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CORROSION RESISTANT ALLOY

Peter Payson, New York, N. Y.

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This invention relates to improved corrosion resistant alloys and particularly to the production of such alloys which are less susceptible than the usual corrosion resistant alloys to intergranular attack when subjected to elevated temperatures.

In the production of alloys resistant to corrosion from ordinary chemicals, food stuffs, oils, etc., it has been the practice to combine chromium, nickel and iron in varying proportions to give the desired characteristics. An example of an alloy of this type is one containing about 16 to 20% chromium, 7 to 10% nickel, over 45% iron, carbon about .15%, manganese less than .75%, sulphur and phosphorus each less than .035%. Considerable variation in the proportions of the constituents present may be made for the production of alloys of particular characteristics and at a suitable cost, a largely sold corrosion resistant alloy being one containing about 18% chromium and 8% nickel.

In using such alloys for the production of equipment for use in chemical industries, it is frequently desirable or necessary to construct large vessels, tanks, tubes and the like by electric arc or gas welding processes or by other heating means. Also, in the use of such equipment in chemical plants, it is often necessary to subject the alloy to elevated temperatures, for example, 1000 to 1600° F., for a considerable period of time.

It has been found that when alloys of the above type are subjected to elevated temperatures for example 1000 to 1600° F., during a welding operation or while in use, the metal in the vicinity of the weld and the other metal subjected to such elevated temperatures will be structurally weakened and will be subject to what is frequently described as "weld decay" or "intergranular corrosion."

For the purpose of testing an alloy to determine whether or not it is subject to intergranular corrosion, it is customary to boil a sample of the alloy to be tested in a solution of copper sulphate and sulphuric acid, usually of the strength of about 10% by weight of each. An alloy which is subject to intergranular corrosion will be, when treated in this manner, put into a condition in which it can be crumbled between the fingers and will not withstand its own weight upon bending, even though the superficial appearance of the material may give no evidence of corrosion whatsoever. The material between the grains or crystals constituting the alloy appears to have been dissolved out without injury to the grains themselves. This test is adopted because it is very drastic in its action and is indicative of the fail-

ures that may be caused when an alloy which has been subjected to temperatures between 1000 to 1600° F. is exposed to electrolytes.

Various means have been tried for minimizing this intergranular corrosion, one of which is to use a very low carbon alloy, for example, below .07% carbon. Such alloys are, however, difficult and expensive to manufacture. Another method sometimes used for lessening intergranular corrosion is to heat the alloy and to quickly cool it from a temperature above 1850° F. Although this treatment may be carried out when dealing with small articles, it is practically impossible, or at least impracticable, to use it when dealing with large tanks or other parts of chemical equipment.

In preparing corrosion resistant alloys to be subjected to welding, it has heretofore been considered advisable to produce an alloy which would be non-magnetic after welding. This may be accomplished with most alloys of this type by the heat treatment mentioned above.

It has now been found that by adding certain elements, including molybdenum, titanium, vanadium, tungsten and silicon either alone or in combination, in amounts varying for example, between about ¼% and 5%, (the amount of added element necessary depending upon the composition of the alloy to which it is added), "Delta" iron is formed in the alloy and apparently carbon is present mainly within the grains or crystals of the Delta iron rather than along the crystal or grain boundaries or in cleavage planes within the crystals, as in the case of alloys previously used for this purpose. Thus when the alloy is heated, to such a temperature that the carbides are precipitated they are precipitated within the grains of "Delta" iron rather than mainly along the grain boundaries or cleavage planes. Thus, when my improved alloys are subjected to temperatures between 1000 to 1600° F. and then to the above mentioned treatment in a copper sulphate-sulphuric acid solution or with other electrolytes, the grain boundaries are not attacked in such a manner as to seriously physically weaken the alloys.

The addition of the elements referred to above in the required quantities causes the appearance of Delta iron in corrosion resistant steel previously free from it and so produces magnetism in the alloy.

