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㉓ Proprietor: **Exxon Research and Engineering Company**
P.O.Box 390 180 Park Avenue
Florham Park New Jersey 07932 (US)

㉔ Inventor: **Ramanarayanan, Trikur Anantharaman**
33 Chestnut Circle
Somerset New Jersey 08873 (US)
Inventor: **Petkovic-Luton, Ruzica**
90 South Woodland Street
Englewood New Jersey 07631 (US)
Inventor: **Ayer, Raghavan**
1670 Shippin Avenue
Stamford Connecticut 06902 (US)

㉕ Representative: **Field, Roger Norton et al**
ESSO Engineering (Europe) Ltd. Patents & Licences
Apex Tower High Street
New Malden Surrey KT3 4DJ (GB)

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Description

This invention relates to alumina-forming nickel-based austenitic alloys having superior oxidation and carburization resistance, superior creep strength, good high temperature ductility, and good microstructural stability.

Various industrial processes, especially chemical processes, create an insatiable demand for alloys which can withstand higher and higher temperatures and environments deleterious to the alloy. One such deleterious environment is a carburizing environment, the effects of which are known to significantly affect plant performance and efficiency in many industrial processes. These effects are evidenced in heat treatment equipment, ethylene pyrolysis tubing, carbon dioxide and helium-cooled nuclear reactors, coal processing plants, and hydrocarbon reformers.

A variety of alloy steels exhibiting both heat and carburization resistance have been developed for use in pyrolysis furnaces for the thermal decomposition of organic compounds, such as the steam cracking of hydrocarbons. Generally, the pyrolysis furnace contains a series of heat-resistance alloy steel tubes in which the reaction occurs. It will be noted that the term "tube" as used herein also includes fittings, pipes and other parts used to contain carburizing materials.

It is well known that alloy steels containing various amounts of nickel, chromium, and silicon, as well as the addition of elements such as tungsten and/or niobium, are frequently used in high temperature applications. However, after extended use at high temperatures, most, if not all, of these known alloys fail to accomplish all of the above objectives.

The major cause of failure, especially in pyrolysis tubes, is creep rupture, brought about by the combined effect of thermal stress and carburization. Carburization of such tubes, which is the diffusion of carbon into the alloy steel causing the formation of additional carbides, principally at the grain boundaries, and the attendant depletion of the matrix in chromium, brings about both a loss of creep strength and embrittlement of the grain boundaries. Once the steel has become embrittled, it is more susceptible to failure by creep rupture at high temperatures, brittle fracture at low temperatures, or both, because of thermal stress.

Although progress has been made in the development of alloy steels capable of withstanding the rigours of high temperature hydrocarbon environments, there still exist a need in the art for the further development of alloy steels having high temperature properties superior to those known in the art.

In accordance with the present invention there is provided alumina-forming nickel-based austenitic alloys having improved oxidation and carburization resistance, improved creep rupture properties, good high temperature ductility, and good microstructural stability. These alloys are

characterized by the following composition (% by weight):

	Cr	20—25
5	Fe	10—15
	Al	3—6
10	Hf	1—2
	W	1.5—3.25
	Nb	1—2
15	Y	0.01—1
	C	0.2—0.3
20	Ni plus impurities	balance

In the drawings

Figure 1 is a graph showing the superior creep strength and ductility of the alloys of the present invention compared with alloys commercially available for high temperature service; and

Figure 2 is a graph which again shows the superior creep and ductility properties of the alloys of the present invention over those conventionally employed. The alloys represented on this graph were first aged at 1000°C for 3,000 to 5,000 hours before testing.

The alloys according to the present invention are particularly adapted to constitute metallic parts to be used on the inside or outside of reforming and steam cracking furnaces wherein there exists an oxidizing and carburizing atmosphere and operating temperatures in the range of about 900°C to about 1100°C.

The alloys of the present invention simultaneously possess the following properties:

- (a) superior oxidation and carburization resistance;
- (b) good creep strength;
- (c) good high temperature ductility; and
- (d) good microstructural stability.

The composition of the alloys of the present invention, by weight percent based on the total weight of the alloy, can be characterized as follows:

50	Cr	20—25	preferably	24—25
	Fe	10—15	preferably	12—14
55	Al	3—6	preferably	4—5
	Hf	1—2	preferably	1.5—2
	W	1.5—3.25	preferably	2.75—3.25
60	Nb	1—2	preferably	1.25—1.75
	Y	0.01—1	preferably	0.5—1
65	C	0.2—0.3	preferably	0.3

The rest being nickel with the usual minimum impurities.

