbon, to damaging carbide precipitation after short periods of heating in the carbide precipitation temperature range is substantially increased if the composition of the steel is so regulated that it falls on the phase boundary line separating fully austenitic steels from steels containing some ferrite. The invention accordingly comprises such steels to which has been imparted resistance to intergranular corrosion after exposure to conventional fabricating heating cycles such as welding and stress-relieving, for example, by balancing the composition of such steels so that they are fully austenitic in the annealed condition by incorporating nickel in such steels in a proportion determined by the proportions of the other constituents and an equation to be given below. While it is generally felt that an austenitic structure is advisable from the standpoint of hot-workability and corrosion resistance, susceptibility to intergranular attack increases as the alloy content of the steel is increased beyond that required by the phase boundary relationship to form a completely austenitic structure.

In general, the method of the invention is applicable to steels containing 16% to 25% chromium, 5% to 25% nickel, and at least 50% iron. Such steels conventionally contain up to 1% silicon and 0.25% to 2.5% manganese, but it is preferred that the silicon and manganese contents do not exceed 0.5% to 1.5% respectively. Carbon may be present up to about 0.06%. Preferably, it

should not exceed 0.04%. Nitrogen may be present up to 0.2%, and it should not be less than 0.10%. Such steels may also contain up to 3% molybdenum.

In regulating the composition of the steel for the purpose of obtaining enhanced resistance to intergranular corrosion, as described herein, it is convenient to have the phase boundary between fully austenitic steels and steels composed of austenite and ferrite expressed mathematically so that the optimum composition can be selected for any given set of conditions. Several such relationships for austenitic chromium-nickel steels may be found in the literature and in general, they reveal the attendant micro-structure for a given composition. These equations show the extent that variations in carbon, nitrogen, manganese, nickel, chromium, silicon, and molybdenum affect the structure balance of a steel. However, it is well recognized that these relationships represent the conditions under which the steels were tested and they do not hold if the conditions differ appreciably from those employed in the development of the equation. For example, an equation developed for wrought metal cannot be applied directly to cast metal or welds because of the differences in homogeniety which exist between the structures and such differences change the value of the constant term in the equation. Another factor influencing the constant term is cold-work. An equation, based on the amount of ferrite present after a given amount of cold-work, will differ significantly in the constant term from one derived on the basis of the amount of ferrite present after annealing only. For these reasons, it is preferred to use the following equation because it is based on the evidence supporting the invention and therefore is more suitable in carrying out the method described herein:

$$\%Ni=\frac{(\%Cr+1.8\ (\%Mo)+2.5\ (\%Si)-16)^2}{12}+13-30\ (\%C)-36\ (\%N)-0.5\ (\%Mn)$$

The equation can be used to determine whether a steel is fully austenitic or partially ferritic in the annealed condition without examining its micro-structure. For example, if the nickel content of the steel is greater than that given by the equation, the steel will be fully austenitic, and if less, it will be partially ferritic.

A feature of the invention is the critical proportioning of the nickel and nitrogen contents. If the nickel content is significantly greater than the amount required to render the steel in the annealed condition completely austenitic in accordance with the phase boundary relationship, the intergranular corrosion resistance of the steel is lowered. It is believed that nickel decreases the tolerance of the steel for carbon. If nitrogen is utilized in conjunction with nickel to form austenite, the resistance of the steels falling on the phase boundary line to intergranular attack can be further increased. Nitrogen does not increase intergranular susceptibility to the same extent as carbon when the periods of heating in the damaging range are short. It is preferred that the nitrogen content be held at about 0.15% for this purpose, but it should not exceed the amount that the steel can safely hold in solution during solidification as otherwise the soundness of the metal will be affected.

The resistance of the steels to intergranular corrosion may be further increased by incorporating molybdenum in the steel. For this purpose, the molybdenum content should exceed about 0.25% and preferably should be held at about 1%. The molybdenum content may be extended to 3% if greater resistance to reducing conditions is desired, but there is some sacrifice in resistance to oxidizing acid conditions when the molybdenum content exceeds about 1%. When nickel is partially replaced with nitrogen, it is advantageous to add at least 0.5% to 1% molybdenum to the steel to offset the loss of resistance to reducing conditions due to the lowering of nickel.