In adding the element to the alloy, it should be added in such quantities that the resultant alloy, when cooled quickly from approximately 1850° to 2100° F., will be magnetic. The resulting alloy will be resistant to intergranular corrosion after

heating at 1000 to 1600° F., for such a period of time as is unavoidable in welding processes and even after heating at such temperatures for long periods.

- To illustrate the application of the above improvement the following table is given:

Steel number	Carbon	Nickel	Chromium	Added element
1	0.09	9.1	17.9	None
2	0.10	19.90	22.7	None
3	0.12	7.2	21.9	None
4	0.12	8.5	19.3	0.66 vanadium
5	0.12	8.3	19.1	1.88 vanadium
6	0.12	8.3	22.0	.78 vanadium
7	0.09	9.7	18.4	1.00 molybdenum
8	0.10	8.2	20.2	3.38 molybdenum
9	0.17	8.4	20.0	3.25 molybdenum
10	0.20	11.2	23.7	2.69 silicon
11	0.21	11.3	23.1	2.27 silicon
12	0.10	8.3	20.5	4.00 tungsten
13	0.10	8.1	21.1	.87 titanium

Each of these alloys may also contain manganese, phosphorus, sulphur or other impurities in the amounts normally found in such alloys, for example the amounts referred to above. Silicon is ordinarily present in corrosion resistant steel alloys and would not be considered as an added element unless present in amounts substantially greater than 0.70%.

These alloy steels were subjected to quick cooling from a temperature of 1850 to 2100° F. and their magnetic properties were tested after such cooling. Later they were reheated to within the range of 1000 to 1600° F. and were subsequently subjected to boiling in a copper sulphate-sulphuric acid solution, as described above.

Steels 1 to 3 are included as illustrative of corrosion resistant alloys of various chromium and nickel contents. No element was added to these alloys. Nos. 1 and 2 were non-magnetic when tested as above described, while No. 3 was magnetic. All of these were found to be subject to intergranular corrosion.

Steels 4, 5 and 6 are examples of alloys to which vanadium has been added in the proportion given. Steel 4 was non-magnetic after being cooled from 1850-2100° F. and was susceptible of intergranular attack when treated as above described. Steel 5 was magnetic after such cooling and was found to be perfectly resistant even after 400 hours of boiling in the copper sulphate-sulphuric acid solution. Steel No. 6 was somewhat magnetic and while not perfectly resistant to chemical action, was highly resistant as compared with No. 4.

Steels 7, 8 and 9 illustrate the addition of molybdenum. No. 7 was non-magnetic and susceptible of intergranular corrosion. Nos. 8 and 9 when treated as described above were magnetic and very highly resistant to intergranular attack.

Steels 10 and 11 illustrate the effect of adding considerable quantities of silicon. No. 10 was magnetic and highly resistant. No. 11 was non-magnetic and was not so highly resistant to intergranular attack.

Steels 12 and 13 are illustrations of the additions of tungsten and titanium, respectively. Each of these alloys were magnetic after cooling from 1850-2100° F. and showed greatly increased resistance to intergranular attack, No. 13 being totally resistant even after 420 hours of boiling in the copper sulphate-sulphuric acid solution.

As illustrated above, the proportions of the added elements must be carefully regulated in order to obtain the full advantage of the improvement. These proportions will vary with the

ratio of carbon, chromium, nickel and iron in the corrosion resistant alloy and should be such that in the particular alloy Delta iron will be formed and the alloy will be magnetic after quickly cooling from 1850° to 2100° F.

