

1

3,574,604

NICKEL-CHROMIUM ALLOYS RESISTANT TO STRESS-CORROSION CRACKING

Harry R. Copson, Mahwah, and Daniel van Rooyen, Ramsey, N.J., assignors to The International Nickel Company Inc., New York, N.Y.

No Drawing. Filed May 26, 1965, Ser. No. 459,110

Int. Cl. C22c 19/00

U.S. Cl. 75-171

4 Claims

ABSTRACT OF THE DISCLOSURE

Intergranular stress-corrosion attack of metal articles in contact with aerated high purity water at elevated temperature is minimized when such articles are formed from nickel-chromium and nickel-chromium-iron alloys of high chromium content.

The present invention relates to nickel-chromium and nickel-chromium-iron base alloys and, more particularly, to minimizing and/or overcoming the vexatious problem of stress-corrosion cracking of such alloys when exposed to a high purity water environment.

In recent years, what must be considered as a unique problem has been reported in the literature as a result of laboratory tests (although the number of such reports has been relatively few) to the effect that nickel-chromium and nickel-chromium-iron alloys, such as those containing, inter alia, 75% to 80% nickel, 14% to 16% chromium and up to 7% to 8% iron, are prone to undergo stress-corrosion attack in pressurized water of high purity at temperatures on the order of about 600° F., e.g., 570° F. to 660° F. That there is a dearth of literature concerning the problem probably stems from the fact that the conditions causing stress-corrosion cracking are unique and specific and are not normally encountered in service. Too, it has been considered that for the most part nickel-chromium and nickel-chromium-iron alloys were thought to be rather immune to this type of corrosive attack. But the possibility of such attack coupled with the gravity of the problem and the expansion of commercial operation dictates that efforts be indeed expended to thwart or minimize the same. Data presented herein confirms that the problem can arise and little emphasis need be added regarding the importance and significance of this phenomenon. Deleterious cracking of components and vessels and the like used in various systems of nuclear equipment wherein high purity water is used, is indeed of no little moment.

Broadly speaking and as is well known to those skilled in the art, stress-corrosion cracking per se is a well known phenomenon. Over the years, a wealth of literature coping with the problem of stress-corrosion cracking of the austenitic nickel-chromium stainless steels has been accumulated, particularly with regard to chloride environments. While known recent avenues of approach for stainless steel were considered in seeking a solution to the problem herein, it was deemed that little by way of substantive merit would be expected, since what is apparently applicable to the stainless steels is not seemingly apposite to the instant situation. Stress-corrosion cracking of the stainless steels in chloride solution is primarily transgranular in nature whereas the subject type of stress-corrosion cracking in nickel-chromium-iron alloys is intergranular. This factor is indicative that cracking is probably associated with some condition at the grain boundaries. Further, it has been found that AISI 304 stainless steel has upon exposure to high purity water of high temperature also suffered stress-corrosion attack of the intergranular type in the sensitized condition.

2

Notwithstanding that the subject problem ostensibly appears to be one intergranular in nature, the conventional methods of overcoming the problem of intergranular corrosion as in connection with the austenitic stainless steels, to wit, the use of either the standard carbide stabilizers or low carbon contents or the use of stabilizing heat treatments, have not proven to be a panacea.

Consideration was also given to the use of materials of very high purity, i.e., the use of extremely pure nickel, chromium and iron and not much else. This pursuit appeals more to theoretical curiosity since it is basically impractical from a commercial viewpoint. Not only is it expensive to use such materials but good commercial practice requires the use of various other elements, notably aluminum and/or titanium, to provide necessary deoxidizing and malleabilizing attributes and to provide, for example, good forging practice. Moreover, it is not unlikely that the mechanical properties of such alloys would be inferior.

