

[54] **HIGH TEMPERATURE
CHROMIUM-NICKEL ALLOY**

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[57] **ABSTRACT**

An alloy containing 45 to 55 percent chromium, 45 to 55 percent nickel, 0.003 to 0.4 percent cerium, up to 1.5 percent titanium, up to 1.5 percent zirconium, and up to 1.5 percent hafnium. The titanium, zirconium and hafnium may be present separately in amounts up to 1.5 percent or they may be present in combination in an amount up to 3.0 percent.

2 Claims, No Drawings

HIGH TEMPERATURE CHROMIUM-NICKEL ALLOY

This invention relates to a high temperature corrosion resistant alloy having a composition within the ranges set forth hereinafter. The term "corrosion" as used herein means the gradual deterioration or breakdown of the alloy by dissolution, oxidation or other means attributable to a chemical process.

High temperature corrosion resistant alloys produce a protective surface coating during service. Stainless steels are examples of alloys which form self-manufactured protective surface oxide scales at high temperatures. While the presence of certain elements in a protective oxide scale is known to increase the degree of protection afforded by the scale, it is necessary to consider other factors when determining the composition of an alloy for high temperature applications requiring corrosion inhibition. Some of these factors are the strength of the scale formed on the substrate, the degree of adherence of the scale to the substrate and the growth stresses in the scale. All of these properties are important in determining the composition of an alloy to be used at high temperatures in corrosion resistant applications.

An alloy having a composition within the ranges of our invention has good corrosion resistance at temperatures up to about 2250°F and has numerous applications in the chemical and petroleum industries where high temperatures are encountered under extremely corrosive conditions for long periods of time. Additionally, alloys within our composition range can be heat treated and worked to produce shapes for fabricating structures.

Our invention consists in an alloy which is more resistant to corrosion at high temperature than presently known alloys. The reason that our alloy is resistant to corrosion at high temperatures is believed to be because the surface oxide layer is highly resistant to spalling and, hence, is more adherent to the substrate than the oxides formed on the surfaces of known high temperature alloys. The advantageous properties of our

increases the adhesion of the outer oxide scale to the metal substrate.

The benefits achieved by the addition of cerium are obtained in a chromium-nickel alloy having at least 45 percent chromium and at least 45 percent nickel. The presence of titanium, zirconium and hafnium either alone or in combination in the alloy is not detrimental since these reactive elements are present in the chromium-nickel matrix without having any appreciable effect on the high temperature corrosion resistance of the alloy.

However, since titanium, zirconium and hafnium are strong nitrogen forming elements, their presence in the alloy prevents the alloy from including excessive amounts of nitrogen in solid solution. The amount of titanium and/or zirconium and/or hafnium required depends upon the amount of nitrogen present in the alloy during the final stages of melting, but it has been determined that 0.3 percent is the effective minimum if these metals are used.

The broad composition range of our novel alloy is as follows:

Element	Percent By Weight
Chromium	45 - 55
Nickel	45 - 55
Cerium	0.003 - 0.4
Titanium	Up to 1.5
Zirconium	Up to 1.5
Hafnium	Up to 1.5
Total of Titanium plus Zirconium plus Hafnium	Up to 3

It should be understood that the method of producing the alloy and the processing to which the alloy is to be subjected must be considered in determining the specific amount of cerium which is added.

The following non-limiting examples show the advantages of alloys within the range of our invention. The chemical analyses of the various heats of the examples are set forth in Table I. In each instance cerium was added after the chromium-nickel alloy was melted and refined.

TABLE I

Heat Number	ANALYSIS - PERCENT BY WEIGHT									
	Cr	Ni	Ce	C	Mg	S	P	Ti	Fe	O
1	50.13	48.86	0.0	0.026	<0.0005	0.010	0.003	0.83	0.21	0.0132
2*	50.0	48.5	0.003	0.068	<0.0005	0.008	—	1.0	0.2	0.0038
3*	50.0	48.5	0.008	0.056	<0.0005	0.008	—	1.0	0.2	0.0040
4	50.06	48.69	0.12	0.034	<0.0005	0.013	0.003	0.87	0.21	0.0029
5	50.02	48.51	0.28	0.050	—	0.011	0.002	0.99	0.20	—
6	49.98	48.53	0.38	0.050	<0.0005	0.008	0.002	1.04	0.19	0.0028

*Nominal composition of chromium, nickel, titanium and iron.

alloy are believed to result from the addition of cerium to the chromium-nickel matrix.

