

June 7, 1966

R. J. QUIGG

3,254,994

ALLOYS HAVING IMPROVED STRESS RUPTURE PROPERTIES

Filed June 24, 1963

Fig. 1

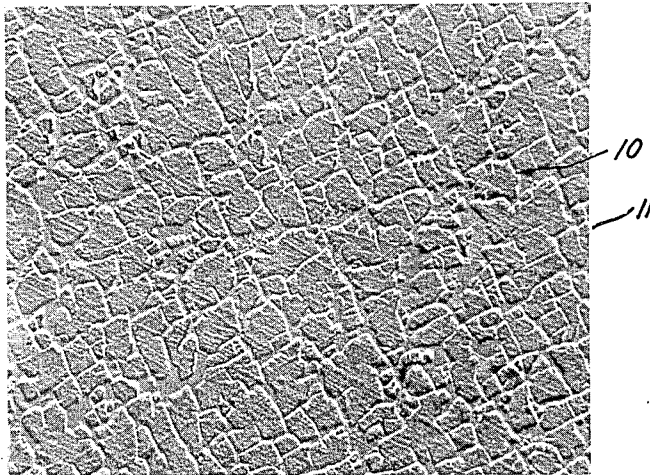
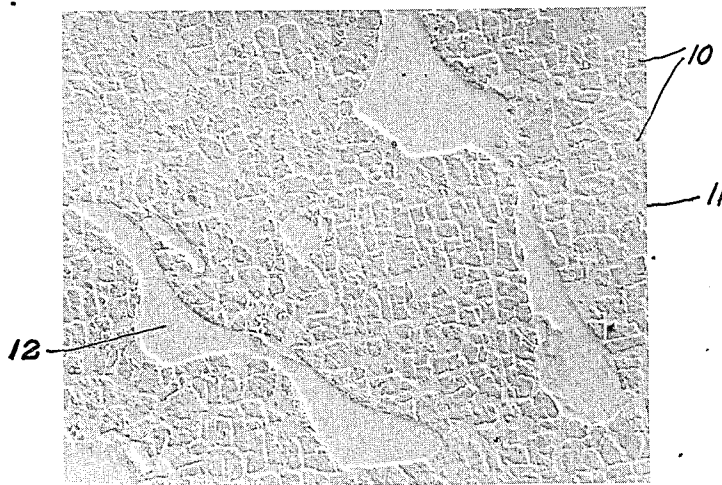


Fig. 2



Inventor
Richard J. Quigg

Hill, Sherman, Merani, Lask & Simpson
by *Httys*

1

2

3,254,994
ALLOYS HAVING IMPROVED STRESS
RUPTURE PROPERTIES

Richard J. Quigg, Euclid, Ohio, assignor to TRW Inc.,
a corporation of Ohio
Filed June 24, 1963, Ser. No. 289,915
8 Claims. (Cl. 75-171)

The present invention relates to improved "super-alloys" having improved stress rupture properties coupled with excellent tensile strength at high temperatures and substantial ductility for alloys of this type.

Many high temperatures applications involved in turbo superchargers, gas turbines, jet aircraft engines, and the like, require materials having the ability to operate under extreme conditions of temperature and stress. For such applications, the stress rupture properties of the alloy are critical, as they frequently spell the difference between acceptability and non-acceptability of a particular alloy regardless of its other physical properties.

Various nickel-chromium base alloys have been suggested for high temperature applications but many of these are deficient in various physical respects. In most cases, they are deficient in stress rupture properties at elevated temperatures. In some cases they are also unacceptable because of their extremely limited ductility, that is, they are quite brittle and difficult to machine.

Some nickel-chromium alloys of the prior art have been suggested for use in high temperature environments where stress rupture properties are important. While these alloys had reasonably high stress rupture properties, it was found that these properties were not always reproducible within the entire ranges set forth for such alloys. It has now been determined that consistently high stress rupture values can be obtained in nickel-chromium alloys by adjustment of the ranges of certain alloying ingredients, by taking steps to control the microstructure of the alloy, and by adjusting the total concentration of aluminum and titanium in the alloy to within carefully controlled limits.