The foregoing approaches serve to focus greater attention on appreciating the significance of the operating environmental conditions which could lead to the type of corrosive attack in question and also understanding the ostensible peculiarities or behavior of nickel-chromium and/or nickel-chromium-iron alloys upon exposure to such conditions. Perhaps it should be mentioned that high purity water as contemplated herein contains not much above a total solids content of less than 1 part per million (p.p.m.) by weight and which has been distilled and/or deionized or otherwise treated such that it will manifest a specific resistance of about 500,000 ohm-cm. or higher. As is appreciated by those skilled in the art, this type of water is used in atomic power equipment including nuclear pressure vessels.

Certain environmental conditions have been established which either promote or are causative of inducing or creating a propensity for detrimental intergranular stress-corrosion cracking to occur in nickel-chromium-iron alloys. Aerated high purity water (in combination with the surface condition of the alloys) is one such condition and temperature is another. Normally, high purity water is devoid of oxygen and it is believed that the usual absence thereof has been responsible, to a considerable degree, for the lack of intergranular stress-corrosion cracking of nickel-chromium and nickel-chromium-iron alloys heretofore on a commercial scale. But the possibilities of oxygen contamination are indeed more than sufficient to warrant the necessity of finding alloys which afford a markedly higher degree of resistance to such attack. As to temperature, if the temperature of the water is at about room temperature, stress-corrosion attack does not appear to be much of a problem. But, in commercial operation the temperature of the high purity water is normally above room temperature and is commonly over 300° F., e.g. about 450° F. or 500° F. to about 660° F. and it is at such temperatures, particularly at the higher temperatures, where the occurrence of intergranular stress-corrosion attack is most likely.

As to the condition of the alloys susceptible to attack and while little is available covering the same in the published literature, it would appear that "crevices" (in combination with aerated, high temperature, high purity water) exert a most pronounced subversive influence in producing stress-corrosion cracking and other forms of corrosion. Whether the crevice by nature be a flaw, crack, sharp indentation or other such surface defect is rather inconsequential. The unfortunate fact remains that it is exceedingly difficult, if not impossible, to avoid or prevent the occurrence thereof. If the alloy is incapable of resisting stress-corrosion attack, there is also at least

the likelihood of greater "crevice buildup" of corroded product. This would obviously interfere in applications requiring moving parts and which of necessity require adherence to observing small clearance tolerances. Thus, it can be reasonably stated without much reservation that the conditions leading to the occurrence of intergranular stress-corrosion cracking of nickel-chromium and nickel-chromium-iron alloys are at hand when aerated high purity water of a temperature of above about 300° F. is brought into contact with certain alloys under stress and containing crevices and the like. It is to be understood, however, that other factors are undoubtedly involved. The present invention is addressed to the foregoing specific problem.

It has now been discovered that nickel-chromium and nickel-chromium-iron alloys wherein the amounts of chromium and/or iron are specially controlled or correlated afford markedly enhanced resistance to intergranular stress-corrosion attack when such alloys are brought into intimate contact with aerated high purity water at a temperature above about 300° F., e.g., 450° F. to about 660° F., notwithstanding the fact that the surface of such alloys contains a surface defect, such as a crevice.

It is an object of the present invention to provide nickel-chromium and nickel-chromium-iron base alloys of special composition which manifest a high overall resistance to stress-corrosion cracking when such alloys are in contact with aerated high purity water at a temperature above about 330° F. and up to at least about 660° F.

It is another object of the present invention to provide a process for accomplishing the foregoing.

Other objects and advantages will become apparent from the following description.

