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NICKEL-CHROMIUM-IRON HEAT RESISTING ALLOYS

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The present invention relates to nickel-chromium-iron alloys particularly suitable for use under carburizing and sulfidizing conditions at elevated temperatures and to articles made thereof.

It is an object of the present invention to provide a nickel-chromium-iron alloy and articles made thereof having high resistance to a carburizing environment at high temperatures.

Another object of the invention is to provide a nickel-chromium-iron alloy and articles made thereof having high sulfidation resisting qualities at high temperatures.

The invention also contemplates providing a special nickel-chromium-iron alloy and articles made thereof having high carburization resistance and high sulfidation resistance at high temperatures and having substantial freedom from embrittlement due to the formation of the sigma phase.

It is another object of the invention to provide a novel, wrought, nickel-chromium-iron alloy having high carburization resistance and high sulfidation resistance at high temperatures as well as having substantial freedom from embrittlement after prolonged heating in a temperature range of about 1200° F. to about 1650° F.

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

Generally speaking, the present invention is based upon the surprising discovery that novel nickel-chromium-iron alloys may be provided having a high resistance to carburizing environments by a higher than usual chromium content and with the nickel content suitably adjusted in special combination with the high chromium content to provide a resistance to structural embrittlement. It has also been found that the novel nickel-chromium-iron alloys, with the special proportioning of their nickel and chromium contents, achieve a superior sulfidation resistance while providing freedom from structural embrittlement. The new nickel-chromium-iron alloys also mitigate the undesirable catalytic behavior which nickel-chromium-iron alloys of higher nickel content may show when in contact with hot hydrocarbons as, for example, in furnace tubing used for the production of ethylene from ethane or propane. The novel composition of this invention also provides resistance to an accelerated type of oxidation known as "green rot" oxidation which is encountered in alloys of higher nickel and lower chromium content.

While the present invention deals primarily with a wrought or forgeable alloy, it is to be understood that the principles expounded would apply similarly to a cast composition.

In general, the alloys should contain sufficient nickel so that no embrittling sigma phase is formed. It has been found by extensive tests that for optimum resistance to carburization and sulfidation these alloys should contain a chromium content of the order of about 30%. It has further been demonstrated that, by providing the alloys with this high chromium content together with an appropriate balancing of the nickel content, they are then

rendered insensitive to embrittlement when subjected to prolonged heating in the temperature range in which the sigma phase may occur. An important purpose of this invention is to provide these high chromium content alloys which offer a resistance to carburization and sulfidation that is much better than for alloys having a lower chromium content. It is to be noted that the lower chromium-containing alloys may be susceptible to embrittlement in the absence of a sufficiently high nickel content to preclude the formation of the sigma phase.

The broad and preferred ranges of the special nickel-chromium-iron alloys of the present invention are given in Table I:

Table I

Elements	Broad Range	Preferred Range
Chromium	27.5 to 33	28 to 32.
Nickel	40 to 50	41 to 47.
Silicon	up to 1.5	up to 0.75.
Carbon	up to 0.5	up to 0.2.
Manganese	up to 2	up to 1.
Iron	Balance	Balance.

When it is stated that iron constitutes the balance, it is to be understood that the balance will be substantially all iron but may contain small amounts of incidental impurities and of other elements as noted hereinafter. In commercial alloys embodying the present invention, the balance may include customary deoxidizing elements in small amounts, for example, titanium up to about 1% and aluminum up to about 0.5%. The alloys may contain up to about 0.4% copper. Nitrogen may be beneficially included in amounts up to about 0.2%.

The nickel content of the special alloys of this invention should be at least 40% to insure that no embrittling sigma phase is formed.

It has been found that if the chromium content of the special alloys of this invention is reduced below about 28%, the alloys are subject to an undesirable increase in carbon content when subjected at high temperatures and for prolonged periods to a carburizing environment. A higher chromium content than about 33% is undesirable because with such higher chromium content alloys no substantial increase is obtained in resistance to carburization, sulfidation, oxidation, etc., at high temperatures.

