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ALLOYS RESISTANT TO CORROSION IN CAUSTIC ALKALIES

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ABSTRACT OF THE DISCLOSURE

Nickel-chromium and nickel-chromium-iron alloys having improved resistance in the stressed condition to stress-corrosion cracking in caustic alkalies such as hot concentrated sodium hydroxide. The presence of fair amounts of iron can be quite detrimental, an adverse effect which is greatly minimized by observing special correlation between iron and chromium, significant percentages of the latter being extremely beneficial.

As is well known to those skilled in the art, nickel-chromium-iron alloys by virtue of their high tensile strength, outstanding resistance to corrosive media generally, good workability, etc., are used commercially in nearly all segments of industry—from food processing equipment to jet engine components, from massive vessels to small intricate components of complex design. In terms of specifics, these alloys have found particular application in severe corrosive environments at elevated temperatures, the caustic alkalies, notably hot caustic soda, being illustrative. It is this type of environment, however, which has given rise to the problem considered herein.

Alloys of the type in question are often employed, for example, in the fabrication of caustic evaporators utilized to concentrate sodium hydroxide. As concentration is increased, the boiling point of the caustic soda rises quite rapidly—increasing the concentration from about 60% to about 90% results in a temperature boost from 320° F. to approximately 570° F. Suffice to say, this presents a most aggressive corrosive environment. In any event, such alloys have on occasion manifested a tendency to stress-corrosion crack when in the stressed condition, particularly in the presence of caustic soda above about 75% concentration.

Now, as is readily recognized, stresses can be induced in metal in any one of several ways. It is quite conventional, for example, in the fabrication of evaporators or other vessels to join metal plates by welding techniques. But by its very nature the welding process brings about residual stresses in the metal. This being the case, in using the higher strength nickel-chromium-iron alloys, it has been thus recommended to first apply a stress-relief treatment. However, as a practical matter, this approach is not without considerable difficulty since to stress-relieve huge pressure vessels such as caustic evaporators obviously presents quite a formidable task.

One way of obviating the drawback inherent in stress-relieving treatments has been to use a specially devised type of nickel characterized by extremely low carbon content (nominally 99.5% nickel plus 0.01% carbon maximum). This material has performed and continues to perform exceptionally well but is attended by the disadvantage of low tensile strength. Where higher strengths would be desirable, if not essential, recourse to some other material would be a necessity. Accordingly, the present invention is addressed to the specific problem, but not limited thereto, of improving the corrosion cracking behavior of stressed nickel-chromium-iron alloys in aggressive environments such as hot (e.g., 500° F. to 600° F.) concentrated (say, above 75%) caustic soda but without incurring appreciable loss in tensile strength.

It has now been discovered that nickel-chromium-iron alloys of controlled chromium and iron contents afford significantly improved resistance to stress-corrosion attack in caustic alkalies, the alloys being in the stressed condition. While the complete theory which might explain the mechanism involved is not yet at hand, it appears that iron exerts a subversive influence, a role quite opposite to that found to be characteristic of chromium.

It is thus an object of the invention to provide alloys of the nickel-chromium and nickel-chromium-iron type which, though they be in the stressed condition, exhibit enhanced resistance to stress-corrosion attack in corrosive media, such as caustic alkalies.

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

Generally speaking and as contemplated herein, stress-corrosion cracking of nickel-chromium and nickel-chromium-iron alloys in caustic alkali solutions is substantially improved with alloys of the following composition (based on weight percent): from 18%, most advantageously at least 26% or 27%, and up to about 35% chromium, up to about 7% iron, the chromium and iron being correlated such that the sum of the chromium minus 2.33 times the iron content exceeds 18%, up to about 0.1% carbon, up to about 3% vanadium, up to about 3% tungsten, up to about 3% molybdenum, the sum of vanadium, tungsten and molybdenum being less than 6%, up to about 1% titanium, up to about 4% aluminum, up to about 1% columbium, up to about 1% tantalum, up to 6% copper, up to 6% cobalt, up to 6% manganese, up to 1% silicon with the balance being 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 constituents, e.g., dexoidizing and cleansing elements, and impurities normally associated therewith in small amounts which do not adversely affect the novel characteristics of the alloys.

In accordance herewith, the presence of iron in amounts which heretofore would be considered rather conventional in alloys of the type under consideration serves to catalyze or otherwise promote the occurrence of stress-corrosion cracking of such alloys when in contact with hot concentrated caustic soda. Equally important, however, has been the discovery that the presence of chromium in substantial amounts greatly minimizes this adverse factor. And this aspect is of utmost significance not only in the fact that stress attack is thwarted but also in the fact that recourse to iron-free alloys is obviated. This is illustrated, for example, by the very practical commercial consideration in that it permits the use of scrap in alloy formulation and also permits the use of ferrochromium in introducing chromium into a melt. These considerations result in a more economical alloy composition than otherwise might be the case. But in consistently achieving best results the percentage of chromium minus 2.33 times the amount of iron must exceed the value of 18%. Otherwise, as will be illustrated herein, premature cracking can easily result.

