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AUSTENITIC CHROMIUM-NICKEL STAINLESS STEELS RESISTANT TO STRESS-CORROSION CRACKING

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The present invention relates to austenitic stainless steels and, more particularly, to overcoming the vexatious problem of stress-corrosion cracking in hot concentrated chloride solution to which the austenitic chromium-nickel stainless steels have been so susceptible heretofore.

The austenitic chromium-nickel stainless steels have been adopted for a vast number of different industrial and commercial applications, a result undoubtedly attributable, inter alia, to their relatively high strength properties at both room and elevated temperatures combined with their inherent ability to be fabricated with relative ease and their resistance to various corrosive environments. With respect to corrosion resistance, there appears to be general agreement that the ability of such steels to resist corrosive media stems from their "passive" nature, i.e., films (generally chromium oxide films) form on the surface of the steels and these films tend to protect the surfaces from penetration by corrodents or to at least greatly inhibit corrosive attack. Unfortunately, these passive films are under certain environments too easily ruptured or removed.

Corrosive activity of austenitic nickel-chromium stainless steels has been classified into four major categories: (1) general corrosion (usually a complete breakdown of the passive or protective film), (2) pitting corrosion (generally the occurrence of localized attack coupled with depth of penetration), (3) stress-corrosion cracking and (4) intergranular corrosion. The present invention is particularly concerned with the prevention of stress-corrosion cracking, a condition which generally arises without any significant occurrence of general corrosion.

As is indicated in the authoritative treatise, "Metals Handbook," 8th Ed., (1961), p. 566, and by practically all other authorities who have grappled with the problem, all commercially available austenitic stainless steels are subject to stress-corrosion cracking. This problem has existed for at least twenty-five years and has been thought to have existed for a longer period except that it went unrecognized as such by earlier investigators. Notwithstanding the numerous articles or treatises (there are at least 250 references to the problem) which have been written concerning the subject, there is no single generally accepted theory which explains the "why" of this phenomenon. To be sure, the theories advanced have been numerous and the following are illustrative of but a few of them: (1) the quasimartensite theory, i.e., plastic deformation results in the formation of a quasi-martensite which is preferentially attacked so as to result in cracking, (2) the plastic deformation theory which involves the formation of crack-sensitive paths wherein precipitates (carbides and nitrides) are formed at stressed areas which are thought to act as cathodes and the contiguous area of the steel as anodes of electrochemical cells entering into progressive corrosion and crack propagation, (3) the restricted slip theory which essentially is a theory of predicting susceptibility to stress-corrosion cracking, i.e., alloys which manifest cross slipping rather easily are considered to possess immunity to cracking, whereas alloys which inherently exhibit a high degree of resistance to slip are considered to be susceptible to cracking. The last might be considered somewhat as a special case of

one of the two most prominent broad theoretical explanations presently in vogue, to wit, the periodic electrochemical-mechanical mechanism. There are other explanations of the problem such as those involving surface films or involving "dislocations," but no one mechanism has achieved general acceptance.

While there may be no single theory which conclusively explains the fundamental nature of stress-corrosion cracking, it can be stated with assurance that if an austenitic chromium-nickel stainless steel is under stress, whether the stress be externally applied and/or residually induced by some processing operation such as quenching or cold-working, and the steel is exposed to certain corrosive media, the conditions are ready-made for failure by stress-corrosion cracking. Chloride solutions, as indicated in the Metals Handbook, are the "worst offenders" and these include the chlorides and other halides of magnesium, calcium, lithium, sodium, etc. Some other solutions have also been known to promote stress-corrosion cracking.

