United States Patent Office

3,664,765

Patented May 23, 1972

3,664,765

NiCrCo ALLOYS TURBINE BLADE WITH CHROMIUM DIFFUSION LAYER

Tsuyoshi Ishimatsu, Tokyo, Takashi Ito, Masamitsu Yano, and Hajime Takeda, Chiba, and Kentaro Nagano, Yokohama, Japan, assignors to Asahi Glass Co., Ltd., Tokyo, Japan

No Drawing. Continuation of application Ser. No. 634,900, May 1, 1967. This application Mar. 9, 1970, Ser. No. 17,014

Claims priority, application Japan, May 4, 1966, 41/28,059; Feb. 24, 1967, 42/11,406

Int. Cl. F01d 5/14

U.S. Cl. 416—241 1 Claim

ABSTRACT OF THE DISCLOSURE

An alloy comprised mainly of chromium, nickel and cobalt and excellent in corrosion- and heat resistance, particularly, an alloy having the high corrosion resistance to a high temperature combustion gas containing sulfur oxides and alkali compounds and suitable for a blade for a gas turbine. The said alloy is provided with a chromium diffusion layer on its surface by a chromizing treatment.

This application is a continuation of copending application Ser. No. 634,900, filed May 1, 1967 and now abandoned.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The present invention relates to alloys having excellent heat- and corrosion resisting properties to combustion gas produced from fuels containing high sulfur, such as C-class heavy oil which contains about 3.5% sulfur as shown in K 2005–1960 JIS (Japanese Industrial Standard). More particularly, it relates to alloys showing sufficient anti-corrosive property in the case where such gases contain some alkali compounds, said alloy having sufficient mechanical strength at high temperatures.

(2) Description of the prior art

The composition of an alloy, namely the kind of elements composing said alloy and proportions of such elements, is determined in accordance with the uses or applications for the alloy.

In other words, the composition of an alloy is determined according to the use so as to impart favorable properties or performances requisite for uses of the alloys. As such properties there may be mentioned, for instance, heat resistance, corrosion resistance, and mechanical strength (i.e. tensile strength, shearing strength, yielding value and creap strength).

The more severe the performance required for the alloy and the higher the number of performances required, the harder it is to fully satisfy those requirements.

Gas turbine blades are caused to revolve at a high velocity in contact with high temperature combustion gas. Therefore, alloys for gas turbine blades are required to

have three properties, i.e. sufficient mechanical strength at high temperatures above 800° C., sufficient heat resistance and sufficient corrosion resistance to high temperature combustion gas and corrosive ash.

As alloys satisfying the above-mentioned three properties, super alloys containing metal elements such as nickel, cobalt, chromium and the like in a high quantity, for instance, Inconel, Udimet, LCN–155 (refer to Table I) and others are well known. These alloys have been widely used for turbine blades.

The turbine blades made of the above-mentioned alloys are durable for a long period of time in the case where fuels containing low or no sulfur like natural gas are employed. However, the turbine blades made of the above described alloys are corroded or give rise to scales on their surfaces where fuels of high sulfur content, such as C-class heavy oil, are employed, thereby becoming frequently impossible to use in a short period of time.

The present inventors have performed numerous experiments and made studies for many years in regard to the causes of such corrosion and such scaling, and have found that:

(1) The occurrence of scales and corrosions becomes especially remarkable in the presence of sulfates of alkali metals, such as Na_2SO_4, $Na_2S_2O_7$, K_2SO_4 and $K_2S_2O_7$.

(2) Sulfates of alkali metals are formed by reaction between sulfur oxides, such as SO_2 and SO_3 produced from combustion of S in the fuel, and alkali compounds contained in the fuel gas.

(3) A very small amount of alkali compounds is present very often in the combustion gas by the following causes:

(a) ash in the fuel,
(b) dusts of alkali compounds,
(c) splash of sea water.

(4) In the case where the turbine is installed near the sea side, the effect of the above-mentioned item (c) is great, and even if alkali content in the air is in the order of 1 mg./m.^{3} or below as Na_2O, when sulfur oxides are present, occurrence of corrosion or formation of scales is remarkably increased.

(5) When the alkali compound is present in the form of NaCl, the action becomes particularly remarkable.

