Patented May 23, 1939 2,159,725

UNITED STATES PATENT OFFICE

2,159,725

CORROSION RESISTANT STEEL

Russell Franks, Niagara Falls, N. Y., assignor to Electro Metallurgical Company, a corporation of West Virginia

No Drawing. Application March 19, 1938, Serial No. 196,909

6 Claims. (Cl. 75—128)

The invention is an article, such as a container, which in normal use is subject to the corrosive action of saline solutions, and this application is in part a continuation of my application Serial No. 84,682, filed June 11, 1936.

Corrosion resistant austenitic steels containing about 18% chromium and about 9% nickel, less than 0.2% carbon, remainder iron, are used extensively to withstand media that rapidly corrode ordinary iron and steel. Despite the excellent resistance of these chromium-nickel steels to uniform general corrosion over the surface of the metal, undesirable deterioration and failure occur from localized attack of saline solutions that exhibits itself in the form of holes or depressed areas, and in many important applications this localized attack renders an article useless long before general deterioration or consumption has occurred.

Two distinct types of localized attack have been observed, the effects of which are readily distinguishable although their causes may be similar. One is characterized by the formation of holes and pits distributed at random over the surface of metal subjected to corrosion although the actual area occupied by these small holes or pits may represent only a fraction of the area constituting the article in question. This type of corrosion is usually referred to as "pitting." The other is "contact corrosion" which occurs only at and adjacent to an area of contact of some object with the corrosion-resisting metal surface. This object may be of the same material or it may constitute another material such as dirt, oil, rust, glass, wood, or even chromium-nickel steel. Although contact corrosion does not ordinarily proceed over the entire surface of the metal the diameters of the corroded areas are as a rule larger than those of the holes produced by pitting. Frequently the affected areas resulting from contact corrosion contain numerous small well-defined pits indicating that contact corrosion in many instances actually accelerates the tendency for the metal to pit.

Attempts have been made to overcome this localized attack by increasing the percentages of chromium and nickel, thereby enhancing the general nobleness of the steel, but steels containing even as much as 25% chromium and 20% nickel are still subject to pitting even though they are somewhat more resistant than the lower alloy steels to contact corrosion.

In the other direction, the nobleness of the steel has been decreased by lowering the chromium and nickel contents to a point where general corrosion proceeds at a moderate rate, but this expedient makes the metal less resistant to contact corrosion and does not eliminate pitting.

I have tested the effect of a great many alloyed additions on the resistance of the austenitic chromium-nickel steels to localized corrosion. Nearly all of those tested have exhibited no substantial beneficial effect. However, certain combinations of alloyed additions in relatively small proportions were found to improve the resistance to this form of corrosion to a surprisingly great degree. Briefly, molybdenum strongly retards pitting, and less strongly retards contact corrosion, and although manganese has little effect in inhibiting either form of attack, a mixture of molybdenum and manganese greatly improves the resistance of the steels to both types of localized corrosion. The data given in Table A show the improvement secured by incorporating these additions in the 18% chromium–9% nickel steels.

Table A

Steel No.	Composition (remainder iron)					
	Percent Cr	Percent Ni	Percent C	Percent Si	Percent Mn	Percent Mo
1	18	9	0.09	0.2	0.6	None
2	18	9	0.07	0.5	0.5	None
3	18	9	0.08	0.3	3	None
4	18	9	0.09	0.3	0.5	2
5	18	9	0.10	0.3	0.5	3.5
6	19	9	0.08	0.4	3.1	2.6

	Condition of sample after—		
	Spraying with 20% NaCl solution for 1 year	Immersion in 10% NaCl+0.5% $FeCl_3$ solution for 5 hours	Immersion in 10% NaCl+5% $FeCl_3$ solution for 1.5 hours
1 and 2	Pitted and severe contact corrosion in 5 months.	Badly pitted	Badly pitted.
3	Slight pitting and contact corrosion.	do	Do.
4	do	Unaffected	Unaffected.
5	Practically unaffected.	Slightly pitted	Slightly pitted.
6	do	Unaffected	Unaffected.

This table shows the results of tests made on different steels using sodium chloride solutions of different strengths with and without additions of ferric chloride. In making these tests, small cylindrical-shaped solid samples approximately ⅞ inch in diameter and 1 inch long were used. Each sample was given a relatively high polish

on all surfaces so that attack could be easily detected. The salt spray tests made with a 20% sodium chloride solution consisted of exposing the sample to the spray from a 20% sodium chloride solution while one surface of the sample was in contact with a glass plate upon which it rested. At the end of a few months in this test a steel sample readily susceptible to localized attack will become pitted on the top surface, whereas the bottom surface in contact with the glass will exhibit both pitting and contact corrosion. The tests made in the 10% sodium chloride solutions containing ferric chloride were employed to detect susceptibility to pitting alone.

It is shown in this table that, at the end of a five-month period, the plain 18% chromium-9% nickel steels were found to be subject to both pitting and contact corrosion in the salt spray test, whereas in the sodium chloride solutions containing ferric chloride in which the samples were simply immersed, pitting occurred in relatively short periods. It is further shown in this table that steels containing molybdenum and low manganese are fairly resistant to pitting but during long periods of exposure gradually become subject to the contact type of attack. Other data in the table indicate that manganese additions in the neighborhood of 3% assist greatly in retarding the development of both pitting and contact corrosion on exposure to the salt spray atmosphere but the chromium-nickel steels containing 3% manganese appear to be quite susceptible to pitting in sodium chloride solutions containing ferric chloride. On the other hand, it is evident that by the incorporation of both molybdenum and manganese the steels are markedly improved with respect to both types of corrosion.