The resistance of the steels to intergranular attack is greatly increased if the carbon content is held at a maximum of 0.04%. Low-carbon steels are particularly required if the steels are to be welded and stress-relieved during fabrication. It has been noted that the short period of heating in the carbide precipitation temperature range during welding coupled with a heat-treatment of 2 hours at 870° C. for the purpose of stress-relieving is far more damaging to the corrosion resistance of the steel than the isothermal heat-treatments normally employed to simulate welding conditions for test purposes. Where particularly heavy sections are involved especially where it is necessary to weld such sections or otherwise heat them to a temperature within the range of 400 to 900° C., it is advisable to keep the carbon less than 0.04%.

As is well understood by those skilled in the art, it is generally not possible to secure an exact composition, and in the endeavor to obtain the preferred composition, the results are likely to vary within certain limits. Deviations within the following ranges are permissible without greatly impairing the resistance of the steel to intergranular corrosion:

Cr±1.0%
Ni±1.0%
Mn±0.5%
Si±0.2%
C±0.005%
N±0.03%
Mo±0.25%

While the method embodying the invention does not necessitate the exclusion of any compositions within the ranges described herein that conform in composition with the requirements of the phase boundary relationship, it is preferred that the compositions fall within the following narrower ranges:

C—0.02% to 0.045%
Mn—0.75% to 1.75%
Si—0.2% to 0.6%
Ni—5% to 12%
Cr—17% to 20%
Mo—0.25% to 3%
N—0.10% to 0.20%

Illustrative examples showing the effect of increasing the total alloy content beyond that necessary to form an austenitic structure on the resistance of the steels to intergranular attack are given in Table I. The steels in Table I were subjected to an accelerated corrosion test consisting of immersing the steel in boiling 65% nitric acid for five periods of 48 hours each after being heated 10 minutes at 1075° C., air-cooling, then 1 hour at 650° C. and air-cooling. The first steel in each series embodies the requirements of this invention; namely, it contains just sufficient nickel in relation to its chromium, silicon, man-

ganese, nitrogen, and carbon contents to render the steel fully austenitic in the annealed condition. In each series, the nickel content was increased beyond the amount required to form an austenitic structure, and it is clearly seen that as the total alloy content of the steel increases it becomes less resistant to intergranular attack in this test medium.

Table I

Composition, Percent—Remainder Fe						Corrosion Rate, Inch Penetration per Month	
Cr	Ni	Mn	Si	C	N	A	B
18.37	10.88	1.09	0.32	0.024	0.029	0.00056	0.00080
18.51	11.82	1.32	0.51	0.023	0.026	0.00058	0.00084
17.92	12.64	1.27	0.50	0.022	0.027	0.00053	0.00069
18.02	14.97	1.43	0.47	0.026	0.027	0.00055	0.00197
20.52	12.71	1.24	0.54	0.028	0.039	0.00053	0.0050
20.36	15.24	1.39	0.47	0.028	0.035	0.00039	0.0125
20.61	18.32	1.35	0.53	0.037	0.034	0.00042	0.0350
18.3	6.5	1.2	0.4	0.030	0.115	0.00088	0.00092
18.3	8.0	1.2	0.4	0.030	0.113	0.00072	0.00074
18.25	10.15	1.24	0.4	0.030	0.110	0.00065	0.00191
18.3	6.5	1.2	0.4	0.033	0.146	0.00099	0.00099
18.3	8.0	1.2	0.4	0.033	0.144	0.00076	0.00081
18.35	10.47	1.20	0.40	0.033	0.153	0.00075	0.00250
18.31	12.50	1.22	0.46	0.033	0.176	0.00062	0.00170

A=Heated 10 minutes at 1075° C. and air-cooled.
B=Heated 10 minutes at 1075° C., air-cooled, then heated 1 hour at 650° C. and air-cooled.