In the composition of the alloys of the present invention:

Chromium (Cr) and aluminum (Al) are jointly responsible for high temperature oxidation and carburization resistance of the alloys. Aluminum in the range of about 3 to 6 wt.%, preferably from about 4 to 5 wt.%, leads to the development of protective Al_2O_3 scales on the alloy surface, provided the chromium level is in excess of 20 wt.%. At lower levels of chromium, aluminum will have a tendency to oxidize internally and a protective Al_2O_3 scale will not develop on the alloy surface. Chromium levels in excess of 25 wt.% will lead to the precipitation of alpha chromium and sigma phases which lead to microstructural instability. Al_2O_3 scales have been found to be more stable than Cr_2O_3 scales (which forms in Al free alloys) at temperatures in excess of about 1050°C.

Chromium also provides strength by virtue of its presence in solid solution and the formation of chromium carbide particles.

Carbon (C) provides strength at elevated temperatures in the presence of carbide forming elements through the formation of finely dispersed alloy carbides in the matrix and discontinuous blocky carbides in the grain boundaries. The latter inhibit grain boundary sliding and thereby constrain matrix deformation at a carbon level of 0.2—0.3. Higher levels of carbon promote the formation of a continuous layer of carbide at grain boundaries which serve as an easy path for crack propagation and thus impart poor ductility.

Hafnium (Hf) additions result in the formation of highly stable hafnium carbides (HfC). These form in preference to chromium carbides during solidification and precipitate as discrete particles at grain boundaries. This process removes carbon from solution and suppresses the precipitation of chromium carbides and thereby promotes the formation of discrete particles of hafnium carbides in preference to the continuous carbide boundary film formed in the absence of hafnium.

Yttrium (Y) in levels less than about 1 wt.% have been shown to significantly improve the adherence of Al_2O_3 scales; therefore, a Y content of about 0.01 to 1 wt.%, preferably about 0.5 to 1 wt.% is employed for use in the present alloys.

Tungsten (W) contributes to solid solution strengthening at high temperatures and 1.5 to 3.25 wt.%, preferably 2.75 to 3.25 wt.% is employed in the alloys of the present invention.

Niobium (Nb), when present in the alloys of the present invention, will form fine niobium carbide precipitates on dislocations in the alloy structure and contributes to the strength of the alloy. Niobium levels of about 1 to 2 wt.% are suitable for use herein, preferred is a niobium content of about 1.25 to 1.75 wt.%.

Nickel constitutes the balance of the alloys with residual impurities at as low a concentration as possible.

The following examples illustrate more fully, the present invention.

Comparative Example A

A coupon measuring 2 cm×1 cm×5 mm was taken from a cast tube comprised of 0.55 wt.% C, 2.31 wt.% Si, 1.21 wt.% Mn, 29.75 wt.% Cr, 28.70 wt.% Ni, balance Fe. The coupon was pack carburized, that is, placed in a carbon bed having access to air, at 1100°C for 72 hours. The coupon was then nickel-plated, cross-sectioned, polished, and examined under a scanning electron microscope. It was observed that carburization occurred throughout the coupon.

Example 1

A coupon having the same dimensions as that of the above Comparative Example was taken from a cast tube comprised of 23.8 wt.% Cr, 12.2 wt.% Fe, 4.8 wt.% Al, 1.23 wt.% Hf, 2.85 wt.% W, 1.68 wt.% Nb, 0.48 wt.% Y, 0.2 wt.% C, and the balance Ni. The coupon was pack carburized at 1100°C for 72 hours. The coupon was then prepared and analyzed as in the above Comparative Example and it was found that a protective Al_2O_3 scale had formed which enabled the coupon to resist carburization.

Example 2

A coupon of the alloy of Example 1 above was oxidized in air at 1100°C for 100 hours. The coupon was then analyzed and it was found that a protective layer of Al_2O_3 had formed on its surface, and that some internal Al_2O_3 stringers were also present. At the chromium and aluminum levels claimed herein, the alloys of the present invention are selectively oxidized to form Al_2O_3 scales which resist further oxidation—thus evidencing the oxidation resistance of the presently claimed alloys.

Example 3

The microstructural stability of the alloy of Example 1 above was determined by studying samples of the alloy after one sample was exposed to air at 1100°C for 1000 hours and another sample was exposed to air at 1175°C for 100 hours. Both samples were found to be structurally stable, that is, the grain structure and precipitates remained unchanged throughout the experiment.

Comparative Examples B and C and Example 4

Three alloy samples, shown in Table I below, were prepared and tested for creep strength and ductility at 1000°C and 3000 psi (206841 mbar) for up to about 700 hours. The results were recorded and are illustrated in Figure 1 herein which shows strain-inch/inch (mm/mm) versus time in hours. It is evidenced by this Figure 1 that the alloy of the present invention is superior to the other two alloys which are representative of those alloys conventionally employed at elevated temperatures.

