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STAINLESS STEEL ALLOY WITH LOW PHOSPHORUS CONTENT

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ABSTRACT OF THE DISCLOSURE

A stainless steel alloy having a content of silicon and phosphorus below a minimal critical limit, and which is highly resistant to intergranular corrosion by boiling nitric acid metallic ion solution having a high oxidation potential.

BACKGROUND OF THE INVENTION

The invention described herein was made in the course of, or under, Contract No. AT(04–3)–189, Project Agreement No. 45, with the United States Atomic Energy Commission.

This invention relates generally to alloys of ferrous materials and to alloys of iron, chromium and nickel, in particular to stainless steel alloys which are highly resistant to intergranular corrosion.

In the processing of expended nuclear reactor fissile fuel, in order to remove the various fission products, nitric acid is generally used to dissolve the fissile fuel, e.g., uranium oxide and fission product material. The process is carried on in large containers fabricated from commercially available stainless steel of the prior art. With high temperatures and high concentrations of nitric acid in the presence of chromium ions or other metallic ions dissolved from the container, cracks develop in the stainless steel caused by intergranular corrosion after a period of time, resulting in a costly replacement of the container. These commercially available stainless or austinitic steel alloys typically contain major amounts of chromium and nickel, with the balance iron, along with small amounts of impurities such as carbon, manganese, sulphur, silicon, phosphorus, nitrogen and oxygen. Although these alloys are initially highly resistant to the corrosive action of acids and alkaline materials, after prolonged exposure they tend to develop cracks or become porous. Such defects result from corrosive attack along the grain boundaries of the individual alloy crystals. This corrosive effect, referred to generally as intergranular corrosion, is aggravated if, e.g., during fabrication, the stainless steel is heated to between 600–700° C. and slowly cooled. In this temperature range, a carbide membrane forms between the grains of the steel alloy which is very susceptible to deterioration by corrosive materials, especially acids. Stainless steels which have been heated to this temperature range and cooled slowly are commonly referred to as "sensitized." Stainless steels which are raised to a temperature above 700° C. and cooled rapidly through this 600–700° temperature range are generally referred to as "non-sensitized." The alloy of the present invention exhibits its high resistance to intergranular corrosion only when fabricated in the manner of the nonsensitized stainless steels, i.e., those which have not been heated to 600–700° C. and slow-cooled.

SUMMARY

The alloy of this invention is a stainlesss steel comprising major amounts of chromium and nickel, with the balance iron, and containing certain impurities in those amounts found in commercial stainless steel; however, the proportions of silicon and phosphorous are severly limited to the point of being substantially absent. The alloy of this

invention is highly resistant to intergranular corrosion in the nonsensitized condition compared with stainless steel alloys of the prior art, especially when exposed to boiling nitric acid metallic ion mixtures, such as obtained with potassium dichromate as employed in dissolving fissile fuels.

It is therefore an object of this invention to provide a stainless steel alloy which is highly resistant to intergranular corrosion in oxidizing acid environment.

It is a further object of this invention to provide a nonsensitized stainless steel alloy which is highly resistant to intergranular corrosion.

It is another object of this invention to provide a stainless steel alloy which is heat treated to reduce its susceptibility to intergranular corrosion, which is highly resistant to intergranular corrosion by boiling nitric acid-potassium dichromate.

Other and more particular objects of this invention will be manifest upon study of the following detailed description.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The typical stainless steel alloys of the prior art and of the present invention are listed in Table I. This list includes the major impurities which might affect the intergranular corrosion-resistant properties of the steel.

Although Table I covers the range of most stainless steel alloys, the general range of composition can extend to from about 14 to 26 weight percent chromium, 0.02 to 0.2 weight percent carbon, 6–22 weight percent nickel, with the remainder iron. It is generally not economical for a stainless steel alloy to contain any higher percentage of chromium and nickel, even though reduction of the silicon and phosphorus content in accordance with this invention would increase the intergranular corrosion resistant properties. Lower percentages of chromium and nickel will, of course, produce less resistance to over-all corrosion. A typical stainless steel alloy will generally contain from about 18–20 weight percent chromium, about 0.06 weight percent carbon, about 8 to 12 weight percent nickel, about 2.0 weight percent manganese, about 0.2 weight percent sulphur, with the balance iron.

Table II is an abridged version of Table I, listing only the chromium, nickel, silicon and phosphorus content along with the corrosion rate arranged to compare the high silicon-phosphorus control impurity samples with the low silicon-phosphorus content stainless steel alloys of the invention.