It has been found that the nickel content within the foregoing ranges depends to some extent on the presence of carbon, titanium and aluminum in the alloys of this invention. While the alloys may be substantially carbon free or may contain carbon up to about 0.5%, with more carbon less nickel is necessary to maintain freedom from embrittlement. However, if the titanium and aluminum content is low or if neither is present, less nickel will be required to ensure freedom from embrittlement.

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

Table II

Elements	Alloy A[1]	Alloy B[1]	Alloy C[1]
Chromium	28.5	28.63	31.22
Nickel	42	42.71	41.76
Titanium		1.06	0.4
Aluminum		0.45	0.38
Silicon	0.5	0.64	0.61
Carbon	0.1	0.05	0.07
Manganese	1	0.85	0.81
Nitrogen	0.1		
Iron	Bal.	Bal.	Bal.

[1] Structurally these alloys are sigma free but contain the non-embrittling phase alpha prime.

It is well recognized that the formation of sigma phase frequently results in serious embrittlement which is reflected in a pronounced decrease in impact resistance.

Portions of several alloys were forged and hot rolled to ¾ inch diameter bars and then cold rolled with an intermediate anneal to ½ inch square bars so that the finished bars received about 23% of cold work. After the cold rolling, a portion of each material was annealed for one hour in the temperature range 1900° to 1975° F. followed by water quenching. A sufficient number of lengths of each material in both the cold worked and annealed conditions adequate for Charpy impact specimens were heated for 100, 500, 1000 and 3000 hours at 1475° F. At the completion of the treatments the specimens were machined into keyhole notched Charpy impact specimens. The Charpy impact values obtained for these alloy specimens are presented in Table III.

Table III

Alloy	Nominal Composition		Charpy Impact in Foot Pounds After Soaking Indicated Hours at 1,475° F.						
	Percent Ni	Percent Cr	Soak Hours	0	100	250	500	1,000	3,000
B	42.7	28.63	Annealed	56	------	36	34	------	------
			Cold Worked	28	------	28	31	------	------
C	41.76	31.22	Annealed	52	------	------	33.5	------	------
			Cold Worked	29.5	------	------	25	------	------
D	46	27	Annealed	49	49	------	46	48.5	45
			Cold Rolled 23%	27	49	------	46	45.5	48
E	46	30	Annealed	48.5	51	------	43.5	44.5	43
			Cold Rolled 23%	33	35	------	37	37.5	37.5
F	46	33	Annealed	50	37	------	36	38	41
			Cold Rolled 23%	33	24	------	25	28	30
G	20	25	Annealed	79	33	------	14	11	9
			Cold Worked	39	11	------	7	7	7

The alloys Nos. B, C, D, E and F have compositions according to this invention. Alloy No. G has a composition outside the scope of the invention but, as this is a widely used heat resistant alloy, it is included here for comparison purposes. When the composition is in accordance with the invention, as illustrated by alloys Nos. B, C, D, E and F, the alloys are substantially insensitive to structural embrittlement when subjected to prolonged heating in the temperature range of about 1000° to 1650° F. in which the sigma phase may occur, as indicated by the foregoing Charpy keyhole notch impact tests.

It will be appreciated that the function of the titanium and aluminum, when used, is to deoxidize and degasify the alloy, and that neither of these elements is essential to this invention. The deoxidation and degasification practice could include instead other elements, for example, calcium and silicon.

The combination of properties obtainable by the invention makes the alloys particularly suitable for a wide variety of articles. Such articles include furnace parts and apparatus subjected to carburizing conditions such as carburizing boxes, baskets and other fixtures for supporting articles to be carburized, cyanide pots and salt bath fixtures, wrought radiant tubes which may be seamless and particularly for use in a carburizing atmosphere, furnace tubing used for the production of ethylene from ethane and propane, thermocouple protection tubes, and furnace parts and apparatus subjected to sulfidation and oxidation at high temperatures. Such articles also may includes cold rolled and hot rolled flats, rounds, sheet and also especially extruded tubing.

It is to be noted that the present invention is not to be confused with an alloy containing nominally 29% chromium and 35% nickel which has exhibited good resistance in several types of carburizing environments but which is structurally unstable and develops the embrittling sigma phase, a deficiency which has been overcome in the present invention by a novel balancing of the nickel and chromium contents.