TABLE I

Comp. Ex. B	Comp. Ex. C	Ex. 4
C—0.11	0.43	0.2
Si—0.88	1.14	—
Cr—24.5	24.0	23.8
Ni—38.7	41.8	balance
Fe—33	30.7	12.2
Mn—1.05	1.45	—
Mo —	1.47	—
Nb—1.49	—	1.68
W —	—	2.85
Y —	—	0.48
Hf —	—	1.23
Al —	—	4.8

Samples of the above alloys were first aged before being tested at 1000°C and 3000 psi (206841 mbar). The alloy corresponding to Comparative B and C were aged at 1000°C for 5000 hours whereas the alloy corresponding to Example 4 was aged at 1000°C for 3000 hours. The results, as illustrated in Figure 2, again demonstrate the superior creep strength and ductility of the presently claimed alloys.

Claims

1. A heat resisting alumina-forming, nickel-based austenitic alloy having improved oxidation and carburization resistance, improved creep strength and good high temperature ductility and microstructural stability consisting of the following elements in the following by-weight proportion ranges:

Cr	20—25 %
Fe	10—15 %
Al	3—6 %
Hf	1—2 %
W	1.5—3.25 %
Nb	1—2 %
Y	0.01—1 %
C	0.2—0.3 %
Ni plus impurities	balance

2. An alloy according to claim 1 in which the chromium content is about 24 to 25 wt. %.

3. An alloy according to claim 1 or 2 wherein the iron content is about 12 to 14 wt. %.

4. An alloy according to any one of claims 1—3 in which the aluminium content is about 4 to 5 wt. %.

5. An alloy according to any one of claims 1—4 in which the hafnium content is about 1.5 to 2 wt. %.

6. An alloy according to any one of claims 1—5 in which the tungsten content is about 2.75 to 3.25 wt. %.

7. An alloy according to any one of claims 1—6 in which the niobium content is about 1.25 to 1.75 wt. %.

8. An alloy according to any one of claims 1—7 in that the yttrium content is about 0.5 to 1 wt. %.

9. An alloy according to any one of claims 1—8 in which the carbon content is about 0.3 wt. %.

Patentansprüche

1. Hitzebeständige, aluminiumoxiddbildende, auf Nickel basierende austenitische Legierung mit verbesserter Oxidations- und Kohlunbeständigkeit, verbesserter Dauerstandfestigkeit und verbesserter Hochtemperatur-duktilität sowie mikrostruktureller Stabilität bestehend aus den folgenden Elementen in den folgenden Gewichtsanteilsbereichen:

Cr	20—25 %
Fe	10—15 %
Al	3—6 %
Hf	1—2 %
W	1,5—3,25 %
Nb	1—2 %
Y	0,01—1 %
C	0,2—0,3 %
Ni plus Verunreinigungen	Rest

2. Legierung nach Anspruch 1, bei der der Chromgehalt etwa 24 bis 25 Gew.% beträgt.

3. Legierung nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß der Eisengehalt etwa 12 bis 14 Gew.% beträgt.

4. Legierung nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß der Aluminiumgehalt etwa 4 bis 5 Gew.% beträgt.

5. Legierung nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß der Hafniumgehalt etwa 1,5 bis 2 Gew.% beträgt.

6. Legierung nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß der Wolframgehalt etwa 2,75 bis 3,25 Gew.% beträgt.

7. Legierung nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß der Niobgehalt etwa 1,25 bis 1,75 Gew.% beträgt.

8. Legierung nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß der Yttriumgehalt etwa 0,5 bis 1 Gew.% beträgt.

9. Legierung nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß der Kohlenstoffgehalt etwa 0,3 Gew.% beträgt.

Revendications

1. Alliage austénitique à base de nickel, formant de l'alumine, résistant à la chaleur, présentant une résistance améliorée à l'oxydation et à la cémentation, une résistance améliorée au fluage et une bonne ductilité à haute température et une stabilité microstructurale, consistant en les éléments suivants, dans les gammes ci-après, en pourcentage en poids:

Cr	20—25 %
Fe	10—15 %
Al	3—6 %
Hf	1—2 %
W	1,5—3,25 %
Nb	1—2 %

Y 0,01—1 %

C 0,2—0,3 %

5 Ni plus impuretés le reste

2. Alliage selon la revendication 1, dans lequel la teneur en chrome est d'environ 24 à 25 % en poids.

10 3. Alliage selon la revendication 1 ou 2, dans lequel la teneur en fer est d'environ 12 à 14 % en poids.

15 4. Alliage selon l'une quelconque des revendications 1 à 3, dans lequel la teneur en aluminium est d'environ 4 à 5 % en poids.