It is known that significant amounts of tungsten are important in alloys of this type to serve as a hardener for the solid solutions existing in the alloy. The present invention goes one step further in determining the correct amount of tungsten which produces the desired hardening properties. The alloys of the present invention also provide a basis for adjusting the aluminum and titanium contents of the alloy such that excellent stress rupture properties, namely, a stress rupture life of at least 100 hours at 1800° F. at an applied stress of 24,000 pounds per square inch can be achieved. The present invention also provides a better understanding of the role of the carbides which should be present for best results, both with regard to their content and their morphology.

An object of the present invention, therefore, is to provide a nickel-chromium base alloy having excellent stress rupture properties at elevated temperatures.

Still another object of the invention is to provide a nickel base alloy containing significant amounts of chromium and tungsten with carefully controlled amounts of aluminum and titanium in order to provide the improved physical properties.

Still another object of the invention is to provide an improved nickel base alloy with particular types of carbide formation which are important in securing the extraordinary physical properties possessed by these alloys.

A further object of the invention is to provide a nickel base alloy of the type described with a chemistry such that it results in the production of dispersed, relatively fine particles of a particular intermetallic com-

pound in a matrix of a solid solution of tungsten and nickel.

The broad range of compositions which I have now found provides the desired physical properties (when the ranges are properly correlated) is given in the following table:

Table I

	Percent
Chromium -----	9-13
Cobalt -----	5-15
Tungsten -----	7-12
Aluminum -----	5.5-7
Titanium -----	0.5-2.0
Columbium, up to -----	2
Carbon -----	0.05-0.25
Boron -----	0.01-0.08
Zirconium -----	0.01-0.20
Nickel, substantially the balance.	

Not only should the chemistry of the alloy be within the range specified above, but it is important, for best results, that the aluminum plus titanium content be in the range from 6.5 to 9%.

Within this broader range, the best alloys which have been produced have analyses within the following narrower ranges:

Table II

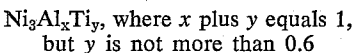
	Percent
Chromium -----	9.5-11.0
Cobalt -----	9.0-11.0
Tungsten -----	8.5-9.5
Aluminum -----	6.0-6.8
Titanium -----	0.75-1.25
Columbium -----	1.2-1.8
Carbon -----	0.085-0.14
Boron -----	0.02-0.04
Zirconium -----	0.07-0.13
Nickel, substantially the balance.	

Of all of the alloys produced according to the present invention, the following specific alloy appears to have the best overall properties:

Table III

	Percent
Chromium -----	10.3
Cobalt -----	10.0
Tungsten -----	9.0
Aluminum -----	6.3
Titanium -----	1.0
Columbium -----	1.5
Carbon -----	0.11
Boron -----	0.03
Zirconium -----	0.10
Nickel -----	Substantially the balance

There is more to the production of a suitable alloy in accordance with this invention than selecting the proper chemistry. It has been found, for example, that the sum of the aluminum and titanium contents must be controlled to the range of 6.5 to 9%, or preferably in the range of 7.25 to 8.25% if the proper microstructure and properties are to be achieved. It is believed that the improved properties of the new alloys are contributable, at least in part, to the production of an intermetallic compound having the following formula:



This intermetallic compound is a face centered cubic structure which constitutes the gamma-prime phase of the nickel-aluminum phase diagram. When too much titanium plus aluminum is present, and insufficient nickel is present to provide the intermediate compound desig-

nated above, the alloy in its as cast condition evidences spherulites of the primary gamma-prime phase which endows the resulting alloy with a brittle structure. Even when the correct range of aluminum plus titanium content is observed, it is important that the titanium concentration not exceed 60% of the total aluminum plus titanium on a molar basis, as otherwise needle-like particles are produced in the microstructure which detract from the physical properties.

It is also important that the nickel-aluminum-titanium phase exist in a properly strengthened solid solution matrix. This strengthening is provided primarily by the relatively high tungsten content of the new alloys although some contribution is made in this regard by the presence of the columbium and to some extent by the cobalt present.

As previously indicated, the extent and the nature of carbide reactions is also of substantial importance in securing the results. The carbide formers present in the composition are essentially the chromium, the columbium, the titanium, and the tungsten. The presence of boron and zirconium influence the production of the proper type of carbide formation which avoids the plate-like structure characteristic of many carbides and provides fine discrete particles of a variety of carbides. Specifically, it has been found that an amount of carbon is necessary to form three different types of carbide systems in the alloy, the first consisting of a mixed carbide of titanium and columbium (TiCb) C, a carbide having the empirical formula $M_{23}C_6$ where M is primarily chromium, and the carbide M'_6C where M' is a combination of tungsten and cobalt. All of these carbides have been identified in the alloy of the present invention by electrolytic digestion followed by X-ray diffraction analysis.