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.

I claim:

1. A carburizing box consisting essentially of an alloy containing about 41% to 47% nickel, about 28% to 32% chromium, with carbon up to about 0.2%, titanium up to about 1%, aluminum up to about 0.5% and the balance substantially all iron, said alloy containing the aforesaid high nickel and chromium contents providing high carburization resistance when subjected in use to prolonged heating at elevated temperatures in a carburizing environment, high sulfidation resisting qualities at high temperatures, and substantial freedom from embrittlement after prolonged heating in a temperature range of about 1200° to 1650° F.

2. A carburizing box consisting essentially of an alloy containing from about 40% to 50% nickel, about 27.5% to 33% chromium, with carbon up to about 0.5%, titanium up to about 1%, aluminum up to about 0.5% and the balance substantially all iron, said alloy containing the aforesaid high nickel and chromium contents providing high carburization resistance when subjected in use to prolonged heating at elevated temperatures in a carburizing environment, substantial freedom from embrittlement after prolonged heating in a temperature range of about 1200° to 1650° F. and high sulfidation resisting qualities at high temperatures.

3. Wrought metal tubing consisting essentially of an alloy containing from about 40% to 50% nickel, about 27.5% to 33% chromium, up to about 1.5% silicon, up to about 2% manganese, up to about 0.5% carbon, up to about 1% titanium, up to about 0.5% aluminum and the balance substantially all iron, said alloy containing the aforesaid high nickel and chromium contents providing high carburization resistance when subjected in use to prolonged heating at elevated temperatures in a carburizing environment, high sulfidation resisting qualities at high temperatures, and substantial freedom from embrittlement after prolonged heating in a temperature range of about 1200° to 1650° F.

4. An article of manufacture subjected in use to prolonged heating at elevated temperatures and made of an alloy containing about 41% to about 47% nickel, about 28% to about 32% chromium, up to about 0.2% carbon, titanium up to about 1%, aluminum up to about 0.5%, and the balance substantially all iron, said alloy containing the aforesaid high nickel and chromium contents providing high carburization resistance when subjected in use to prolonged heating at elevated temperatures in a carburizing environment, high sulfidation re-

sisting qualities at high temperatures, and substantial freedom from embrittlement after prolonged heating in a temperature range of about 1200° to 1650° F.

5. An article of manufacture subjected in use to prolonged heating at elevated temperatures and made of an alloy containing about 40% to about 50% nickel, about 27.5% to about 33% chromium, up to about 0.5% carbon, titanium up to about 1%, aluminum up to about 0.5%, and the balance substantially all iron, said alloy containing the aforesaid high nickel and chromium contents providing high carburization resistance when subjected in use to prolonged heating at elevated temperatures in a carburizing environment, high sulfidation resisting qualities at high temperatures, and substantial freedom from embrittlement after prolonged heating in a temperature range of about 1200° to 1650° F.

6. An alloy suitable for articles subjected in use to prolonged heating at elevated temperatures, said alloy containing about 41.7% to about 47% nickel, about 28% to about 32% chromium, up to about 0.75% silicon, up to about 0.2% carbon, up to about 1% manganese, up to about 1% titanium, up to about 0.5% aluminum and the balance substantially all iron, said alloy containing the aforesaid high nickel and chromium contents providing high carburization resistance when subjected in use to prolonged heating at elevated temperatures in a carburizing environment, high sulfidation resisting qualities at high temperatures, and substantial freedom from embrittlement after prolonged heating in a temperature range of about 1200° to 1650° F.

7. An alloy subjected in use to prolonged heating at elevated temperatures, said alloy containing about 40% to about 50% nickel, about 27.5% to about 33% chromium, up to about 1.5% silicon, up to about 0.5% carbon, up to about 2% manganese, up to about 1% titanium, up to about 0.5% aluminum and the balance substantially all iron, said alloy containing the aforesaid high nickel and chromium contents providing high carburization resistance when subjected in use to prolonged heating at elevated temperatures in a carburizing environment, high sulfidation resisting qualities at high temperatures, and substantial freedom from embrittlement after prolonged heating in a temperature range of about 1200° to 1650° F.

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