As described above, the higher the number of performance required for the alloy and the more severe the performance required, the more difficult it is to sufficiently satisfy the all of these requirements.

For instance, Inconel–700 possesses sufficient mechanical strength at high temperatures, sufficient heat resistance and sufficient corrosion resistance against high temperature combustion gases and possesses the above-mentioned three performances ordinarily requisite as alloy for turbine blades:

However, Inconel–700 is not sufficiently resistant to combustion gases containing sulfur oxides and alkali compounds and is remarkably corroded in a relatively short period of time.

In addition, when said turbine blades are exposed to such a gas, scales are formed on the surface, thereby resulting in lowering the efficiency of the turbine.

It may be possible to determine the composition of an alloy so as to exhibit sufficient corrosion resistance to combustion gases containing sulfur oxides and alkali compounds. However, it is difficult to determine the alloy composition so as to have such corrosion resistance, in addition to the three performances described above. Still more is it very difficult to determine the alloy composition so as not to scale, even when exposed to combustion gas containing sulfur oxides and alkali compounds, in addition to the said four performances in total.

Under the above-mentioned circumstances, alloys have not been known which satisfy five requirements in the total as described above.

Accordingly, fuel with high sulfur content such as C-class heavy oil is cheap but even when its use is economically desirable, such a fuel has not been used.

BRIEF SUMMARY OF THE INVENTION

According to this invention there is provided alloys having five performances as described above.

Furthermore, according to the present invention, it is also possible to make the cheap sulfur-containing fuel useful as a gas turbine fuel.

It is an object of the present invention to provide an alloy having five performances as set forth hereinbefore.

Another object of the present invention is to provide turbines blades having the above-mentioned five performances.

A further object of the present invention is to make the cheap sulfur-containing fuel useful as a gas turbine fuel.

The present inventors have also executed laborious studies for the purpose of accomplishing the above-mentioned objects, which are difficult to achieve by mere selection of alloy composition, through alloys for and surface treatment of alloys or turbine blades.

As a result, the following facts have been made clear:

(1) The result of a corrosion test, wherein test pieces are heated at higher temperature for a relatively short period of time in an atmosphere containing far more quantity of sulfur oxide and alkali compound as compared with combustion gases actually used (hereinafter referred to as "accelerating test"), is not always coincident with the result of a test wherein test pieces are actually used as a turbine blade for an extended period of time (hereinafter referred to as "practical test").

(2) Two kinds of alloys of the identical series which respectively are subjected to the same surface treatment show sometimes corrosion resistances different widely from each other.

For instance, an alloy formed with an aluminum diffusion layer on the surface of Inconel–700 (called alloy-1) shows a better result in the accelerating test, as compared with an alloy formed with a chromium diffusion layer on the surface of Inconel–700 (called alloy-2), while in the practical test, said alloy-1 shows far inferior result as compared with said alloy-2.

Although the alloy–2 shows a good result in the practical test, the alloy having a chromium diffusion layer on the surface of Inconel–X (called alloy-3) shows extremely bad results.

At the present stage of the investigation, it is not definitely evident why the above-mentioned results (1) and (2) are obtained.

However, it has been proved from the result of experiments up to the present that alloys satisfying the hereinbefore described five performances can be obtained by forming a chromium diffusion layer by means of chromizing method on the surface of an alloy (hereinafter referred to as "base alloy") composed mainly of Cr, Ni and Co and having the following composition:

	Percent by wt.
Cr+Ni+Co	above 74
Cr	13 to 22
Ni	above 18
Co	above 11

The typical alloys, which satisfy the above described conditions and are able to provide preferable results, are Inconel–700, S–816, S–816B and Udimet, the compositions of these alloys being shown in Table I.

The present invention is a novel proposition based on the results of investigations as described above.

DETAILED DESCRIPTION INCLUDING PREFERRED EMBODIMENTS

Names of base alloys for accomplishing the above described objects and standard composition ranges of their principal constituents are shown in Table I. As can be seen from Table I, these alloys contain some by-constituents in addition to Cr, Ni and Co and as can also be seen by comparing Table I with Table II, these alloys contain, in some cases, some by-constituents which are not shown in Table I.