Table III is an abridged version of Table I, listing two typical commercial stainless steel alloys arranged to compare the commercial purity alloys with alloys of similar impurity content, with the exception that the silicon content is limited to below 2000 p.p.m. by weight, and the phosphorus content is kept below about 20–21 p.p.m. by weight.

These alloys were all fabricated from high purity starting materials, and with alloying agents added in controlled amounts. It can be seen, however, that other processes may be used to make the alloy of this invention, e.g., by selectively reducing the silicon and phosphorus content.

The sample alloys listed in Table I were all placed in a boiling mixture of 5 normal nitric acid and 0.4 normal chromium^{+6} ions (added as potassium dichromate) for a maximum of 100 hours. The weight loss caused by corrosion was measured and the weight loss rate was calculated in milligrams per square centimeter per hour (mg./cm.^{2}-h.).

Although a nitric acid-chromium^{+6} ion solution is used to test the alloys listed in Table I, a similar corrosive environment can be obtained using other metallic ions and methods.

The intergranular corrosion process rate has been found to be directly proportional to the oxidation potential between the corrosive solution and the alloy. A low oxidation potential will produce a low corrosion rate, while a high oxidation potential will produce a high corrosion rate. Using hydrogen as the potential base, a typical oxidation potential that produces a high corrosion rate for alloys listed in Table I will range from 1.1 to 1.3 volts. This oxidation potential can be obtained either by adding metallic ions to the solution or using the metal alloy as an electrode in a manner similar to the electrode in an electrolytic plating process wherein the direction of current causes material of the alloy to go into solution, rather than receive material out of solution.

For the nitric acid-chromium^{+6} ion solution of the concentrations noted above, the oxidation potential is about 1.2 volts. Other metallic ions, such as manganese^{+7}, cerium^{+4} or iron^{+3} in the proper and sufficient concentration will also produce highly oxidizing solutions, having oxidation potentials with the alloys of Table I in the range between 1.1 and 1.3 volts.

Therefore, the alloy of this invention is not to be limited to characteristics in a nitric acid-chromium^{+6} solution environment, but rather to a highly oxidizing solution containing metallic ions producing a high oxidation potential.

In observing the samples of Table I after being subjected to the corrosive environment, it was noted that generally those samples having a corrosion rate below about 0.5 to 0.6 mg./cm.^{2}-h. showed no evidence of intergranular corrosion, but rather an over-all attack on the surface of the sample. In contrast, it was noted that generally those samples having a corrosion rate above about 0.5 to 0.6 mg./cm.^{2}-h. exhibited progressively greater intergranular corrosion for increases in weight loss rate. All samples were tested for a maximum of 100 hours. It can be seen that, for longer periods of sustained exposure, even the low silicon-phosphorus alloys will eventually exhibit intergranular corrosion. However, compared with stainless steel alloys of the commercial varieties and having relatively elevated silicon-phosphorus content, the alloys in Table II and Table III show a substantial reduced rate for the low silicon, low phosphorus alloy of this invention. This rate is reduced by about a factor of 10.

From Tables II and III, it can be seen that generally, having due regard for experimental accuracy, the beneficial effects of reduced silicon and phosphorus appear when the silicon content is below about 2000 p.p.m., and the phosphorus content is below about 20 p.p.m. Greater intergranular corrosion can be predicted with certainty for alloys with silicon and phosphorus contents higher than these specific critical limit values.

Although the foregoing embodiment has been described in detail, there are obviously many other embodiments and variations in configuration which can be made by a person skilled in the art without departing from the spirit and scope or principle of this invention. Therefore this invention is not to be limited except in accordance with the scope of the appended claims.