5. Alliage selon l'une quelconque des revendications 1 à 4, dans lequel la teneur en hafnium est d'environ 1,5 à 2 % en poids.

20 6. Alliage selon l'une quelconque des revendications 1 à 5, dans lequel la teneur en tungstène est d'environ 2,75 à 3,25 % en poids.

7. Alliage selon l'une quelconque des revendications 1 à 6, dans lequel la teneur en niobium est d'environ 1,25 à 1,75 % en poids.

25 8. Alliage selon l'une quelconque des revendications 1 à 7, dans lequel la teneur en yttrium est d'environ 0,5 à 1 % en poids.

30 9. Alliage selon l'une quelconque des revendications 1 à 8, dans lequel la teneur en carbone est d'environ 0,3 % en poids.

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FIG.1

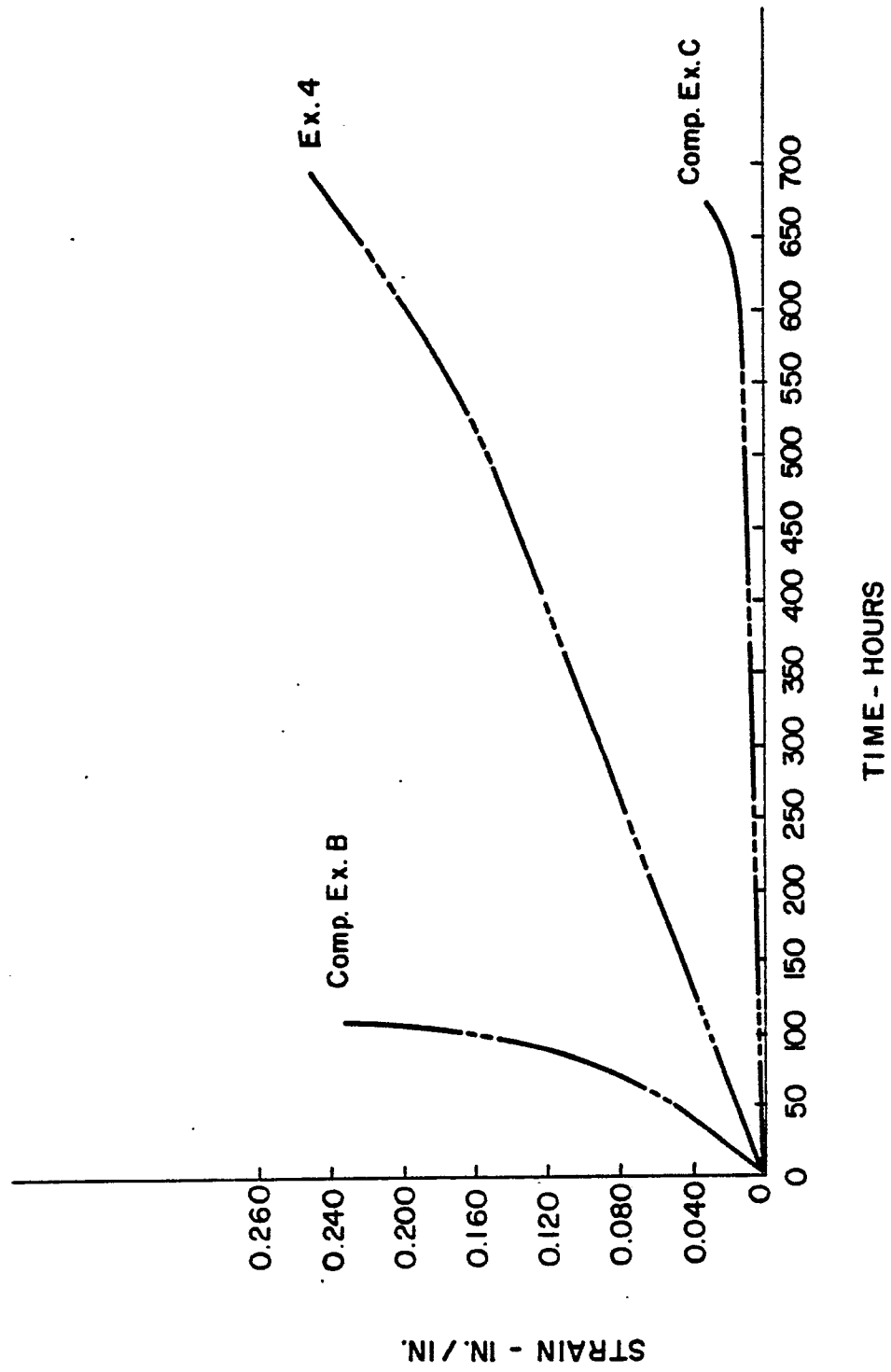


FIG. 2