Among these by-constituents, there are those which are contained necessarily in the steps of manufacturing the alloy (hereinafter referred to as by-constituents A) and those which are added in order to enhance the properties of alloy (hereinafter referred to as by constituents B).

Further, with regard to these by-constituents, names of the by-constituents A and their composition ranges are given in the following:

	Percent by wt.
C	below 0.4
P	below 0.03
S	below 0.03

Names and the composition ranges of the by-constituents B are shown as follows:

	Percent by wt.
Si	below 1.5
Mn	below 2
Mo	below 6
Ti	below 4
Al	below 5
Fe	below 4
W	below 8
Nb	below 4
V	below 1
B	below 0.1

Further, the detailed properties of the above described alloys are described in

"Engineering Alloys" (the Fourth edition), by Norman E. Woldman, published by Reinhold Publishing Corp. Chapman & Hall Ltd., London, and "bal" in Table I and II means a balance, i.e. percent remainder left after other constituents have been subduced from 100.

TABLE I

Name of alloy	Constituent										
	C	Si	Mn	Cr	Ni	Co	Mo	Ti	Al	Fe	Other
Inconel-700[a]	<0.16			13–17	Bal	23–34			2.5–3.5	<4	
Inconel-700[b]	<0.1		1	15	48	28	3	2.5	2.5	1	
S-816	0.3–0.45			18–22	18–22	38	3.5–5			4	W: 3.5–8; Nb: 2.5–4.
S-816 B	0.4	0.3	1.5	20	20	Bal	4				W: 4; Nb: 4; B: 0.1.
Udimet-41	0.09			19	Bal	11	10	3	1.5		
Udimet-500	<0.15	<0.75	<0.75	15–20	Bal	13–20	3–5	2.5–3.2	2.5–3.2	<4	
Udimet-520	<0.05	<0.75	<0.75	19	Bal	12	6	3	2		W: 1; B: 0.05.
Udimet-600	<0.1	<0.75	<0.75	15–20	Bal	13–20		2.5–3.2	3.8–4.6	<4	B: <0.04.
Udimet-700	<0.15	<0.75	<0.75	13–17	Bal	17–20	4.5–5.7	3–4	3.7–4.7	<1	B: <0.1.

A method widely known as chromizing method is utilized for forming a chromium diffusion layer on the surface of such a base alloy. The chromizing method is a method wherein the metal or alloy, that is, the substances to be treated (hereinafter simply referred to as a base alloy) is brought into contact with the vapor of CrX_2 (wherein X is Cl, I or F), at high temperature, in a reducing atmosphere such as hydrogen gas, carbon monoxide gas or hydrocarbon or in a neutral atmosphere such as argon, to deposit Cr on the base alloy by decomposition of CrX_2, and the thus deposited Cr diffuses and penetrates into the base alloy to form a Cr diffusion layer on the surface of the base alloy.

It is desirable to make the thickness of the Cr diffusion layer commonly to be the order of 40 to 150μ. The diffusion layer obtained by the chromizing method has a high Cr content on the surface and the Cr content decreases gradually towards the base alloy, and the composition of the diffusion layer approaches rapidly to the composition of the base alloy on the boundary surface of both portions. Particularly good result can be obtained when the Cr content of the diffusion layer is above 40% and the Cr content of the surface of the said layer is from 60 to 95%.

As the chromizing methods, there are the following

(1) powder method, and
(2) gas method

and the most widely used method is the former powder method.

(1) Powder method

The powder method is a method wherein a base alloy is embedded in a mixture of finely divided powders of Cr or Cr-Fe alloy and a small quantity of NH_4X (wherein X is Cl, I or F) and heated in a reducing atmosphere such as a hydrogen stream. In this case, NH_4X reacts with fine powders of Cr or Cr-Fe alloy to produce CrX_2, and CrX_1 vapor thus produced comes into contact with the mother alloy to form the diffusion layer.

Further, a coagulation-preventing agent such as, for instance, kaolin or alumina is usually mixed in an amount of 0.5 to 2 times the quantity of Cr or Cr-Fe alloy powder with the Cr or Cr-Fe alloy powder in order to prevent the latter from adhering to the surface of the base alloy.