The above illustrations have been given in connection with steels containing .09 to .21% carbon, since, as indicated above, certain chromium-nickel-iron alloys containing less than .07% carbon are essentially free from intergranular attack and may not require the additional element. The alloys used usually contain at least about 45% iron, about 16 to 30% chromium, about 7 to 20% nickel, and the carbon should be less than about .25%. An increase in the carbon content of the steel makes it necessary to add increased amounts of the added element in order to produce a ferritic or magnetic condition when the alloy is cooled from 1850-2100° F. The chromium and nickel are usually present in such proportions that without the addition of the added element a non-magnetic alloy would be produced when cooled from 1850-2100° F., that is such that the alloy, without the added element would be austenitic.

As illustrated in Examples 4, 5 and 6 an increase in the chromium content over the 18% chromium-8% nickel ratio makes it unnecessary to add as much of the added element in order to produce an alloy which is magnetic upon cooling from 1850-2100° F. and which is resistant to intergranular attack.

I have also found that an alloy which is highly resistant to intergranular attack can be produced by adding titanium in amounts insufficient to produce a magnetic alloy when cooled quickly from 1850-2100° F. The following is an example of such an alloy:

Carbon	Silicon	Nickel	Chromium	Titanium
.09	.65	9.89	17.90	.70

Although specific examples have been given in describing the invention, it is not intended to thereby limit it to the particular proportions given, it being apparent that the invention may be utilized with many different concentrations of ingredients in the alloys. The terms used in describing the invention have been used in their descriptive sense and not as terms of limitation and it is intended that all equivalents of these terms should be included within the scope of the claims. In using the terms "molybdenum-silicon element" in the appended claims, it is intended to include molybdenum, titanium, zirconium, vanadium, tungsten and silicon or their equivalents either alone or in combinations of two or more.

What I claim is:

1. A corrosion resisting alloy steel article, at least a portion of which is exposed in use to temperatures of about 1000 to 1600° F. and thereafter without subsequent heating and quenching from a higher temperature, to liquid media inducing intergranular attack, said article being resistant to said attack, said steel containing: about 16 to 30% chromium, about 7 to 20% nickel, from about .07 to under .25% carbon in proportions to form austenite when cooled quickly from about 1850 to 2100° F., an effective amount up to about 5% molybdenum and an effective amount up to about 5% silicon, the molybdenum and silicon being present in such proportions as to form a resulting alloy steel containing delta ferrite.

2. A fabricated corrosion resisting alloy steel article, at least a portion of which is exposed during fabrication to temperatures of about 1000 to 1600° F. and thereafter without subsequent heating and quenching from a higher temperature, to media inducing intergranular attack, said article being resistant to said attack, said steel containing: about 16 to 30% chromium, about 7 to 20% nickel, from about .07 to under .25% carbon in proportions to form austenite when cooled quickly from about 1850 to 2100° F., an effective amount up to about 5% molybdenum and an effective amount up to about 5% silicon, the molybdenum and silicon being present in such proportions as to form a resulting alloy steel containing delta ferrite.

3. A corrosion resisting alloy steel article, at least a portion of which is exposed in use to temperatures of about 1000 to 1600° F. and thereafter without subsequent heating and quenching from a higher temperature, to liquid media inducing intergranular attack, said article being resistant to said attack, said steel containing: about 16 to 30% chromium, about 7 to 20%

nickel, from about .07 to under .25% carbon in proportions to form austenite when cooled quickly from about 1850 to 2100° F., and an effective amount up to about 5% molybdenum, the molybdenum being present in such proportion as to form a resulting alloy steel containing delta ferrite.

4. A fabricated corrosion resisting alloy steel article, at least a portion of which is exposed during fabrication to temperatures of about 1000 to 1600° F. and thereafter without subsequent heating and quenching from a higher temperature, to media inducing intergranular attack, said article being resistant to said attack, said steel containing: about 16 to 30% chromium, about 7 to 20% nickel, from about .07 to under .25% carbon in proportions to form austenite when cooled quickly from about 1850 to 2100° F., and an effective amount up to about 5% molybdenum, the molybdenum being present in such proportion as to form a resulting alloy steel containing delta ferrite.

PETER PAYSON.