To the foregoing should be added that, apart from iron content, certain other elements, at least when present in relatively high amounts, manifest a propensity to bring about cracking in hot caustic soda. Vanadium, tungsten, molybdenum, columbium and tantalum were notable in this regard, with tantalum and columbium being exceptionally detrimental. Vanadium, tungsten and molybdenum impart high strength characteristics and can be present in the alloys for this purpose. It is of benefit, however,

that these three elements individually not exceed about 2%, e.g., 0.5% to 2%, the total not being in excess of 5%.

For the purpose of giving those skilled in the art a better appreciation of the invention, the following illustrative information and data are given.

A substantial number of alloys was prepared, processed, and tested, the compositions of the alloys being set forth in Table I. Ingots obtained upon melting and cooling were (a) soaked at about 2200° F. to 2300° F. for about two hours, (b) forged to a thickness of one inch, (c) reheated to about 2200° F. and hot rolled to a thickness of about ¼ inch, (d) annealed for one hour at about 2100° F. followed by a water quench, (e) cold rolled about 40% to a thickness of 0.15 inch, (f) again annealed at 2100° F. and water quenched, and then (g) machined into specimen blanks approximately 3.25 inches in length, 0.5 inch in width and 0.12 inch in thickness. Before machining, a substantial number of the specimens was subjected to an additional heat treatment consisting of heat-at 1250° F. for about two hours followed by air cooling. Thus, samples were tested in the annealed and/or the annealed plus heat treated (H.T.) conditions.

To simulate commercial conditions, the single U-bends were suspended on a fixture and then placed in a metal beaker filled with reagent grade sodium hydroxide pellets, the beaker containing enough water to make a ninety weight percent caustic solution at test temperature. The beaker was put into an autoclave and 150 pounds per square inch (p.s.i.) overpressure of air was introduced. Thereafter, the autoclave was sealed and brought to the test temperature of about 572° F., at which temperature the caustic was molten. The overpressure of air was employed in view of the fact that in a caustic evaporator air is present plus the fact this also made for an exceptionally severe (probably too severe) environment for purposes of test. The test was conducted for seven days, after which the specimens were sectioned and given a thorough metallographic examination at a magnification of at least 125×. Depth of crack was determined.

With regard to the data given in Table I, the symbol "OK" denotes that no cracking was observed either visually or metallographically; 1/30, for example, indicates cracking visually observed and depth of crack was 30 mils; *m*/110 indicates the crack was not visually observed but was detected metallographically with crack depth being 110 mils. Alloys A through O, 5 and 10 are outside the scope of the invention but afford a good basis of comparison with alloys 1 through 4, 6 through 9 and 11 through 16, with alloys are within the invention.

TABLE I

Alloy	Percent					Stress cracking results	
	Cr	Fe	C	Ni	Other	Annealed	Annealed plus H.T.
A	15.9	7.3	0.01	Balance			1/210
B	16.2	0.1	0.02	do			1/40
C	20.0	7.0	0.01	do	1.2 TA		1/108
D	26.6	12.0	0.06	do			1/120; 1/120
E	24.0	7.5	0.09	do	1.7 Mo		1/20
F	26.9	11.3	0.06	do	5.8 Mo		1/120
G	27.0	<0.1	0.05	do	5.6 Mo		1/80
H	26.7	2.0	0.06	do	4.9 Cb		1/120
I	27.4	3.1	0.06	do	4.0 Ti		1/120
J	25.8	<0.1	0.05	do	8.2 Ta		1/120
K	19.1	1.8	0.03	do	0.5 V	*m*/20	OK
L	27.3	<0.1	0.05	do	6.7 V		1/95; 1/60
M	27.8	<0.1	0.05	do	7.3 W		*m*/5; 1/12
N	24.7	<0.1	0.05	do	10.0 W		1/40, 1/35
O	28.1	<0.1	0.05	do	4.8 Cb		1/120; 1/120
1	27.5	<0.1	0.06	do			OK; OK
2	25.9	0.4	0.04	do			*m*/1; *m*/0.5
3	25.8	0.8	0.04	do			*m*/0.5; *m*/0.5
4	27.0	2.4	0.06	do			*m*/2.5; *m*/2.5
5	26.5	7.9	0.05	do			1/40; OK
6	29.5	<0.1	0.05	do			OK; OK
7	28.5	0.4	0.05	do			*m*/1; OK
8	28.2	0.8	0.05	do			*m*/1; *m*/2
9	27.9	2.2	0.05	do			*m*/5; *m*/2
10	29.5	7.3	0.06	do			1/45; 1/40
11	20.6	<0.1	0.06	do		OK	*m*/3
12	24.8	<0.1	0.05	do		OK	OK
13	24.8	<0.1	0.06	do		OK	OK
14	24.4	0.9	0.05	do	1.4 V	OK	OK
15	25.9	<0.1	0.06	do	5.9 Co		OK
16	26.5	3.3	0.06	do	3.8 Al		*m*/5