As there have been a number of theories to explain stress-corrosion, so too have there been a number of proposals for overcoming the problem, none of which has been completely satisfactory since the difficulty is presently ever the more to the forefront of long-time unresolved problems. For example, it has been suggested to avoid using a material susceptible to stress-corrosion cracking under conditions of intended use. In this connection, the use of ferritic stainless steels has been given consideration since the ferritic types are ostensibly rather immune to stress-corrosion cracking. To do so, however, would be to lose all the advantages of the austenitic stainless steels. It has also been suggested to avoid contact between austenitic stainless steels and chlorides. This is hardly a panacea, although it might circumvent the problem. The use of inhibitors, e.g., chromates, phosphates, and oxygen scavengers, has been urged, but this approach has not proven successful and brings into play other undesirable problems. Changes in design, processing conditions and/or fabrication have been proposed. For example, the use of high temperature stress-relieving treatments has been advanced in an effort to minimize the effect of residual stresses, it being considered that residual stresses are more causative of stress-corrosion cracking than stresses externally applied. This approach has not proven to be the answer, partly because it is difficult to reduce and to maintain the stresses at a low level. Another proposal is the use of the well-known cathodic protection principle. This is based upon the consideration that stress-corrosion cracking is of an electrochemical nature and the use of protective currents should assist in preventing cracking. The difficulties arising from this approach including the impracticability of carrying it out on a commercial scale, are well known and will not be dwelt upon herein. In addition, stress-corrosion cracking still occurs. Other proposals include change of alloy composition, e.g., maintaining the carbon and nitrogen contents at very low levels in 18–8 stainless steel and cold working. Actually, this results in a ferritic stainless steel or one very high in ferrite.

Of all proposals, considerable interest has been shown with regard to purity of composition with emphasis on keeping the nitrogen (a known subversive performer) content at a low level, e.g., 0.01% to 0.02% or lower. This involves the use of materials of very high purity plus the application of expensive processing techniques, e.g., vacuum treatment. This approach appeals to theory but involves substantial additional costs which render it uneconomical from a commercial viewpoint. The austenitic stainless steels are relatively expensive. To increase the cost through the use of high purity materials and expensive vacuum treatments would be quite disadvantageous. In addition, there is considerable conflict

as to whether "purity" is the answer. In any event, a more practical solution is required and it is to this aspect that the instant invention is directed.

Although many attempts were made to overcome the problem of stress-corrosion cracking in austenitic chromium-nickel stainless steels, none, as far as we are aware, was entirely successful when carried into practice commercially on an industrial scale. This includes those proposals involving the beneficial effects of nickel, carbon or silicon and low amounts of nitrogen.

It has now been discovered that the problem of stress-corrosion cracking of austenitic stainless steels can be overcome or greatly minimized while utilizing standard air-melting techniques (as opposed to expensive vacuum techniques) and commercially pure grades of materials (as opposed to high purity materials) provided the steels are of specially controlled composition as set forth hereinafter. It has been further found that certain elements, notably phosphorus, promote the susceptibility of austenitic stainless steels to stress-corrosion cracking. However, in accordance with the invention, the presence of controlled amounts of phosphorus is not harmful and can be readily tolerated, thus avoiding questionable recourse to the use of pure materials or to undesirable processing techniques to rid the steels of phosphorus. In addition, because of the specially balanced composition of the steels within the invention, larger amounts of nitrogen can be present than otherwise might be the case.

It is an object of the invention to provide austenitic chromium-nickel stainless steels which greatly resist stress-corrosion cracking notwithstanding that the steels are highly stressed and in contact with corrosive solutions, including chloride solutions, which are known to be causative of stress-corrosion cracking.

Generally speaking and in accordance with the present invention, it has been found that stress-corrosion cracking of austenitic chromium-nickel stainless steels can be eliminated or greatly minimized with steels of the following most advantageous composition: about 20% to about 30% nickel, about 16% to about 25% chromium, at least 0.07% and up to 0.09% carbon, up to about 1.5% silicon, phosphorus in an amount up to not more than 0.015%, nitrogen in an amount up to 0.035%, the sum of the phosphorus plus nitrogen being not more than 0.045%, and the balance essentially iron. Phosphorus, among other elements, has been found to exert a pronounced adverse influence in the resistance of austenitic chromium-nickel stainless steels to stress-corrosion cracking. However, provided that the phosphorus content is controlled in accordance with the invention and provided the composition of the steels is otherwise critically balanced, the detrimental effect of phosphorus is overcome. This avoids use of processing techniques to eliminate phosphorus and is thus beneficial in maintaining the cost of producing the steels at an economic level. In addition, it has been found that what might have heretofore been considered as a relatively high and detrimental amount of nitrogen, e.g., 0.035%, can be present in the austenitic steels of the instant invention provided that the composition is critically balanced. A particular feature and advantage of the invention is that air-melting practices and commercial grades of materials can be employed. These factors greatly contribute to maintaining the economic competitiveness of the steels.

Satisfactory results can also be achieved with austenitic stainless steels of the following composition: at least 19% and up to about 35% nickel, about 15% to about 30% chromium, at least 0.07% and up to not more than 0.1% carbon, up to about 1.6% silicon, phosphorus in an amount up to not more than 0.018%, nitrogen in an amount up to 0.045% but preferably not greater than 0.04%, the sum of the phosphorus plus nitrogen being controlled such that it does not exceed 0.055%, and the balance essentially iron.