The most usually used NH_4X is NH_4Cl and about 2 to 4% of NH_4Cl is added to Cr or Cr-Fe alloy. The heating temperature ranges from 950° C. to 1100° C. and the heating time is in the range from 5 to 10 hours.

A method wherein NH_4I is used as NH_4X has been developed by Diffusion Alloy Co. Ltd., England. About 0.3% of NH_4I is added to Cr or Cr-Fe alloy, in which case the heating temperature is in the range from 900° C. to 950° C. and heating temperature ranges from 5 to 10 hours.

A method wherein NH_4F is used as NH_4X has been developed by Office National d'Etudes et de Recherches Aeronautiques, France. About 10 to 20% of NH_4F is added to Cr or Cr-Fe alloy, in which case the heating temperature is from 980 to 1050° C. and the heating time is from 5 to 7 hours.

(2) Gas method

The gas method is a method wherein Cr or Cr-Fe alloy is caused to react with dry HCl at high temperature to produce $CrCl_2$ and a chromium diffusion layer is formed by bringing the vapor of $CrCl_2$ thus obtained into contact with a base alloy.

A method called "BDS method" has been developed as one of the gas methods, wherein $CrCl_2$ vapor generated is once absorbed in alumina or the like and the base alloy is embedded in alumina, in which $CrCl_2$ thus obtained has been absorbed, and then heated. The BDS method is the most practical method of the gas methods.

In the BDS method, Cr or Cr-Fe alloy is mixed with porous porcelain powder, alumina or the like, through which mixture dry HCl gas is passed at about 1,000° C. to generate $CrCl_2$. The porcelain powder, alumina or the like are saturated with thus generated $CrCl_2$ and a base alloy is embedded in the thus obtained powders, and heated at about 1,000° C. for several hours.

When the base alloy is subjected to the chromizing treatment as described above, sometimes the mechanical strength decreases to some extent. In such a case, the mechanical strength of the base alloy can be restored by reheating the alloy at a temperature somewhat higher than the chromizing temperature (for instance, at 1,170° C. for Inconel–700) for about 2 hours and cooling in air, and further reheating at a temperature somewhat lower than the chromizing temperature (for instance, at 820° C. for Inconel–700) for about 20 hours and cooling in air.

It is preferable to heat the said base alloy in a reducing or neutral atmosphere.

This invention is further described with reference to the following example which is illustrative but not limitative thereof.

EXAMPLE

In the following Table II, names and compositions of base alloys, and chromizing methods applied to the base alloys and the results obtained when the base alloys having Cr-layer thus formed are actually used for turbine blades are shown.

Furthermore, of chromizing methods,

P means the powder method, and
G means the gas method.

The conditions of treatments, conditions of the operation of turbine are given in detail as follows:

(1) Conditions of treatment in the powder method

A base alloy is embedded in a mixture of powders of alloy which is composed of 60% Cr and 40% Fe in weight of 10% of 30 to 40 mesh (Tyler sieve scale mesh), 20% of 40 to 60 mesh, 60% of 60 to 80 mesh and 10% of 80 to 120 mesh in size, fine alumina powder (about 30 to 60 mesh) in equal quantity of the alloy powder and NH_4Cl in the quantity of 3% of the alloy powder in weight, and then heated them in the hydrogen stream at the temperature and for the time shown in Table II.

(2) Gas method

Through a mixture consisting of a powdered Cr–Fe alloy of 60% Cr, and 40% Fe in weight of about 20 to 30 mesh in size and a fine alumina powder of about 0.2 to 0.6 inch in diameter in equal quantity, dry HCl is passed at 1,000° C. to convert Cr to $CrCl_2$ until alumina powder is saturated with thus generated $CrCl_2$. A base alloy is then embedded in the thus obtained powders and heated in the hydrogen stream at the temperature and for the time shown in Table II.

(3) The operating conditions for turbine

Combustion gas at 800° C. generated from combustion of C-class heavy oil with sulfur content of 3.5% (several mg. of sodium is also contained in 1 m.^{3} of combustion gas as Na_2O) is used for continuous running for 10,000 hours.