When sufficient manganese is incorporated, the effect is to offset the tendency for the ferritic constituent to develop in the austenitic chromium-nickel steels as a result of the molybdenum addition, thereby permitting the manganese-bearing steels to be rolled directly from ingots of large size into articles of commerce. Without sufficient manganese present, the molybdenum-bearing chromium-nickel steels tend to check during the hot rolling or forging processes because of the excessive quantities of the ferritic constituent that is present in the cast chromium-nickel steels containing molybdenum. While it is true that the amount of the ferritic constituent can be reduced by increasing the carbon and nickel contents and reducing the chromium content of the steels, this results in decreased resistance to general over-all corrosion. Thus, the manganese performs another important function by permitting the fabrication of articles of low carbon content that also contain optimum percentages of chromium.

The invention comprises a novel article, such as a container, which in normal use is subject to the corrosive action of saline solutions, that would (because of localized contact between the metal of the inside of the container and a solid object, or because of the presence of a small crevice in the container, or because the solution has a pH less than 7, or for more than one of these reasons) normally produce localized attack of an article composed of ordinary austenitic chromium-nickel steel, (18% chromium, 9% nickel, 0.1% carbon, less than 1% each of silicon and manganese, remainder iron). The novel article is composed of an austenitic chromium-nickel steel containing about 16% to 30% chromium, about 7% to 20% nickel, carbon in amounts not exceeding 0.20%, and effective amounts of molybdenum and manganese that serve to inhibit the localized corrosive attack. The molybdenum is suitably present in an amount of about 2% to 5% of the steel and the manganese should be present to the extent of between 1.50% and 5%, although it is preferable to have present at least 2% manganese. The usual amount of silicon present in commercial steel may also be included, but it is preferred that the silicon content be kept below 1%.

The preferred range of compositions is as follows:

	Per cent
Chromium	16 to 24
Nickel	8 to 14
Carbon	Not over 0.12
Molybdenum	2.50 to 4
Manganese	2 to 4
Silicon	Not over 0.5
Iron	The remainder

The steel of which the container of the present invention is composed is adapted to fabrication by ordinary methods, by forging and rolling, and by welding, riveting, and similar joining means. The steels are also soft, ductile and tough, possess excellent strength, and maintain their excellent corrosion resistant properties even after cold rolling if the cold work is applied uniformly to the section. One of the most important applications of the container is to hold and resist the action of sea water or water containing other chlorides such as exist in industrial applications. Usually in these instances the corroding media have a pH value less than 7, a condition which causes pitting to take place readily in the plain chromium-nickel steels.

I claim:

1. A container for saline solutions composed of an austenitic steel containing 16% to 30% chromium, 7% to 20% nickel, 2% to 5% molybdenum, 1.5% to 5% manganese, carbon in an amount less than 0.2%, silicon in an amount not exceeding 1%, the remainder iron; the molybdenum and manganese acting to impart to such container resistance to localized attack by saline solutions.

2. A container for saline solutions that normally would produce localized attack of a container composed of an austenitic chromium-nickel steel containing no molybdenum and less than 1.5% manganese, such container being resistant to the localized attack of saline solutions and being composed of an austenitic steel containing 16% to 24% chromium, 8% to 14% nickel, 2.5% to 4% molybdenum, 2% to 4% manganese, carbon in an amount not exceeding 0.12%, silicon in an amount not exceeding 0.5%, the remainder iron.

3. Article which in normal use is subjected to the prolonged action of saline solutions under conditions which tend to produce localized corrosion of the pitting and contact types in austenitic chromium-nickel steels containing no molybdenum and less than 1.5% manganese, which article is composed of an alloy steel comprising 16% to 30% chromium, 7% to 20% nickel, 2% to 5% molybdenum, 1.5% to 5% manganese, carbon in an amount not exceeding 0.2%, silicon in an amount not exceeding 1%, the remainder iron; the molybdenum and manganese acting to impart improved resistance to said localized corrosion.

4. Article which in normal use is subjected to the localized corrosive action of prolonged con-

tact with sea water, at least a portion of such water in contact with the article having a pH less than 7, which article is composed of a fully austenitic alloy steel comprising 16% to 24% chromium, 8% to 14% nickel, 2.5% to 4% molybdenum, 2% to 4% manganese, carbon in an amount not exceeding 0.12%, silicon in an amount not exceeding 0.5%, the remainder iron; the molybdenum and manganese acting to impart improved resistance to said localized corrosive action.

5. Articles which in normal use are subjected to the prolonged action of saline solutions under conditions which, because of localized contact between said article and a solid object or because the solution has a pH less than 7, or both, tend to produce localized corrosion of the pitting and contact types in austenitic chromium-nickel steels containing no molybdenum and less than 1.5% manganese, which articles are composed of an alloy steel comprising 16% to 30% chromium, 7% to 20% nickel, 2% to 5% molybdenum, 1.5% to 5% manganese, carbon in an amount not exceeding 0.2%, silicon in an amount not exceeding 1%, the remainder iron; the molybdenum and manganese acting to impart resistance to said localized corrosion.

6. Articles which in normal use are subject to the localized corrosive action of prolonged contact with sea water having a pH less than 7, which articles are composed of an alloy steel comprising 16% to 24% chromium, 8% to 14% nickel, 2.5% to 4% molybdenum, 2% to 4% manganese, carbon in an amount not exceeding 0.12%, silicon in an amount not exceeding 0.5%, the remainder iron; the molybdenum and manganese acting to impart resistance to said localized corrosive action.

RUSSELL FRANKS.