In carrying the invention into practice, it is most important that special attention be given to controlling the nickel, carbon and phosphorus contents. As will be demonstrated hereinafter, should the nickel content fall below 19%, e.g., 18%, stress-corrosion cracking can occur. Amounts of nickel higher than 35% are unnecessary and only increase cost. The minimum carbon content is exceedingly important. As will become clear from data presented herein, carbon contents of 0.06% and lower are unsatisfactory and result in stress-corrosion cracking in air melted austenitic chromium-nickel stainless steels made from materials of commercial purity. Carbon above 0.1% intensifies susceptibility to intergranular corrosion. Above 0.1% carbon, too great an amount of chromium is taken up in the form of chromium carbides. This depletes the grain boundaries of the austenitic steels of chromium and promotes greater susceptibility to intergranular corrosion. It might be considered that carbide stabilizers such as columbium and titanium might be employed to counteract this effect. The diffculty here is that the columbium and/or titanium would tie up the carbon (columbium and/or titanium carbides would preferentially form as opposed to chromium carbides) to the extent that while the steels might be immune to intergranular corrosion, they would be susceptible to stress-corrosion cracking. The effort would be self-defeating. Phosphorus, a subversive promoter, should not exceed 0.018%. It has been found, for example, that even in high-purity vacuum-treated austenitic stainless steels, 0.023% phosphorus is most harmful since it actively promotes stress-corrosion cracking. As those skilled in the art will appreciate, the AISI commercial grades of austenitic stainless steels contain up to 0.2% phosphorus. Phosphorus contents of the order of 0.2% and higher have been known to impart beneficial effects to austenitic stainless steels. For example, it has been indicated that even 0.12% phosphorus improves stress-rupture properties at high temperatures. However, in accordance with the invention, such amounts of phosphorus are detrimental. Nitrogen is present in austenitic chromium-nickel stainless steels and is known to act subversively. There are prior references indicating that nitrogen should be maintained at a very low level; however, it has now been found that in the steels provided in accordance with this invention, comparatively high amounts of nitrogen, i.e., up to 0.045%, can be present. However, the total phosphorus and nitrogen contents should not exceed 0.055% and it is most advantageous that the sum not exceed 0.045%. Additionally, if the phosphorus content is on the high side, it is preferable to maintain the nitrogen content on the low side and vice versa.

For the purpose of giving those skilled in the art a better understanding and/or appreciation of the invention, there is given hereinafter data which are illustrative of the advantages embodied by the stainless steels having compositions within the invention. However, it should be mentioned that the test employed in connection with the data, to wit, immersion of stressed U-bend specimens in boiling concentrated magnesium chloride, has been criticized as being too severe on the grounds that such severe conditions would not be encountered in usual commercial applications. In addition, the tests conducted in accordance with the invention have been continued for longer time periods than are usually considered necessary. If the stainless steels will withstand what is considered to be a severe test, then it would seem that the results thereby obtained would be a more critical indicator as to reliability, particularly from the commercial viewpoint.

In addition to using air melting practice in combination with commercial grades of materials, e.g., Armco iron and ferrochromium, specimens for test were also prepared using materials of high purity (electrolytic iron electrolytic chromium) and vacuum melting technique. Because of availability, carbonyl or electro-nickel was

used in the tests. Initially, ingots were prepared from compositions as set forth in the appropriate Tables hereinafter. The ingots were machined and ground to remove all surface defects and contamination, were heated in air to a temperature of about 2150° F. and were then forged in air to ¾ inch slabs. All surfaces were again machined to a depth of ⅛ inch to insure removal of any contaminating effect that might have been introduced from the forging operations.

A number of test specimens were machined from the forgings and subjected to the U-bend, magnesium chloride test. Other specimens of the forged material were cut into ¼ inch x ½ inch slices and cold-rolled about 40% and subjected to test in the cold-rolled condition. In addition, cold-rolled specimens were also annealed in an argon atmosphere for one hour at 1950° F. and water quenched. These too were subjected to the U-bend, magnesium chloride test. In some cases the forgings were hot-rolled prior to cold rolling. All specimens were finish ground to about 40 microinches or finer to avoid possible surface contamination. Still other specimens were sensitized, i.e., subjected to an intermediate temperature treatment, e.g., about 1250° F., and then subjected to test in the sensitized condition. This was conducted with the view that austenitic stainless steels, as a commercial proposition, are often subjected to the so-termed "sensitization" treatment (as by an intermediate heat treatment or welding operation) and this could affect susceptibility to stress-corrosion cracking. Thus, specimens were tested in at least one or more of four different conditions so as to intensify and diversify test conditions, thereby avoiding reliance on the possibility that stress-corrosion cracking might not occur in one condition without knowing whether it would occur in one of the others.

