United States Patent [19]

Costin et al.

[11] **3,881,918**

[45] **May 6, 1975**

[54] **COBALT-BASE SUPERALLOY**

[75] Inventors: **Darryl J. Costin; James B. Ford,** both of Columbus, Ohio

[73] Assignee: **Owens-Corning Fiberglas Corporation,** Toledo, Ohio

[22] Filed: **May 9, 1974**

[21] Appl. No.: **468,360**

[52] **U.S. Cl.** **75/171**

[51] **Int. Cl.** **C22c 19/00**

[58] **Field of Search** 75/171, 170; 148/32, 32.5

[56] **References Cited**

UNITED STATES PATENTS

3,418,111 12/1968 Herchenroeder 75/171

Primary Examiner—R. Dean

Attorney, Agent, or Firm—Carl G. Staelin; John W. Overman; Philip R. Cloutier

[57] **ABSTRACT**

A cobalt-base superalloy, especially suitable for use in high temperature oxidizing environments is provided by combining constituent elements at defined amounts to form a composition which provides a balance of properties to the alloy especially high stress rupture strength and oxidation resistance at temperatures of at least 2,000 F.

8 Claims, No Drawings

COBALT-BASE SUPERALLOY

BACKGROUND OF THE INVENTION

This invention relates to a cobalt-base superalloy for use at temperatures of at least 2,000°F. More particularly, the invention relates to an alloy composed primarily of cobalt and chromium, but also includes nickel, tungsten, zirconium, silicon, iron and carbon with minor amounts of yttrium and dysprosium. The alloy is particularly suited for high temperature apparatus used in oxidizing environments.

Nickel and cobalt-base alloys, referred to as superalloys, find wide application in jet engines and in chemical industries where high temperature corrosive and oxidizing environments are common. Nickel base superalloys are generally limited to temperatures below 2,000°F, because higher temperatures cause the solution of $\gamma'(Ni_3Al)$, the main strengthening ingredient in the nickel-base superalloys; the overall effect of which is to significantly lower the high temperature stress rupture strength of the alloys. Cobalt-base superalloys generally exhibit somewhat higher elevated temperature stress rupture strength than nickel base superalloys beyond 2000°F; however, the oxidation resistance of the cobalt-base superalloys is generally inferior to that of comparable nickel-base superalloys.

Alloys shown in the prior art generally demonstrate either exceptional high temperature stress rupture strength or exceptional high temperature oxidation resistance. The prior art reveals compositions for alloys having superior high temperature oxidation resistance as shown in U.S. Pat. No. 3,418,111, but these alloys exhibit inferior high temperature stress rupture strength.

The alloys of this invention, however, exhibit a superior balance between high stress rupture strength and oxidation resistance at high temperatures of at least 2,000°F.

In evaluating the strength of an alloy, the inherent stress rupture capability of the alloy is an important criteria in the utility of the alloy at high temperatures. In a typical stress rupture test, which is widely used in the industry, time to failure is measured as a function of load and temperature. The ability of the alloy to withstand high stresses at high temperatures without failure is desirable and necessary in the utility of these alloys.

In addition to strength, the alloy must also possess the ability to resist corrosive attack in oxidizing atmospheres. The oxidation resistance of an alloy is manifested by the protective nature of the oxide film formed on the surface of the alloy when exposed to high temperatures in oxidizing environments. Oxidation resistance of an alloy is typically measured with the aid of a Thermogravimetric Analyzer (TGA) in which the change in weight of an alloy sample is measured as a function of time at a constant temperature and partial pressure of oxygen. The ability of the alloy to withstand the corrosive attack of oxidizing atmospheres at high temperatures is necessary in the utility of these alloys.

Strength alone or in combination with poor oxidation resistance makes an alloy less desirable for operation in high temperature oxidizing environments. Consequently, the composition of an alloy which finds use in such environments must combine high temperature oxidation resistance, without the employment of external coatings, and high temperature stress rupture strength, yielding an alloy having improved service life.