Many tests have shown that the method of improving intergranular corrosion resistance described herein is applicable to a wide variety of compositions falling within the limits of composition set forth above. Several examples of steels containing nitrogen or molybdenum or both are given in Table II to illustrate further the invention. The steels in Table II were also tested in boiling 65% nitric acid, but, in these tests, the samples were exposed for three periods of 48 hours each after heating 15 minutes at 1125° C., air-cooling, then heated 2 hours at 650° C. and air-cooling. As in Table I, the first steel in each series is in accordance with the invention. Again it is seen that as the total alloy content is raised above the amount required to form an austenitic structure, in these cases by increasing nickel, resistance to intergranular attack decreases. It will be apparent that steels made by the method described herein need not be annealed after being exposed to the detrimental range for short periods of time as in welding, to avoid subsequent intergranular attack in service.

In Table III are typical examples of steels made in accordance with the invention, and the accompanying corrosion data illustrate the excellent resistance to intergranular corrosion exhibited by these steels after heating for short periods of time in the detrimental temperature range. The corrodent employed in the tests consisted of 10% nitric acid-3% hydrofluoric acid heated to 70° C., and the tests were conducted for 5 periods of 1 hour each. This solution is extremely corrosive and provides a sensitive and rapid test for revealing intergranular susceptibility due to carbide precipitation at the grain boundaries. Prior to heating in the detrimental range, the test samples were held 15 minutes at 1125° C. and air-cooled. The composition of the steels included in the table meets the requirements of the phase boundary relationship for a completely austenitic structure, and they fall within the allowable variation limits described above. These data clearly indicate that steels made in accordance with this invention so effectively retard carbide precipitation that, when heated in the detrimental temperature range for short periods of time as in welding, they will retain substantially all of their initial corrosion resistance in subsequent exposure to severe corrosive conditions. In this respect, the steels containing in excess of 0.10% nitrogen and 0.5% molybdenum are especially noteworthy.

Table II

Composition, Percent—Remainder Fe							Corrosion Rate, Inch Penetration per Month	
Cr	Ni	Mn	Si	Mo	C	N	A	B
18	5.0	1.5	0.5	------	0.057	0.145	0.00113	0.0021
18	6.0	1.5	0.5	------	0.051	0.145	0.00101	0.0049
18	7.0	1.5	0.5	------	0.051	0.144	0.00086	0.0054
18	6.0	1.5	0.5	0.5	0.060	0.166	0.00094	0.00108
18	8.0	1.5	0.5	0.5	0.050	0.158	0.00088	0.00180
18	10.0	1.5	0.5	0.5	0.060	0.139	0.00079	0.00825
18	7.0	1.5	0.5	1.0	0.06	0.17	0.00085	0.00098
18	9.0	1.5	0.5	1.0	0.06	0.13	0.00079	0.00379
18	10.5	1.5	0.5	1.0	0.058	0.04	0.00057	0.00191
18	15.0	1.5	0.5	1.0	0.050	0.04	0.00088	0.00420
18	9.0	1.5	0.5	2.0	0.054	0.166	0.00076	0.00120
18	11.5	1.5	0.5	2.0	0.042	0.159	0.00141	0.00830

A=Heated 15 minutes at 1125° C. and air-cooled.
B=Heated 15 minutes at 1125° C., air-cooled, then heated 2 hours at 650° C. and air-cooled.

Table III

Percent Composition, Remainder Fe and 18% Cr						Corrosion Rate, Inch Penetration per month			
Ni	Mn	Si	Mo	C	N	A	B	C	D
6.0	1.5	0.5	------	0.032	0.144	0.91	0.87	0.75	0.94
6.0	1.5	0.5	0.5	0.036	0.16	0.46	0.52	0.51	0.53
7.0	1.5	0.5	1.0	0.039	0.17	0.37	0.35	0.36	0.35
7.0	1.5	0.5	1.0	0.047	0.17	0.31	0.34	------	------
9.0	1.5	0.5	2.0	0.051	0.167	0.11	0.13	0.13	0.12
10.0	1.5	0.5	3.0	0.041	0.135	0.04	0.05	0.03	0.03

A=Heated 15 minutes at 1125° C. and air-cooled.
B=Heated 15 minutes at 1125° C. and air-cooled, heated 2 hours at 650° C. and air-cooled.
C=Heated 15 minutes at 1125° C. and air-cooled, heated ½ hour at 750° C. and air-cooled.
D=Heated 15 minutes at 1125° C. and air-cooled, heated 2 hours at 870° C. and air-cooled.