The test specimens were formed in the configuration of a U-bend by taking specimen samples of about 6 inches long, ½ inch wide and about ⅛ inch thick, and bending them over a mandrel using a tensile test machine. This induced considerable stress in the specimens and the specimens were then placed in a vise and the legs of the U-bends were drawn about parallel to each other by tightening the vise. Bolts were inserted through holes near the ends of the legs of the specimens. Boiling concentrated magnesium chloride was used as the corrosive agent because of its known severity in promoting stress-corrosion cracking. The solutions were of about 42% concentration and the boiling point was adjusted to 154° C. Five liter flasks equipped with reflux condensers held the magnesium chloride. Four test specimens of at least one of the groups (forged, cold-rolled, annealed or sensitized) under test were suspended in each flask with the apices of the bends and about half of the legs immersed in the solution. The time required for cracking was the criterion employed in determining susceptibility or resistance to stress-corrosion cracking. The specimens were usually removed from test every second or third day and examined under a magnifier for cracks. When cracking was evident, the specimens were removed from test. When no cracking occurred in a period of about two weeks, fresh magnesium chloride solutions were used to replace the old solutions. Generally, if no stress-corrosion cracking was evident after a period of thirty days (720 hours), testing was suspended although in some instances it was continued for a longer period of time. After removal from the test solution, micro-examination was made of all specimens and the apices of the bends were examined in longitudinal cross-section near the surface and along the center line to confirm the presence or absence of the cracks.

As mentioned hereinbefore, it has been found that phosphorus is a potent promoter of the susceptibility of austenitic chromium-nickel stainless steels. This is true notwithstanding that highly pure materials and vacuum techniques are employed. In this connection, vacuum melting, electrolytic iron, electrolytic chromium and carbonyl nickel were used in the preparation of the austenitic stainless steels having compositions shown in Table I.

TABLE I

Chemical Composition

Alloy No.	Percent Ni	Percent Cr	Percent C	Percent Si	Percent P	Percent N
1	20.6	16.3	0.001	<0.01	0.003	0.0001
2	20.3	17.1	0.004	0.04	0.002	0.0001
3	20.8	18.1	0.003	0.06	0.003	0.0032
4	20.1	17.9	0.002	0.01	0.023	0.0048
5	20.3	18.1	0.003	0.01	0.065	0.0004
6	21.0	18.8	0.006	0.02	0.35	0.0007
7	46.8	17.9	0.003	0.18	0.13	0.0537

The results of the test are given in Table I–A. The period to crack is given as of the day cracking was observed, but since inspection was usually made every second or third day, cracking could have taken place before the day indicated. For example, if cracking time is given as 15 days, cracking could have occurred between the 13th and 15th day. In addition, failure of any specimen in this multiple test (including other results given herein) is taken as showing that the stainless steel involved is unsatisfactory and is not in accordance with the invention.

TABLE I–A

Cracking Time

Alloy No.	Forged				Cold Rolled				Cold Rolled and Annealed				Sensitized				Percent Cracked	Average Life-to-Crack in Days
1	30	OK	OK	OK	15	15	OK	OK	3	4	11	30	—	—	—	—	58	21.5
2	11	11	OK	OK	21	21	21	28	10	20	30	30	—	—	—	—	83	20
3	21	OK	OK	OK	24	OK	OK	OK	21	21	23	30	—	—	—	—	50	25.4
4	1	1	2	2	3	3	6	OK	6	6	6	6	—	—	—	—	92	6
5	1	1	1	1	1	1	1	1	1	1	1	1	—	—	—	—	100	1
6	1	1	1	1	1	1	1	1	1	1	1	1	—	—	—	—	100	1
7	3	3	3	3	6	6	6	6	3	3	3	3	—	—	—	—	100	4