The alloy of this invention is particularly useful in high temperature oxidizing environments which exist in chemical, aerospace and other industries. These environments require alloys to possess a high resistance to corrosive attack in oxidizing atmospheres and a high load bearing ability at high temperatures.

Consequently, it is an object of this invention to provide a cobalt-base superalloy for use in high temperature oxidizing environments and in high stress conditions.

It is another object of this invention to provide an alloy composition which provides and balances the properties of high temperature stress rupture strength and high temperature oxidation resistance.

It is a further object of this invention to provide high temperature, load bearing apparatus, which apparatus is fabricated from an alloy possessing oxidation resistance and high stress rupture strength at temperatures at and above 2,000°F.

These and other objects will be readily apparent from the following detailed description which is intended only to illustrate and disclose the invention.

SUMMARY OF THE INVENTION

The cobalt-base superally according to the invention consists essentially of certain balanced amounts of chromium, nickel, tungsten, zirconium, silicon, iron, and carbon along with essential amounts of yttrium and dysprosium. More specifically, the alloy of this invention comprises in percent by weight* a chromium content of about 22.5 to 29.0; a nickel content of about 8.0 to 10.5; a tungsten content of about 6.0 to 9.0; a zirconium content of about 0.80 to 2.0; a silicon content of about 0.80 to 1.5; an iron content of about 0.35 to 0.50; a carbon content of about 0.25 to 0.45; a yttrium content of about 0.10 to 0.15; a dysprosium content of about 0.05 to 0.15; and a cobalt content being essentially the balance. A number of impurities are also found in the alloy, which impurities can be tolerated up to certain indicated levels without adversely affecting the alloy's properties and/or the performance of apparatus fabricated from the alloy at high temperatures. The impurities of the alloy consist essentially of aluminum, titanium, sulfur and phosphorus. These impurities are introduced into the alloy with the charge materials and their amounts must be strictly controlled to keep the respective amounts below the following percent by weight: aluminum, 0.10; titanium 0.10; sulfur 0.015 and phosphorus, 0.015.

*Unless expressly stated otherwise, all percents herein and in the appended claims are expressed as percents by weight.

In practicing the invention, this cobalt-base superalloy comprises a critical chromium content in order to form a protective oxide, which oxide imparts oxidation resistance to the alloy. It is well known that trivalent Cr^{+++}ions diffuse more slowly in a Cr_2O_3 lattice than divalent Co^{++} ions do in a CoO lattice. Therefore, for diffusion controlled oxidation, the Cr_2O_3 lattice, or external scales, provide more resistance to oxidation than the CoO lattice, or external scales. As a consequence, more cobalt-base superalloys contain large amounts (approximately 30 percent) of chromium in order to promote Cr_2O_3 films upon oxidation. However, in a spinel lattice, wherein the nonstochiometric composition may range from $CoCr_2O_4$ to $Co_{1.3}Cr_{1.8}O_4$ (at 1 atmosphere oxygen at 1,200°–1,400 °C), the diffusivities of both chromium and cobalt are much lower than in either CoO or Cr_2O_3. It has been theorized therefore, that

the $CoCr_2O_4$ spinel lattice should provide more protection than the Cr_2O_3 lattice for diffusion controlled oxidation. Oxdiation maps predict that the critical range for the chromium content that will give rise to the formation of a spinel lattice upon oxidation in the cobalt-base alloy is between 13 weight percent and 28 weight percent chromium. Preferred chromium contents are in the higher range—22.5 to 29.0 weight percent chromium. If the chromium content is too low, an alloy having unacceptable high temperature oxidation resistance results. Practice has revealed that a chromium content less than about 22.5 percent by weight leads to poor oxidation resistance at high temperatures. On the other hand, if there is a significant excess of chromium present, the alloy will be charcterized by poor strength and phase instability.

Nickel is included in the alloy to stabilize the face centered cubic phase of high temperatures, thereby preventing allotropic phase transformation from occurring. Nickel contents in the alloy of from 8.0 to 10.5 weight percent serve this purpose.