Generally speaking and in accordance with the present invention, stress-corrosion cracking of nickel-chromium and nickel-chromium-iron alloys to be brought into contact with aerated high purity water, the temperature of the water being from above about 300° F. to about 660° F., e.g., 450° F. or 500° F. to about 660° F., can be greatly minimized by utilizing alloys of the following composition (based on weight percent): about 14% to about 35% chromium, up to about 50% iron, with the proviso that when the iron is present in an amount above about 0.5%, the chromium is at least 20%, at least one element selected from the group consisting of aluminum and titanium, the aluminum being present in an amount up to 0.5%, e.g., about 0.01% to 0.4%, and the titanium being present in an amount up to about 0.5%, e.g., about 0.01% to 0.4%, up to about 1% silicon, e.g., about 0.05% to 0.5% silicon, up to about 0.15% carbon, e.g., up to 0.1% carbon, and the balance essentially nickel. The use of the expression "balance" or "balance essentially" in referring to the nickel content of the alloys, as will be understood by those skilled in the art, does not exclude the presence of other elements commonly present as incidental elements, e.g., deoxidizing and cleansing elements, and impurities normally associated therewith in small amounts which do not adversely affect the novel characteristics of the alloys. In this regard, it is preferred that elements such as phosphorus and sulfur be maintained at low levels as is consistent with commercial practice. Manganese can be present in amounts up to at least 2%, e.g., 0.1% to 1%.

In accordance with the present invention, it has been found that relatively high amounts of chromium, e.g., above 20%, exert a most beneficial effect in minimizing intergranular stress-corrosion cracking in nickel-chromium and nickel-chromium-iron alloys. The theoretical explanation for this phenomenon is not completely understood, particularly when viewed in the light of the conventional amounts of chromium, e.g., 14% to 16%, widely used in nickel-chromium-iron alloys of the substantially non-age hardening type. The amount of chromium contemplated herein can be less than 20% provided the iron content of

the alloys is less than about 0.5%, e.g., less than 0.35% iron. Low iron contents also favorably contribute to resisting intergranular stress-corrosion cracking. The benefit conferred by either high chromium or low iron or both can be further increased by maintaining the carbon content below about 0.05%, e.g., below 0.03%.

In carrying the invention into practice, it is advantageous in obtaining optimum results that alloy compositions falling within the following ranges be employed: about 20% to about 30% chromium, up to about 10% iron, with the proviso that when the iron content is above about 0.35%, the chromium is at least 22%, at least one element selected from the group consisting of aluminum and titanium, the aluminum being from about 0.03% to 0.2% and the titanium being from about 0.03% to 0.3%, silicon in an amount up to about 0.35%, up to about 0.05% carbon and preferably not more than 0.03% carbon, the balance being essentially nickel. To facilitate ease of processing and to provide optimum deoxidizing and/or malleabilizing characteristics, it is preferred that both aluminum and titanium be present in a total amount of at least 0.2%. For optimum results, the chromium content is advantageously at least 23% or 24% regardless of the iron content.

From a practical commercial point of view, alloys of the type under consideration are commonly, as is well known to those skilled in the art, produced and/or sold in the so-called "annealed" condition. That is to say, the alloys are generally subjected to an anneal heat treatment within the temperature range of 1500° F. to 2100° F., usually about 1600° F. to 1900° F., and thereafter cooled as by quenching. Intergranular stress-corrosion cracking can occur in this condition but this is only one aspect of the situation, albeit an important one. Frequently, such alloys are "sensitized" or used in applications whereby they become sensitized. For example, alloys contemplated herein are often welded to form a welded structure; however, as a result of the welding operation, the alloys pass through (upon cooling) a "sensitizing" temperature range of below about 1500° F., to 800° F., e.g., about 1450° F. to 850° F. While an alloy might manifest good resistance to intergranular stress-corrosion cracking in the annealed condition, it may very well show cracking in the sensitized condition. This fact is illustrated herein and, thus, consideration should be given to both conditions (annealed and sensitized).

For the purpose of giving those skilled in the art a better understanding and/or appreciation of the invention, the following illustrative data are given:

A number of alloy test specimens were prepared having compositions given in Table I, Alloys A through I being outside the invention and Alloys Nos. 1 through 6 being within the scope thereof:

TABLE I

	Chemical composition, percent							
	Cr	Fe	C	Al	Ti	Si	Ni	Other
Alloy:								
A-----	16.3	7.0	0.04	0.11	0.30	0.21	Balance	
B-----	16.2	7.5	0.07	0.09	0.26	0.22	do	
C-----	16.2	7.4	0.06	0.09	0.26	0.21	do	
D-----	15.9	7.3	0.06	0.10	0.28	0.20	do	0.9 Cb
E-----	16.4	7.0	0.005	0.11	0.38	0.25	do	2.85 Cb
F-----	16.4	7.1	0.06	0.12	0.28	0.18	do	1.05 W
G-----	16.4	7.4	0.05	0.12	0.28	0.20	do	1.7 Mo
H-----	14.9	6.7	0.05	0.17	0.34	0.20	do	7.5 Mo
I-----	16.2	7.1	0.04	0.12	0.27	0.26	do	0.3 Ta
1-----	24.0	6.4	0.04	0.10	0.27	0.23	do	
2-----	23.8	7.1	0.03	0.12	0.24	0.26	do	
3-----	20.5	7.2	0.04	0.10	0.27	0.23	do	
4-----	20.6	0.12	0.06	0.12	0.29	0.20	do	
5-----	24.8	0.06	0.06	0.14	0.30	0.21	do	
6-----	16.2	0.12	0.02	0.08	0.33	0.23	do	

The alloys of Table I were prepared using vacuum melting techniques and using materials of relatively high purity. After removing surface defects from the cast ingots, the alloys were heated to about 2200° F. and forged to flats (1 inch by 3.5 inches by 10 inches). After

reheating to 2150° F., the flats were hot rolled to a thickness of about 0.2 inch. Subsequent to conventional processing, including cold rolling to provide specimens about 0.12 inch thick, the alloys were subjected to various treatments. Three different treatments were employed, one consisting of solution heat treating at about 2050° F. for one hour followed by a water quench. The second treatment consisted of a sensitizing treatment whereby the specimen was heated to a temperature of about 1250° F., held at this temperature for about two hours and then air cooled. The third heat treatment was a thermomechanical treatment whereby the strips were cold reduced by about 40% to 50%, annealed at about 1600° F. for about four hours and then water quenched. This third treatment was investigated since it is not uncommon to cold work such alloys and thereafter anneal to obtain a desired level of mechanical or other properties. Thus, three specimens (strips) of each alloy composition were prepared, one being subjected to the solution anneal treatment, the second being subjected to the sensitizing treatment and the third to the thermomechanical treatment (often referred to as a stabilizing treatment).

Standard autoclave testing techniques were employed and duplicate U-bend test specimens of each alloy were used. These specimens were formed by bending two flat strips simultaneously around a mandrel and inserting a bolt through the parallel legs thereof. The flat strips were about 3/8 inch in width, 0.12 inch thick and about 3.25 inches long. Prior to bending about the mandrel, an area about 0.005 inch deep and about 1 inch long was ground in the center portion of one strip. On bending about the mandrel, a tapered crevice was formed.

The test solution was aerated high purity water (air saturated at one atmosphere) with the pH thereof having been adjusted to about pH 10.0. This test solution was placed in the autoclave and a head spaced having additional air was maintained. The test specimens were immersed in the solution and the autoclave sealed and brought to a test temperature of about 600° F. to 660° F. The autoclaves were opened about every two weeks and the specimens inspected for cracks, whereafter the tests were restarted with fresh solution in those instances where cracking was not visually observed. The tests were conducted generally over a period of eight weeks and both visual and metallographic examinations of the specimens were made. In this connection, if a specimen did not exhibit visual cracking, the metallographic examination was not then made; however, any specimen which did not manifest visual cracking during the full eight week period was thereafter examined metallographically. The results are reported in Table II wherein the numerals indicate the time of cracking; for example, the numerals 2 and 4 indicate the specimens cracked within the first and second two week periods, respectively.