The data in Tables I and I–A illustrate the detrimental effect of phosphorus under what might be considered as the most favorable conditions, to wit, vacuum melting and the use of extremely pure materials. When the phosphorus content was rather low as in Alloys 1, 2 and 3, the average life-to-crack was comparatively high (20–25 days). However, as the phosphorus content was increased, cracks became evident almost immediately. For example, Alloy No. 4 containing 0.023% phosphorus cracked in less than 6 days and Alloy No. 5 containing 0.065% phosphorus cracked in less than a day. Regarding Alloys Nos. 1 and 2, it can be stated that these austenitic steels were of high purity; nevertheless, they cracked and this is indicative that the use of high purity materials alone in producing austentic chromium-nickel steels will not provide resistance to stress-corrosion cracking as contemplated by the present invention.

Not only must the phosphorus content be controlled, but, as mentioned above herein, the alloy composition

as a whole must be critically balanced. This is particularly apropos regarding the nickel, carbon, nitrogen or nitrogen plus phosphorus contents. As will be seen from data presented hereinbelow, small amounts of such elements can greatly affect the results obtained. In this connection, several austenitic chromium-nickel stainless steels having compositions given in Table II were subjected to test and the results are given in Table II–A. It might be pointed out that in the main Alloys Nos. 8 through 20 reflect the importance of a minimum carbon content of 0.07%, Alloys Nos. 21 and 22 illustrate the effect of nickel contents below 19%, Alloys Nos. 23 through 26 and Alloy No. 27 show the effect of high nickel contents in austenitic alloy steels otherwise outside the invention and Alloys Nos. 27 through 31 are a further indication of the necessity of maintaining a proper correlation in the amounts of nickel, carbon, phosphorus and nitrogen.

TABLE II

Chemical Composition [1]

Alloy No.	Ni, percent	Cr, percent	C, percent	Si, percent	P, percent	N, percent
8	20.0	17.7	0.02	0.66	0.007	0.027
9	20.3	17.8	0.02	0.36	0.013	0.026
10	20.0	17.8	0.03	0.23	0.008	0.013
11	20.0	18.5	0.03	0.74	0.009	0.015
12	20.0	18.1	0.04	0.17	0.007	0.025
13	20.2	17.5	0.04	0.09	0.009	0.022
14	20.1	17.3	0.05	0.22	0.009	0.024
15	20.0	18.8	0.06	0.46	0.008	0.018
16	19.9	18.0	0.06	0.16	0.007	0.032
17	20.0	17.2	0.06	0.50	0.01	0.016
18	20.0	17.5	0.07	0.11	0.007	0.024
19	20.0	17.5	0.07	0.53	0.008	0.019
20	19.9	19.0	0.08	0.65	0.009	0.018
21	15.9	17.7	0.08	0.09	0.011	0.015
22	18.2	17.6	0.06	1.50	0.008	0.01
23	21.71	17.9	0.015	0.72	0.012	0.032
24	25.68	17.8	0.013	0.90	0.011	0.025
25	27.41	17.4	0.013	0.80	0.013	0.022
7	46.8	17.9	0.003	0.18	0.13	0.0537
26	20.42	18.0	0.08	1.61	0.013	0.029
27	19.9	17.7	0.08	0.32	0.016	0.002
28	20.0	17.7	0.08	0.56	0.015	0.048
29 [2]	19.73	17.7	0.08	0.64	0.012	0.043
30	20.0	18.1	0.10	0.075	0.012	0.026

[1] Allo, steels air melted using Armco iron and ferrochromium except Alloys Nos. 7 and 27 which were vacuum melted using electrolytic iron and electrolytic chromium.

[2] Contained 0.1 percent aluminum. Steels otherwise contained less than 0.03 percent aluminum except No. 28 which contained 0.034 percent aluminum.

Table II–A reflects that all the austenitic chromium-nickel stainless steels containing less than 0.07% carbon (Alloys Nos. 8 through 17, and 22 through 25 and 7) cracked regardless of nickel content; similarly, the steels containing less than 19% nickel (Alloys Nos. 21 and 22) cracked regardless of carbon content. Increasing the nickel content from 21.71% to 46% in steels containing less than 0.07% carbon (Alloys Nos. 23 through 25 and Alloy No. 7) did not prevent the occurrence of cracking within the 30-day period. It is also to be noted that ⅙ of the specimens of Alloy No. 28 cracked and this alloy contained a total of 0.063% of phosphorus plus nitrogen. No cracking occurred in Alloy No. 29 which was otherwise similar to Alloy No. 28 except that it contained a total of 0.055% phosphorus plus nitrogen. It is much preferred that the total content of phosphorus and nitrogen be controlled such that it does not exceed 0.055% and preferably not more than 0.045%.