The inclusion of tungsten in the alloy composition is important to obtain high temperature stress rupture strength in the alloy. An excess of tungsten in the composition results in a loss of oxidation resistance and causes phase instability, whereas an insufficient amount of tungsten does not impart the desired stress rupture properties to the alloy. In order to impart high stress rupture strength to the alloy without sacrificing oxidation resistance, the amount of tungsten used in the composition was found to be about 6.0 to 9.0 percent by weight.

Zirconium at a level corresponding to at least 0.80 percent by weight must be present to obtain high temperature stress rupture strength. When the zirconium level exceeds the upper limit of the range, the melting point of the alloy is lowered, thereby resulting in a loss of high temperature strength. Zirconium reacts with carbon to form MC carbides, which strengthen the alloy matrix at high temperatures.

Silicon is included in the alloy composition in order to impart oxidation resistant characteristics to the alloy. However, it was found that much like chromium, silicon in excess results in poor strength and phase instability. A silicon content of about 1.0 percent by weight yields an alloy having optimum properties, by striking a balance between stress rupture strength and oxidation resistance. Silicon is also present to facilitate the casting of the alloy, by improving the alloy's fluidity during casting processes.

Iron is included in the alloy composition as an impurity, and should be maintained at a level below 0.5 percent by weight, lest deterioration of stress rupture properties will result.

Carbon is present in the alloy composition to promote the formation of carbides, in the form of small discrete particles for stress rupture strengthening. Only a small amount of carbon is necessary to fulfill this requirement. It has been found that when an excess volume of carbides are present, the oxidation resistance drops to an unacceptable level. A carbon content between 0.25 percent and 0.45 percent has been found to impart this alloy with a maximum level of oxidation resistance, while maintaining a sufficient amount of carbides to obtain excellent stress rupture strength.

It was found that combinations of rare earth additions improve the oxidation resistance of the cobalt-base superalloy and particularly improve the oxide scale adherence, which improves oxidation resistance. It is believed that the rare earth additions act as a vacancy sink, the overall effect of which is to reduce "vacancy pile up" in the subscale, which improves the adherence of the oxide scale to the alloy. A large improvement in scale adherence was observed to occur in the alloys of this invention with combined additions of about 0.15 weight percent yttrium and about 0.10 weight percent dysprosium.

The alloy of this invention may be prepared in accordance with recognized present-day melt procedures for superalloys. Desirably the constituents used are in master alloys to avoid unwanted impurities and to carefully control the final alloy composition. Preferably the melting is accomplished with a neutral crucible under vacuum. However, if desired, the charge when in a molten state, may be protected by an argon atmosphere. Other and additional charges of chromium, carbon, silicon, tungsten, zirconium, and the like required to arrive at the desired alloy composition may then be added when the melt temperature is about 2,800°F to about 2,900°F. Alternatively, these elements may be added with the original charge of chromium and cobalt.

It has been found that the time of addition of yttrium and dysprosium to the molten bath is critical. Specifically the combined yttrium and dysprosium charge additions should be made immediately prior to pouring in order to prevent appreciable oxidation losses of the rare earth elements. Heating is continued, and generally the melt is between about 2,910°F and 3,020°F when poured.

Fabricated articles are usually made from the cobalt-base superalloys of this invention by vacuum investment casting. Such articles include hardware or apparatus such as impellars or the like which are capable of withstanding high bearing loads at high temperatures. The alloy as cast can be welded and machined.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The cobalt-base superalloy of this invention has a composition falling within the range as shown below:

EXAMPLE I

Element	Percent by Weight
Chromium	22.5 – 29.0
Nickel	8.0 – 10.5
Tungsten	6.0 – 9.0
Zirconium	0.8 – 2.0
Silicon	0.8 – 1.5
Iron	0.35 – 0.50
Carbon	0.25 – 0.45
Yttrium	0.10 – 0.15
Dysprosium	0.05 – 0.15
Cobalt	Balance

Iron, aluminum, titanium, sulfur and phosphorous are impurities that are introduced with the charge materials and can be tolerated to a degree without adversely affecting the properties of this alloy, especially high temperature stress rupture strength and resistance to oxidation at high temperatures. The following indicated amounts of these impurities, when not exceeded do not affect the properties of this alloy: iron — 0.50 percent by weight, aluminum — 0.10 percent by weight; titanium — 0.10 percent by weight; sulfur —

0.015 percent by weight; and phosphorus — 0.015 percent by weight.