The addition of small amounts of cerium to a chromium-nickel alloy decreases the oxidation rate of the alloy by a substantial amount, and, thus, the alloy is better able to resist corrosion at high temperatures. Analysis of outer oxide scale formed on alloys in accordance with our invention shows that the scale is substantially completely Cr_2O_3 which indicates that the cerium does not diffuse into the outer scale. It is believed that the cerium forms a thin, non-uniform, discontinuous oxide layer between the outer oxide scale and the metal substrate. Thus, an additional barrier to diffusion of oxygen and chromium is produced on the metal surface. By forming an intermediate oxide layer, the cerium has a substantial effect upon oxide spallation and

A consideration of the analyses of the various heats shows that the amount of cerium in the alloy progressively lowers the oxygen content of the alloy. The alloys containing the lower amounts of cerium showed good hot workability, but ingots containing over 0.12 percent cerium were not workable even though the oxygen content was lower than in the ingots containing the smaller amounts of cerium.

In order to show the effect of cerium on oxidation resistance, a number of tests were conducted to determine the weight change and oxide scale adherence characteristics of our alloy including various amounts of cerium. A series of oxidation tests were conducted for various time periods at 1,800°F and 2,000°F with temperature cycling. The results of these tests are shown in Tables II, III and IV.

TABLE II

OXIDATION WEIGHT CHANGE AT 1800°F						
Sample*	Condition	Cerium (%)	Weight Change** (mg/cm²)			Condition of Oxide Scale
			45 Hours	108 Hours	205 Hours	
Heat 1	Wrought	0.0	0.0	-5.50	-6.51	All Spalled
Heat 3	Wrought	0.008	+0.21	+0.34	+0.22	Partially Spalled
Heat 4A	As-Cast	0.12	+0.59	+0.80	+1.07	Adherent
Heat 4B	As-Cast	0.12	+0.59	+0.89	+1.10	Adherent
Heat 5A	As-Cast	0.28	+0.73	+0.99	+1.27	Adherent
Heat 5B	As-Cast	0.28	+0.77	+0.99	+1.29	Adherent
Heat 6A	As-Cast	0.38	+0.66	+0.92	+1.25	Adherent
Heat 6B	As-Cast	0.38	+0.65	+0.95	+1.26	Adherent

*(1) Specimen size: .25"×.75"×1.5".
(2) Oxidation test carried out in box furnace with specimens in quartz containers.
(3) Weights measured at room temperature in as-cooled conditions.
**Three cycles of 45, 63 and 97 hours.

TABLE III

OXIDATION WEIGHT CHANGE AFTER 63 HOURS AT 2000°F				
Sample*	Condition	Cerium (%)	Weight Change (mg/cm²)	Condition of Oxide Scale
Heat 1	Wrought	0.0	-6.9	All Spalled
Heat 2	As-Cast	0.003	-8.2	All Spalled
Heat 3	As-Cast	0.008	-4.3	Partially Spalled
Heat 4	As-Cast	0.12	+1.5	Adherent
Heat 6	As-Cast	0.38	+1.4	Adherent

*(1) Specimen size: .25"×.75"×1.5".
(2) Oxidizing media: Air in box furnace.
(3) Weights measured at room temperature.

TABLE IV

OXIDATION WEIGHT CHANGE AFTER 430 HOURS AT 2000°F				
Sample*	Condition	Cerium (%)	Weight Change (mg/cm²)	Condition of Oxide Scale
Heat 1	Wrought	0.0	-16.22	All Spalled
Heat 2	As-Cast	0.003	-3.71	Partially Spalled
Heat 2	Wrought	0.003	-5.63	Partially Spalled
Heat 5	As-Cast	0.28	+11.93	Adherent
Heat 6	As-Cast	0.38	+5.00	Adherent

*(1) Specimen size: Approximately 0.3"×0.750"×1.00".
(2) Oxidation test carried out in box furnace.
(3) Weights measured at room temperature.

The tabulations in the above tables show that increased amounts of cerium promote adherence of the oxide scale to the substrate. Thus, scale formed on specimens with no cerium spalled off in large platelets, while the samples containing small amounts of cerium

showed partial spalling in small platelets, and the samples with larger amounts of cerium showed no spalling at all.

The results of continuous weight gain measurements due to oxidation are set forth in Tables V through IX.

TABLE V

CONTINUOUS WEIGHT GAIN FOR OXIDATION AT 1750°F			
Time (Hours)	Weight Gain* (mg/cm²)		
	0% Cerium (Heat 1)	0.008% Cerium (Heat 3)	0.28% Cerium (Heat 5)
0.1	0	0.011	-0.023
0.2	0.020	0.031	-0.012
0.3	0.111	0.053	
0.4	0.162	0.077	
0.5		0.110	0.046
0.75		0.187	0.093
1.0	0.243	0.220	0.139
1.5		0.265	0.197
2.0		0.297	
2.5	0.394	0.330	0.232
3.0	0.425	0.352	0.294

*(1) Total surface area of specimens: Approximately 9.5 cm².
(2) Specimen condition: As-cast.
(3) Dry air flow: 5.25 liters per minute; Dew point: 100°F.
(4) Weights measured at 1750°F during testing.