In the following Table II, by "excellent" is it meant that adhesion of scale and corrosion scarcely occurs; by "bad" is it meant that remarkable adhesion of scale and corrosion occurs, and by "fairly good" is it meant that a little adhesion of scale and corrosion occurs.

Mark * in the composition represents by-constituents which are not shown in Table I of standard compositions or that the analytical values of composition of alloys available on the market are slightly different from the corresponding standard composition.

TABLE II

Name of alloy	Constituent											Chromizing method	Temp. (° C.)	Time (hr.)	Thickness of the diffusion layer (μ)	Cr Concentration (percent)		Results
	C	Si	Mn	Cr	Ni	Co	Mo	Ti	Al	Fe	Other					In the diffusion layer	At the surface of layer	
Inconel-700 =	0.13	*0.3	*0.1	15	46	29	*3.0	*2.2	3.0	0.8		P	1,050	10	70	65	80	Excellent.
Inconel-700 =	0.08		0.6	14.5	47.6	28.3	3.2	2.5	2.3	0.92		G	1,000	5	60	70	84	Do.
Inconel-700 =	0.13	*0.3	*0.1	15	46	29	*3.0	*2.2	3.0	0.8		No chromizing						Bad.
Inconel-X	0.04	0.3	0.7	15	73			2.5	0.9	7.0	Nb: 0.9	P	1,050	10	35	34	50	Bad.
S-816	0.4	*0.7	*1.5	20	20.7	38	4.0			3.7	W: 7.0; Nb: 4.0	P	1,050	10	60	70	85	Excellent.
S-816 B	0.38	0.3	1.45	19.8	20.1	Bal	3.9				W: 4.1; Nb: 3.7; B: 0.12	G	1,000	5	55	75	89	Do.
Udimet-41	0.08			19.3	Bal	10.8	10.4	3.2	1.5			P	1,080	10	90	85	103	Do.
Udiment-500	0.10	0.67	0.59	17.5	Bal	16.5	4.0	3.0	2.75		B: 0.047	P	1,080	10	95	80	100	Do.
Udiment-520	0.03	0.55	0.60	19.3	Bal	11.8	5.6	2.7	2.1		W: 0.96; B: 0.046	G	1,000	5	58	74	87	Do
Udiment-600	0.83	0.72	0.66	19.7	Bal	17.6		2.7	3.9	2.6	B: 0.02	P	1,080	10	89	86	104	Do
Udiment-700	0.13	0.56	0.72	16.6	Bal	18.3	5.2	3.1	4.5	0.6	B: 0.08	P	1,080	10	100	80	98	Do
S-816	0.4	*0.7	*1.5	20	20.7	38	4.0			3.7	W: 7.0; Nb: 4.0	P	1,000	7	30	35	50	Fairly good.

We claim:

1. In a gas turbine, gas turbine blades having high resistance to heat and to corrosion under exposure to the hot products of combustion containing sulfur oxide and alkali metal compounds, aid turbine blade being an alloy selected from the group consisting of Inconel 700, S–816, S–816B, Udimet 41, Udimet 500, Udimet 520, Udimet 600 and Udimet 700, said blade having on its surface a chromium diffusion layer formed by chromizing treatment, said layer being from 40 to 150μ in thickness and having a chromium content of 40% by weight, the concentration of chromium in the surface of said layer being from 60 to 95% by weight.

References Cited

UNITED STATES PATENTS

2,875,090	2/1959	Galmiche	117—107.2
3,065,108	11/1962	Seelig et al.	117—107.2
3,240,572	3/1966	Faber	416—241 X
3,257,230	6/1966	Wachtell et al.	117—107.2
3,290,126	12/1966	Monson	117—102.2
3,293,030	12/1966	Child et al.	75—171

OTHER REFERENCES

Alloy Digest, Udimet 500, published by Engineering Alloys Digest, Inc., Upper Montclair, N.J., October 1956.

Alloy Digest, Udimet 600, published by Engineering Alloys Digest, Inc., Upper Montclair, N.J., October 1958.

Alloy Digest, Udimet 700, published by Engineering Alloys Digest, Inc., Upper Montclair, N.J., March 1959.

L. DEWAYNE RUTLEDGE, Primary Examiner

G. K. WHITE, Assistant Examiner

U.S. Cl. X.R.

148—31.5, 39