TABLE II

	Cracking time					
	1st treatment		2nd treatment		3rd treatment	
	Visual	Metallographic	Visual	Metallographic	Visual	Metallographic
Alloy:						
A.....	OK, OK	C*, OK	2, 2	C, C	OK, OK	C*, OK
B.....	OK, OK	OK, OK	2, 2	C, C	8, OK	C*, C*
C.....	8, OK	C, OK	2, 2	C, C	OK, OK	C*, OK
D.....	8, OK	C*, OK	4, OK	C, OK	OK, OK	C, C
E.....	OK, OK	OK, OK	8, OK	C*, OK	8, OK	C, OK
F.....	OK, OK	C*, C*	2, OK	C, OK	OK, OK	C*, C*
G.....	OK, OK	OK, OK	OK, OK	OK, OK	2, OK	C, OK
H.....	OK, OK	OK, OK	OK, OK	C*, OK	2, 4	C, C
I.....	OK, OK	OK, OK	4, OK	C, OK	8, OK	C, C*
1.....	OK, OK	OK, OK	OK, OK	OK, OK	OK, OK	OK, OK
2.....	OK, OK	OK, OK	OK, OK	OK, OK	OK, OK	OK, OK
3.....	OK, OK	OK, OK	OK, OK	C, OK	OK, OK	OK, OK
4.....	OK, OK	OK, OK	OK, OK	OK, OK	OK, OK	OK, OK
5.....	OK, OK	OK, OK	OK, OK	OK, OK	OK, OK	OK, OK
6.....	OK, OK	OK, OK	OK, OK	OK, OK	OK, OK	OK, OK

NOTE:

C=cracks extended more than 1/2 through specimen.
C*=shallow cracks usually about 1 to 2 grains deep.

The data of Tables I and II illustrate the marked superiority of alloys within the present invention. It is clear that Alloys A, B, and C (which can be considered as "Controls") readily cracked under at least two conditions of testing, particularly in the sensitized condition. Alloys D through I reflect that elements such as columbium, tungsten, molybdenum and tantalum did not overcome this propensity to manifest undesirable stress-corrosion cracking. By way of contrast, Alloys Nos. 1 through 6 were greatly superior in this respect. Except for the amount of chromium, Alloys Nos. 1 and 2 were very close in composition to Alloys A, B and C. However, the former, which contained over 23% chromium, did not crack whereas the latter were quite unsatisfactory in comparison therewith. Only one specimen of Alloy No. 3 exhibited any degree of cracking and that was in the last phase of completion of the test. This alloy contained 20.5% chromium. Broadly, this alloy is within the scope of the present invention although as indicated hereinbefore, it is much preferred to use a chromium content of at least 23%. Alloy No. 4, which was quite similar to Alloy No. 3, did not manifest any cracking but it will be noted that the iron content thereof was 0.12% as opposed to 7.2% for Alloy No. 3. This clearly reflects the benefit, as indicated above herein, of using low iron contents. However, it must be recognized that for intended commercial applications it might often be necessary to use higher amounts of iron, to wit, 5% to 15%. Where this is necessary, then, of course, at least 20% and preferably at least 23% chromium should be present in the alloy. Alloy No. 6 contained a low iron content and cracking was not observed. Because of the catastrophic effects that could ensue should intergranular stress-corrosion cracking occur in a nuclear environment and particularly the propagation of the cracking, it is quite advantageous to use a chromium content of not less than 24% and an iron content of not more than 0.35%.

It has also been found, and it is an additional feature of the instant invention, that substantial amounts of elements such as molybdenum can be tolerated provided the chromium content is not less than 20%. This is manifested by the data in Tables III and IV (data on tantalum being included), the alloys having been prepared and tested in the manner set forth in connection with Tables I and II:

TABLE III

	Chemical composition, percent							
	Cr	Fe	C	Al	Ti	Si	Ni	Other
Alloy:								
G.....	16.4	7.4	0.05	0.12	0.28	0.20	Balance	1.7 Mo
7.....	24.0	7.5	0.09	0.19	0.37	-----	do.....	1.7 Mo
H.....	14.9	6.7	0.05	0.17	0.34	0.20	do.....	7.5 Mo
8.....	22.0	6.9	0.08	0.18	0.35	0.21	do.....	7.7 Mo
I.....	16.2	7.1	0.04	0.12	0.27	0.26	do.....	0.3 Ta
9.....	20.0	7.0	0.005	0.17	0.29	0.23	do.....	1.2 Ta