The data in Table I clearly reflect the improvement in results attainable by using high chromium contents and controlled percentages of iron. Alloys 1 through 5 indicate the effect of increased iron (from <0.1% to 7.9%) on a series of alloys of similar chromium content, about 26% to 27.5%. This effect is confirmed by a comparison of alloys 6 through 10. (In construing the results, a satisfactory alloy is deemed to be one manifesting a crack depth of not more than about 10 mils.) Alloys 5 and 10 exhibited the greatest susceptibility to cracking. And it will be noted that each of these alloys (which are without the invention) failed to satisfy the relationship—percent Cr—2.33×percent Fe≧18%. It should be added that alloys G, H, I, J, L and N illustrate the subversive effects characteristic of substantial amounts of molybdenum, columbium, titanium, vanadium and tungsten, respectively, notwithstanding that the chromium, iron relationship was met in each instance. Alloy 6 even when exposed for an additional seven-day period failed to crack. Thus, alloys containing at least 28% or 29% chromium afford exceptionally good resistance to attack. It might be added that an iron content of 0.5% or 1% and up to about 5% or 6% can be utilized to advantage for reasons previously indicated herein; however, it is of benefit to limit the iron content to 3%.

While the foregoing has been set forth in connection with alloys resistant to hot caustic, the invention contemplates use of the alloys in other applications where resistance to various corrosive media is necessary. In addition to being useful in the construction and fabrication of vessels and containers generally, particularly those useful in storing or handling alkalies, including hot caustic, the alloys are also deemed useful in the production of tubes, piping, evaporators bellows, and steam lines, casting components for pumps, etc.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations thereof 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.

I claim:

1. A process for improving the resistance of nickel-chromium and nickel-chromium-iron metal articles to stress-corrosion cracking in caustic alkalies such as hot concentrated sodium hydroxide, which comprises flowing caustic alkali past and in contact with a metal article formed from an alloy containing from 18% to 35% chromium, up to about 7% iron, the chromium and iron being correlated such that the sum of the chromium minus 2.33 times the iron content exceeds 18%, up to about 0.1% carbon, up to about 3% each of vanadium, tungsten and molybdenum, the sum of the vanadium, tungsten and molybdenum being less than about 6%, up to 1% titanium, up to about 4% aluminum, up to about 1% columbium, up to about 1% tantalum, up to about 6% each of copper, cobalt and manganese, up to about 1% silicon, and the balance essentially nickel.

2. A process in accordance with claim 1 in which the metal article is formed from an alloy containing at least 26% chromium.

3. A process in accordance with claim 1 in which the metal article is formed from an alloy containing at least 29% chromium.

4. A process in accordance with claim 1 in which the metal article is formed from an alloy containing at least 1% iron and at least 28% chromium.

5. A process in accordance with claim 1 in which the metal article is formed from an alloy containing up to 2% each of vanadium, tungsten and molybdenum with the proviso that the total of these constituents does not exceed 5%.

6. A process in accordance with claim 1 in which the metal article is formed from an alloy containing from 0.5% to 3% iron.

7. A process in accordance with claim 5 in which the metal article is formed from an alloy containing at least 28% chromium, 0.5% to 2% of metal from the group consisting of vanadium, tungsten, and molybdenum, and 0.5% to 3% iron.

8. A process in accordance with claim 1 in which the caustic alkali is sodium hydroxide.

9. A process in accordance with claim 2 in which the caustic alkali is hot sodium hydroxide of at least 75% concentration.

10. A process in accordance with claim 4 in which the caustic alkali is hot sodium hydroxide of at least 75% concentration.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,565,611 Dated February 23, 1971

Inventor(s) GEORGE ECONOMY

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 38, for "dexoidizing" read --deoxidizing--.
Column 3, line 49, for "heat-" read --heating--.
Column 4, line 3, for "with" read --which--.
Column 4, Table I, under heading "Annealed plus H.T." Allc
for "1/210" read --1/120--; same column heading, Alloy
for "1/40 1/35" read --1/40; 1/35--.
Column 4, line 67, for "evaporators" read --evaporator--.

Signed and sealed this 4th day of January 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Pat