In addition to the foregoing and in accordance with the invention, elements other than phosphorus have to be controlled in order to avoid the subversive influence which they exert with respect to the resistance of austenitic chromium-nickel stainless steels to stress-corrosion cracking. These elements include aluminum, molybdenum, bismuth, arsenic and antimony. As a general rule, the latter three elements are not normally found present to any appreciable degree in (or at least are not intentionally added to) austenitic chromium-nickel stainless steels. However, to avoid stress-corrosion cracking, the amounts of bismuth, arsenic and antimony should not exceed 0.015%, 0.015%, and 0.015%, respectively. Molybdenum is quite often added to stainless steels for a number of reasons. In accordance with the invention, the amount of molybdenum should be controlled so as not to exceed 0.075% and preferably not more than 0.05%.

With respect to aluminum it has been found that amounts thereof in the range of about 0.03% to about 0.06% adversely affect resistance to stress-corrosion cracking of austenitic chromium-nickel stainless steels. Amounts of aluminum below 0.03% or appreciably above 0.06%, e.g., 0.1% to 0.2%, can, in accordance with the invention, be tolerated. This effect of aluminum while not understood is shown in Tables III and III–A.

TABLE II–A

Cracking Time

Alloy No.	Forged				Cold Rolled				Cold Rolled and Annealed				Sensitized				Percent Cracked	Average Life-to-Crack in Days
8	1	1	1	1	1	1	1	1	1	4	4	4	—	—	—	—	100	1.75
9	—	—	—	—	2	2	2	2	2	2	2	2	2	2	2	2	100	2.0
10	—	—	—	—	7	7	7	9	6	6	6	8	5	5	5	5	100	6.33
11	—	—	—	—	5	13	13	18	6	6	6	6	5	5	5	7	100	7.9
12	12	12	12	12	9	17	27	30	7	11	11	12	—	—	—	—	100	14.3
13	—	—	—	—	4	4	4	7	7	7	9	11	2	2	5	5	100	5.55
14	—	—	—	—	OK	OK	OK	OK	OK	OK	OK	OK	20	OK	OK	OK	8	29.2
15	—	—	—	—	OK	OK	OK	OK	OK	OK	OK	OK	21	OK	OK	OK	12.5	29.3
16	20	20	25	25	OK	OK	OK	OK	29	29	OK	OK	—	—	—	—	50	27.3
17	—	—	—	—	OK	OK	OK	OK	29	OK	OK	OK	OK	OK	OK	OK	8	29.9
18	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	—	—	—	—	0	>30
19	—	—	—	—	OK	OK	OK	OK	—	—	—	—	OK	OK	OK	OK	0	>30
20	—	—	—	—	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	0	>30
21	—	—	—	—	16	23	23	23	30	30	30	30	11	11	23	—	100	22.7
22	—	—	—	—	21	30	OK	OK	4	4	4	4	11	11	11	11	83	14.2
23	—	—	—	—	5	5	5	5	5	5	6	6	4	4	4	4	100	4.9
24	—	—	—	—	10	10	12	12	5	5	5	5	4	4	4	4	100	6.5
25	—	—	—	—	30	30	30	30	7	7	7	9	7	7	7	7	100	14.8
7	3	3	3	3	6	6	6	6	3	3	3	3	—	—	—	—	100	4.0
26	—	—	—	—	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	0	>30
27	—	—	—	—	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	0	>30
28	—	—	—	—	OK	OK	OK	OK	OK	OK	30	30	OK	OK	OK	OK	16.6	30
29	—	—	—	—	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	0	>30
30	—	—	—	—	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	0	>30

TABLE III

Chemical Composition

Alloy No.	Percent Ni	Percent Cr	Percent C	Percent Si	Percent P	Percent N	Percent Al
32	21.7	17.3	0.002	0.03	0.006	0.001	<0.01
33	21.7	17.2	0.007	<0.09	0.007	0.006	0.04
34	19.1	18.3	0.05	0.01	0.001	0.0005	0.03
35	21.4	16.9	0.04	0.42	0.012	0.038	0.05
36	23.8	16.4	0.09	0.63	0.013	0.037	0.04
29	19.73	17.7	0.08	0.64	0.012	0.043	0.1