TABLE VI

CONTINUOUS WEIGHT GAIN FOR OXIDATION AT 2000°F, 0% CERIUM (HEAT 1)		
Time (Hours)	Weight Gain* (mg/cm²)	
0.1		0.32
0.5		0.92
1.0		1.30
2.0		1.89
17.7		4.76
26.3		5.54
41.8		6.71
50.5		7.18
65.7		8.00
74.5		8.39
90.5		9.04
98.5		9.37

*(1) Specimen size: 2.046"×0.361"×0.091".
(2) Specimen condition: As-cast.
(3) Dry air flow: 5.25 liters per minute; Dew point: 100°F.
(4) Weights measured at 2000°F during testing.

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TABLE VII

CONTINUOUS WEIGHT GAIN FOR OXIDATION AT 2000°F, 0.03% CERIUM (HEAT 2)	
Time (Hours)	Weight Gain* (mg/cm ²)
0.1	0.36
0.2	0.58
0.5	0.86
1.0	1.25
2.1	1.68
4.0	2.19
19.2	3.94
92.9	6.97
99.9	7.21

- *(1) Specimen size: 1.718"×0.271"×0.101".
 (2) Specimen condition: As-Cast.
 (3) Dry air flow: 5.25 liters per minute; Dew point: 100°F.
 (4) Weights measured at 2000°F during testing.

TABLE VIII

CONTINUOUS WEIGHT GAIN FOR OXIDATION AT 2000°F, 0.008% CERIUM (HEAT 3)	
Time (Hours)	Weight Gain* (mg/cm ²)
0.1	0.31
0.2	0.57
0.5	0.78
1.0	1.00
2.0	1.47
3.3	1.82
18.5	3.34
27.3	3.81
42.7	4.40
67.2	5.07
75.1	5.19
90.5	5.47
99.3	5.60

- *(1) Specimen size: 2.107"×0.377"×0.100".
 (2) Specimen condition: As-cast.
 (3) Dry air flow: 5.25 liters per minute; Dew point: 100°F.
 (4) Weights measured at 2000°F during testing.

TABLE IX

CONTINUOUS WEIGHT GAIN FOR OXIDATION AT 2000°F, 0.28% CERIUM (HEAT 5)	
Time (Hours)	Weight Gain* (mg/cm ²)
0.1	0.20
0.2	0.25
0.5	0.48
1.0	0.57
2.0	0.81
4.0	1.08
8.0	1.34
23.2	1.82
32.0	1.91
47.3	2.14

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TABLE IX-Continued

CONTINUOUS WEIGHT GAIN FOR OXIDATION AT 2000°F, 0.28% CERIUM (HEAT 5)	
Time (Hours)	Weight Gain* (mg/cm ²)
71.1	2.19
80.0	2.26
95.2	2.28
100.8	2.31

- *(1) Specimen size: 2.108"×0.313"×0.085".
 (2) Specimen condition: As-cast.
 (3) Dry air flow: 5.25 liters per minute; Dew point: 100°F.
 (4) Weights measured at 2000°F during testing.

The results of the tests at 1,750°F are not as accurate as those at 2,000°F due to smaller changes in weight, but this series of tests shows the general trend in the change of weight due to oxidation as more cerium is included in the alloy. The tests at 2,000°F (Tables VI – IX) clearly show the beneficial effect of cerium in retarding the rate of oxidation. The samples containing cerium form progressively thinner and more adherent scale as the cerium content was increased.

Based upon the test results shown in Tables II – IX, it may be concluded that cerium increases the adherence of the oxide scale to the metal substrate and decreases the thickness of the scale.

The alloy of our invention may be used for a number of different applications such as, for example, metal fired heaters, reactor vessels for treating pulping liquors, refinery heaters, acid handling equipment and metallurgical heat treating furnace components.

While we have described a preferred embodiment of our invention, it may otherwise embodied within the scope of the appended claims.

1. A high temperature corrosion resistant alloy consisting essentially of 45 – 55 percent chromium, 45 – 55 percent nickel, 0.003 – 0.4 percent cerium and between 0.3 percent and 3.0 percent of at least one of the metals selected from the group consisting of titanium, zirconium and hafnium, there being no more than 1.5 percent of any one of said metals.

2. A high temperature corrosion resistant alloy consisting essentially of 45 – 55 percent chromium, 45 – 55 percent nickel, 0.003 – 0.4 percent cerium and between 0.3 percent and 1.5 percent titanium.

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