Specific examples of the alloys of this invention were prepared according to the above-described procedure. These alloys consisted essentially of the following weight percentages.

EXAMPLE II

Element	Percent by Weight
Chromium	25.0
Nickel	10.0
Tungsten	3.0
Zirconium	1.0
Silicon	1.0
Iron	0.5 maximum
Carbon	0.3
Yttrium	0.15
Dysprosium	0.10
Cobalt	Balance

EXAMPLE III

Element	Percent by Weight
Chromium	28.5
Nickel	9.5
Tungsten	8.2
Zirconium	1.4
Silicon	1.0
Iron	0.5 maximum
Carbon	0.35
Yttrium	0.10
Dysprosium	0.09
Cobalt	Balance

EXAMPLE IV

Elements	Percent by Weight
Chromium	23.5
Nickel	8.5
Tungsten	7.1
Zirconium	0.85
Silicon	1.3
Iron	0.5 maximum
Carbon	0.27
Yttrium	0.13
Dysprosium	0.06
Cobalt	Balance

Vacuum investment castings of the above alloys into stress rupture bars and oxidation samples were produced. These stress rupture bars and oxidation samples were tested and evaluated and compared to stress rupture bars and oxidation samples of cobalt-base alloys disclosed in U.S. Pat. No. 3,418,111, specifically Haynes Alloy 188. Haynes Alloy 188 is known to possess excellent stress rupture strength and oxidation resistance to 2,000°F. The tables below show the results of the testing.

TABLE I (Isothermal Oxidation)

Alloy	Temp. (°F)	Time (Hrs)	Weight Change/Area (mg/Cm^2)
Haynes 188	2000	30	4.251
Example II	2000	30	3.442
Haynes 188	2000	50	4.979
Example II	2000	50	3.981
Haynes 188	2000	74	5.414
Example II	2000	74	4.495

TABLE II (Stress Rupture)

Alloy	Temp. (°F)	Stress (psi)	Avg. Rupture Life (Hrs)
Haynes 188*	2000	2000	261.6
Example II**	2000	2000	11,200
Haynes 188*	2000	2400	62.2
Example II**	2000	2400	4,490
Haynes 188*	2000	3200	21.1
Example II**	2000	3200	1,050

*Sheet
**Vacuum Cast Bars

The above tables illustrate the superiority of the alloys of this invention over Haynes Alloy 188 which is used as a comparison in the industry.

Table I illustrates the superior oxidation resistance of an alloy of this invention when compared against Haynes Alloy 188, at temperatures of 2,000°F. The continuous weight change of the samples, as a function of time, were produced from a conventional TGA apparatus. The slope of the (weight change/area)^2 versus time curve generated in this oxidation study gives some indication of the rate of oxidation. The respective slope is referred to as the parabolic rate constant, such that the higher the parabolic rate constant, the higher the rate of oxidation. At 2,000°F. the parabolic rate constant for Haynes Alloy 188, was determined to be 0.312 $Mg^2/Cm^4/Hr$, as compared to a parabolic rate constant of 0.183 $Mg^2/Cm^4/Hr$ for an alloy of this invention (Example II). Therefore, an alloy of this invention (Example II) exhibits a 41.5 percent reduction in oxidation rate over that of Haynes Alloy 188 at 2,000°F.

Table II illustrates the excellent high temperature stress rupture life of an alloy of this invention (Example II).