TABLE III-A

Cracking Time

Alloy No.	Forged				Cold Rolled				Cold Rolled and Annealed				Sensitized				Percent Cracked	Average Life-to-Crack in Days
32	OK	OK	OK	OK	9	9	30	30	13	14	30	OK	—	—	—	—	58	23.8
33	2	2	2	2	4	4	6	OK	2	2	2	OK	—	—	—	—	83	7.3
34	—	—	—	—	14	14	14	30	9	9	20	22	OK	OK	OK	OK	67	21
35	—	—	—	—	14	21	21	21	13	13	13	13	3	6	7	7	100	12.6
36	—	—	—	—	OK	OK	OK	OK	15	15	29	29	OK	OK	OK	OK	33	27.3
29	—	—	—	—	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	0	>30

Alloy No. 33, which was prepared with high purity materials and vacuum treated (as was Alloy No. 32), showed a considerable decrease in resistance to stress-corrosion cracking with an aluminum content of 0.04% as against Alloy No. 32 which contained 0.01% aluminum. A similar pattern of behavior is shown by Alloys Nos. 34 through 36 and 29. It is to be particularly noted that Alloy No. 36 which would be otherwise within the invention except that it contained 0.04% aluminum failed whereas Alloy No. 29 which is within the invention and quite similar in composition to Alloy No. 36 except that it contained 0.1% aluminum completely resisted cracking during the test.

With regard to other elements that can be present in the stainless steels contemplated in accordance with the invention, it is to be pointed out that manganese should not be present in an amount greater than 0.7% and advantageously should not exceed 0.2% if stress-corrosion cracking is to be avoided. In addition, it is preferred that copper should not be present in an amount greater than 0.2% and it is more preferred to maintain copper at less than 0.1%.

It is to be observed that the present invention provides austenitic chromium-nickel stainless steels highly resistant to stress-corrosion cracking when subjected to stress and in contact with halide solutions. Thus, the steels, in addition to being highly useful for high temperature applications, are especially suitable in the chemical processing industry where stress-corrosion cracking has heretofore been so prominent. It is to be further pointed out that no impairment in mechanical properties of the austenitic steels within the invention is encountered. Actually, the mechanical properties show an improvement over the properties of the typical AISI grades of austenitic chromium-nickel stainless steels.

It is to be noted that the present invention is not to be confused with the published compositions of the well-known AISI grades of austenitic chromium-nickel stainless steels. These AISI grades are usually reported as nominal compositions. For example, the aforementioned Metals Handbook lists the AISI grades in terms of nominal compositions, but, as referred to before herein, indicates that they suffer from stress-corrosion cracking.

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. An austenitic chromium-nickel stainless steel highly resistant to stress-corrosion cracking when subjected to stress and in contact with halide solutions, said steel consisting essentially of about 20% to 30% nickel, about 16% to about 25% chromium, at least 0.07% and up to 0.09% carbon, up to 1.5% silicon, phosphorus in an amount up to not more than 0.015%, nitrogen in an mount up to not more than 0.035%, the sum of the phosphorus plus nitrogen not exceeding 0.045%, up to 0.7% manganese and the balance essentially iron.

2. The austenitic stainless steel set forth in claim 1 wherein the manganese content is not greater than 0.2%.

3. An austenitic chromium-nickel stainless steel highly resistant to stress-corrosion cracking when subjected to stress and in contact with halide solutions, said steel consisting essentially of from 19% to about 35% nickel, about 15% to about 30% chromium, at least 0.07% and up to 0.1% carbon, up to 1.6% silicon, phosphorus in an amount up to not more than 0.018%, nitrogen in an amount up to not more than 0.045%, the sum of the phosphorus plus nitrogen not exceeding 0.055%, up to 0.7% manganese, and the balance essentially iron.

4. The austenitic stainless steel set forth in claim 3 wherein the manganese content is not greater than 0.2%.

References Cited in the file of this patent

UNITED STATES PATENTS

3,118,761 Hull ---------- Jan. 24, 1964

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,159,479 December 1, 1964

Harry R. Copson et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 52, after "approach" insert a comma; column 7, line 13, for "Alloy No. 27" read -- Alloy No. 7 --; same column 7, TABLE II, footnote 1, line 1 thereof, for "Allo" read -- Alloy --; column 10, line 7, for "compositions" read -- composition --; line 41, for "mount" read -- amount --.

Signed and sealed this 3rd day of August 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
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