TABLE IV

	Cracking time					
	1st treatment		2nd treatment		3rd treatment	
	Visual	Metal-lographic	Visual	Metal-lographic	Visual	Metal-lographic
Alloy:						
G.....	OK, OK	OK, OK	OK, OK	OK, OK	2, OK	C, OK
7.....	OK, OK	OK, OK	OK, OK	OK, OK	OK, OK	OK, OK
H.....	OK, OK	OK, OK	OK, OK	C*, OK	2, 4	C, C
8.....	OK, OK	OK, OK	OK, OK	OK, OK	OK, OK	OK, OK
I.....	OK, OK	OK, OK	4, OK	C, OK	8, OK	C, C*
9.....	OK, OK	OK, OK	OK, OK	OK, OK	OK, OK	OK, OK

NOTE:

C=cracks extended more than $\frac{1}{2}$ through specimen.

C*=shallow cracks usually about 1 to 2 grains deep.

Whereas Alloy G containing 1.7% molybdenum cracked in a relatively short period in the stabilized condition (3rd Treatment), Alloy No. 8 containing 7.7% molybdenum exhibited a much greater resistance to cracking and this is deemed attributable to the higher chromium content. Further, as indicated above herein, alloys containing a relatively high amount of chromium, to wit, at least 20% chromium, together with low carbon contents, i.e., below 0.03%, also exhibit improved resistance to intergranular stress-corrosion cracking. This is illustrated by Alloy No. 9.

It is to be observed that the present invention provides nickel-chromium and nickel-chromium-iron alloys highly resistant to intergranular stress-corrosion cracking when in contact with pressurized, aerated water at a temperature of above about 300° F. to about 660° F., notwithstanding that the surface of the alloys be characterized by a crevice or some such similar surface defect. The invention is also applicable in minimizing intergranular stress-corrosion cracking in aerated high purity water at surface areas which do not contain obvious crevices. Pressure vessels, heat exchangers, steam generation surfaces, tubing, etc., are illustrative of the type of articles which can be fabricated from the alloys of the invention. However, the present invention should not be confused with nickel-chromium and nickel-chromium-iron alloys of the age hardening type and which contain substantial amounts of precipitation hardening ingredients such as aluminum and titanium. The alloys of the present invention are, as a practical matter, of the non-age hardening type.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A process for minimizing intergranular stress-corro-

sion cracking of metal articles when in contact with aerated high purity water at a temperature of about 300° F. to about 660° F. which comprises flowing high purity water past and in contact with such a metal article, the article being formed from an alloy containing at least 23% and up to 35% chromium, up to 25% iron, at least one element selected from the group consisting of up to 0.5% aluminum and up to 0.5% titanium, the sum of aluminum and titanium being at least about 0.2%, up to 1% silicon, up to 0.15% carbon, and the balance essentially nickel.

2. A process in accordance with claim 1 in which the metal article is formed from an alloy which contains up to about 10% iron, 0.01% to 0.4% aluminum, 0.01% to 0.4% titanium, 0.05% to 0.5% silicon and up to 0.1% carbon.

3. A nickel-chromium alloy characterized by improved resistance to intergranular stress-corrosion cracking particularly when in contact with aerated high purity water at a temperature of about 300° F. to 660° F., said alloy consisting essentially of about 24% to 35% chromium, up to 10% iron, at least one element selected from the group consisting of up to 0.5% aluminum and up to 0.5% titanium, the sum of aluminum and titanium being at least about 0.2%, up to 1% silicon, up to 0.15% carbon, and the balance essentially nickel.

4. An alloy in accordance with claim 3 in which both aluminum and titanium are present in a total amount of at least 0.2%.

References Cited

UNITED STATES PATENTS

1,542,232 6/1925 Girin 75—128

RICHARD O. DEAN, Primary Examiner

U.S. Cl. X.R.

75—124, 128; 176—88