The excellent resistance of steels made in accordance with the invention to intergranular corrosion is further illustrated in Table IV. The corrodent in these tests consisted of boiling 65% nitric acid, and the tests were conducted for 5 periods of 48 hours each. The corrosion rates after the fifth test period are given in the table. These data show that the steels contemplated by the present invention are well suited for service in nitric acid after exposure to the detrimental temperature range for limited periods of heating when properly selected with respect to molybdenum content.

Table IV

Percent Composition, Remainder Fe and 18% Cr						Corrosion Rate, Inch Penetration per month			
Ni	Mn	Si	Mo	C	N	A	B	C	D
6.0	1.5	0.5	------	0.032	0.144	0.00094	0.00103	0.00090	0.00094
6.0	1.5	0.5	0.5	0.036	0.16	0.00099	0.00145	0.00111	0.00092
6.5	1.5	0.5	0.5	0.042	0.140	0.00068	0.00240	0.00205	0.00092
7.0	1.5	0.5	1.0	0.039	0.170	0.00113	0.00135	0.00108	0.00090
9.0	1.5	0.5	2.0	0.051	0.167	0.00079	0.00250	0.00470	0.00150

A=Heated 15 minutes at 1125° C. and air-cooled.
B=Heated 15 minutes at 1125° C., air-cooled, then heated 2 hours at 650° C. and air-cooled.
C=Heated 15 minutes at 1125° C., air-cooled, then heated ½ hour at 750° C. and air-cooled.
D=Heated 15 minutes at 1125° C., air-cooled, then heated 2 hours at 870° C. and air-cooled.

In the process of proving this invention, a large number of steels have been made and tested for the purpose of establishing the limits of the invention. The data obtained permit the conclusion that steels made in accordance with the invention possess superior resistance to intergranular attack. While an improvement is derived in every case, it will be apparent that not all steels embodying the invention will possess the same degree of intergranular corrosion resistance. It will be apparent, for example, that alloy constituents such as nitrogen and molybdenum, may be used with beneficial results. It will also be apparent that, while the maximum permissible carbon content varies with composition, for extremely severe conditions it is preferable to keep the carbon at about 0.04%. And finally, it will be apparent that the choice of composition will depend on the service conditions to be encountered.

This invention is in part a continuation of our application Serial No. 748,110, filed May 14, 1947, now abandoned.

We claim:

1. Chromium-nickel steel fully austenitic in the annealed condition and containing 16% to 25% chromium; 5% to 25% nickel; up to 3% molybdenum; 0.02% to 0.06% carbon; 0.25% to 2.5% manganese; up to 1% silicon; and 0.1% to 0.2% nitrogen, the remainder iron, the nickel content of such steel being substantially equal to:

$$\frac{(\%Cr+1.8\,(\%Mo)+2.5\,(\%Si)-16)^2}{12}+13-30\,(\%C)-36\,(\%N)-0.5\,(\%Mn)$$

2. Chromium-nickel steel fully austenitic in the annealed condition and containing 17% to 20% chromium; 5% to 12% nickel; 0.25% to 3% molybdenum; 0.02% to 0.045% carbon; 0.75% to 1.75% manganese; 0.2% to 0.6% silicon; and 0.1% to 0.2% nitrogen, the remainder iron, the nickel content of such steel being substantially equal to:

$$\frac{(\%Cr+1.8\,(\%Mo)+2.5\,(\%Si)-16)^2}{12}+13-30\,(\%C)-36\,(\%N)-0.5\,(\%Mn)$$

and such steel being characterized by resistance to intergranular corrosion after exposure to conventional fabricating heating cycles.

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