TABLE I

Alloy Designation	Wt. percent		P.p.m. (by weight)							Corrosion Rate, mg./cm.^{2}-h.
	Cr	Ni	Mn	Si	C*	S	P*	N	O*	
1	15.5	13.1	5	10	38	80	15	11	172	0.45
2-Mn	14.8	12.9	140	1	34	10	10	22	221	0.47
3-Mn	14.8	13.0	1.46×10^3	1	18	29	12	17	200	0.53
5-Mn	13.3	11.6	2.63×10^4	10	19	51	15	15	145	0.47
2-Si	15.0	13.5	5	2×10^2	46	70	14	8	179	0.45
3-Si	15.2	13.6	5	1.8×10^3	35	70	13	8	89	0.50
4-Si	15.1	13.4	5	2.8×10^3	31	60	9	8	59	1.35
5-Si	15.4	13.6	5	9.5×10^3	39	40	9	7	74	4.30
7-Si	16.0	12.6	20	4.8×10^3	34	20	17	16	75	1.75
2-C	15.5	13.1	5	10	100	10	19	11	142	0.50
3-C	15.3	12.8	5	10	92	40	18	15	83	0.50
4-C	15.4	12.6	5	10	159	10	20	10	24	0.50
5-C	15.3	12.6	5	10	545	10	21	11	31	0.75
6-C	15.5	12.9	5	10	1.48×10^3	100	17	16	84	0.48
2-P	14.7	12.0	5	10	24	40	100	9	207	2.10
3-P	14.6	12.0	5	20	25	50	245	7	215	3.30
4-P	14.6	12.0	5	20	35	40	920	14	199	8.20
5-P	14.4	12.0	2	25	31	40	220	6	219	0.95
5-N	14.8	12.5	1	20	35	30	20	427	224	0.88
5-O	11.9	14.5	N.D.	5	17	23	5	51	667	0.44
Commercial Pur., 16-12	16.6	11.5	5.8×10^3	4.7×10^3	360	160	204	222	27	4.4
304 Stnls. Stl., Low Si, P	19.0	7.8	1.56×10^4	10	313	170	14	123	197	.87
16-12, Low Si, P	16.5	11.7	9.9×10^3	5	544	140	21	142	45	0.53
Commercial Pur., 304 Stainless Steel	19.0	8.5	$.2\times10^4$	4.3×10^3	623	130	190	318	166	8.0

*Average numbers of 2 or more analyses. N.D. not detected.

TABLE II

Low Silicon-Phosphorous						High Silicon-Phosphorous					
Alloy Designation	Chrom. wt. percent	Nickel wt. percent	Silicon, p.p.m.	Phosph., p.p.m.	Corros. Rate, mg./cm.^{2}-h.	Corros. Rate, mg./cm.^{2}-h.	Phosph., p.p.m.	Silicon, p.p.m.	Nickel, wt. percent	Chrom. wt. percent	Alloy Designation
2-Mn	14.8	12.9	1	10	0.47	0.88	20	20	12.5	14.8	5-N
3-Mn	14.8	13.0	1	12	0.53	3.30	245	20	12.0	14.6	3-P
5-O	11.9	14.5	5	5	0.44	2.10	110	10	12.0	14.7	2-P
1	15.5	13.1	10	15	0.45	0.95	220	25	12.0	14.4	5-P
5-Mn	13.3	11.6	10	15	0.47	3.30	245	2.0	12.0	14.6	3-P
6-C	15.5	12.9	10	17	0.48	1.35	9	2.8×10^3	13.4	15.1	4-Si
3-C	15.3	12.8	10	18	0.50	1.75	17	4.8×10^3	12.6	16.0	7-Si
2-C	15.5	13.1	10	19	0.50	4.30	9	9.5×10^3	13.6	15.4	5-Si
4-C	15.4	12.6	10	20	0.50	0.75	21	10	12.6	15.3	5-C
2-Si	15.0	13.5	2×10^2	14	0.45						
3-Si	15.2	13.6	1.8×10^3	13	0.50						

TABLE III

Low Silicon-Phosphorous						High Silicon-Phosphorous					
Alloy Designation	Chrom. wt. percent	Nickel wt. percent	Silicon, p.p.m.	Phosph., p.p.m.	Corros. Rate, mg./cm.^{2}-h.	Corros. Rate, mg./cm.^{2}-h.	Phosph., p.p.m.	Silicon, p.p.m.	Nickel, wt. percent	Chrom. wt. percent	Alloy Designation
Low Si-P Comm. 16-12 Alloy.	16.5	11.7	5	21	0.53	4.4	204	4.7×10^3	11.5	16.6	Commercial Pur., 16-12 Alloy.
Low Si-P, Type 304 ss.	19.0	7.8	10	14	0.87	8.0	190	4.3×10^3	8.5	19.0	Commercial Pur., 304 ss.

I claim:

1. A stainless steel alloy having a high resistance to intergranular corrosion by boiling nitric acid-metallic ion mixtures having a high oxidation potential, consisting essentially of iron, chromium, nickel, and minor amounts of impurities selected from the group consisting of carbon, manganese, sulphur, silicon, phosphorus, nitrogen and oxygen, in which the chromium content is from about 14 to 26 weight percent, the carbon content is from about 0.02 to 0.2 weight percent, the nickel content is from about 6 to 22 weight percent, the content of silicon is from 1 to 2000 p.p.m. by weight, and the content of phosphorus is from about 5 to 20 p.p.m. by weight.

2. A stainless steel alloy as described in claim 1, additionally including a manganese content of about 2.0 weight percent, and a sulphur content of about 0.2 weight percent, and wherein the chromium content is from about 18 to 20 weight percent, the carbon content is about 0.06 weight percent, and the nickel content is from about 8 to 12 weight percent.

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