We claim:

1. High temperature, load-bearing oxidation resistant apparatus in the form of vacuum investment castings, said apparatus being fabricated from an alloy consisting essentially of:

Element	Percent by Weight
Chromium	22.5 - 29.0
Nickel	8.0 - 10.5
Tungsten	6.0 - 9.0
Zirconium	0.8 - 2.0
Silicon	0.8 - 1.5
Iron	0.35 - 0.50
Carbon	0.25 - 0.45
Yttrium	0.10 - 0.15
Dysprosium	0.05 - 0.15
Cobalt	Balance

wherein the alloy possess high temperature stress rupture strength and oxidation resistance.

2. High temperature, load-bearing, oxidation resistant apparatus in the form of vacuum investment casting, said apparatus being fabricated from an alloy consisting essentially of:

Element	Percent by Weight
Chromium	25.0
Nickel	10.0
Tungsten	8.0
Zirconium	1.0
Silicon	1.0
Iron	0.5 maximum
Carbon	0.3
Yttrium	0.15
Dysprosium	0.10
Cobalt	Balance

wherein the alloy posses high temperature stress rupture strength and oxidation resistance.

3. High temperature, load-bearing, oxidation resistant apparatus in the form of vacuum investment casting, said apparatus being fabricated from an alloy consisting essentially of:

Element	Percent by Weight
Chromium	28.5
Nickel	9.5
Tungsten	8.2
Zirconium	1.4
Silicon	1.0
Iron	0.5 maximum
Carbon	0.35
Yttrium	0.10
Dysprosium	0.09
Cobalt	Balance

wherein the alloy possess high temperature stress rupture strength and oxidation resistance.

4. High temperature, load-bearing, oxidation resistant apparatus in the form of vacuum investment casting, said apparatus being fabricated from an alloy consisting essentially of:

Element	Percent by Weight
Chromium	23.5
Nickel	8.5
Tungsten	7.1
Zirconium	0.85
Silicon	1.3
Iron	0.5 maximum
Carbon	0.27
Yttrium	0.13
Dysprosium	0.06
Cobalt	Balance

wherein the alloy possess high temperature stress rupture strength and oxidation resistance.

5. An alloy suitable for vacuum investment casting, consisting essentially of:

Element	Percent by Weight
Chromium	22.5 – 29.0
Nickel	8.0 – 10.5
Tungsten	6.0 – 9.0
Zirconium	0.8 – 2.0
Silicon	0.8 – 1.5
Iron	0.35 – 0.50
Carbon	0.25 – 0.45
Yttrium	0.10 – 0.15
Dysprosium	0.05 – 0.15
Cobalt	Balance

said alloy being characterized by resistance to oxidation and by having high stress rupture strength at temperatures of at least 2,000°F.

6. An alloy suitable for vacuum investment casting, consisting essentially of:

Element	Percent by Weight
Chromium	25.0
Nickel	10.0
Tungsten	8.0
Zirconium	1.0
Silicon	1.0
Iron	0.5 maximum
Carbon	0.3
-Continued	
Element	Percent by Weight
Yttrium	0.15
Dysprosium	0.10
Cobalt	Balance

said alloy being characterized by resistance to oxidation and by having high stress rupture strength at temperatures of at least 2,000°F.

7. An alloy suitable for vacuum investment casting, consisting essentially of:

Element	Percent by Weight
Chromium	23.5
Nickel	8.5
Tungsten	7.1
Zirconium	0.85
Silicon	1.3
Iron	0.5 maximum
Carbon	0.27
Yttrium	0.13
Dysprosium	0.06
Cobalt	Balance

said alloy being characterized by resistance to oxidation and by having high stress rupture strength at temperatures of at least 2,000°F.

8. An alloy suitable for vacuum investment casting, consisting essentially of:

Element	Percent by Weight
Chromium	23.5
Nickel	8.5
Tungsten	7.1
Zirconium	0.85
Silicon	1.3
Iron	0.5 maximum
Carbon	0.27
Yttrium	0.13
Dysprosium	0.06
Cobalt	Balance

said alloy being characterized by resistance to oxidation and by having high stress rupture strength at temperatures of at least 2,000°F.

* * * * *