The microstructure of the alloys of the present invention is shown in FIGURES 1 and 2 of the drawings which are actual electron photomicrographs of the new material in the as cast condition, at magnifications of 6,000 times. From these two photomicrographs, it will be seen that the intermetallic compound exists as widely dispersed, symmetrical fine particles 10 of the intermetallic in a nickel-tungsten solid solution 11. The fine particles 10 of the intermetallic compound are usually somewhat square and average about 1 micron across. The micrograph of FIGURE 2 indicates a typical carbide formation 12 in the as cast structure of the alloy.

The alloys of the present invention all meet a minimum stress rupture life of 100 hours at 1800° F. at a stress of 24,000 pounds per square inch. The stress rupture tests were conducted on standard lever arm Arcweld creep testing units controlled to plus or minus 3° F.

The presence of columbium is particularly important for stress rupture life. The first 0.5% of this element seems to be the most important. For example, an alloy of the type described with no columbium had a stress rupture value of 21,000 p.s.i., with a columbium content of 0.59% the same alloy had a value of 24,000 p.s.i., at a Cb content of 1.2-1.8%, the alloy had a value of 25,000 p.s.i.

Typical stress rupture properties at other temperatures are given in the following table:

Table IV

Temp., ° F.:	Stress at 100 hr. life, p.s.i.
1200	119,000
1300	107,000
1400	90,000
1500	74,000
1600	57,000
1700	39,000
1750	33,000
1800	25,000
1850	21,000
1900	16,000

Some typical tensile properties for a composition given in Table III are reproduced below:

Table V

Temp. ° F.:	Ultimate strength, (kp.s.i.)
75	130.5
1200	127.1
1300	129.2
1400	131.8
1500	113.6
1600	97.0
1700	74.6
1800	53.0
1900	38.5
2000	21.5

The ductility of the alloys is quite good considering the strength properties. The alloys evidence a minimum elongation of about 4% at room temperature and usually 5 to 6%. Even at temperatures of 1200 to 1600° F., and at slow stress rates, the elongation is still on the order of 2%.

The oxidation resistance of the new material at 2,000° F. is very good. Heating of the alloys in air to 2,100° F. and holding for up to 50 hours results in a weight gain of less than 1.5 milligrams per square centimeter.

The thermal fatigue resistance is also very good. Utilizing a cycle of 15 seconds at heat and 15 seconds of air blast with no externally applied load, the following results have been obtained.

Table VI

Temp. ° F.:	Cycles to first crack
2000 (no cracks, discontinued)	6000
2000	4300
2000	5900
2150	2400
2150	1700

The alloys of the present invention should be vacuum cast and cooled at a slow cooling rate.

From the foregoing, it will be understood that the alloys of the present invention have improved stress rupture properties at high temperatures making them ideally suited for the manufacture of jet engine parts and the like. It should also be evident that various modifications can be made in the details of the present invention without departing from the scope of the invention.

I claim as my invention:

1. An alloy having improved stress rupture properties at high temperatures and consisting essentially of the following analysis:

	Percent
Chromium	9-13
Cobalt	5-15
Tungsten	7-12
Aluminum	5.5-7
Titanium	0.5-2.0
Columbium, up to	2
Carbon	0.05-0.25
Boron	0.01-0.08
Zirconium	0.01-0.20
Nickel	Substantially the balance

said alloy having an aluminum plus titanium content of from 6.5 to 9% and having sufficient nickel present to provide the compound $Ni_3Al_xTi_y$ where x plus y equals 1, but y is not greater than 0.6, said alloy in the as cast condition having a stress rupture life of at least 100 hours at 1800° F. at an applied stress of 24,000 p.s.i.

5

2. The alloy of claim 1 in which the microstructure of the alloy includes dispersed relatively symmetrical fine particles of said $\text{Ni}_3\text{Al}_x\text{Ti}_y$ in a matrix of a solid solution of tungsten and nickel.

3. An alloy having improved stress rupture properties at high temperatures consisting essentially of the following analysis:

	Percent
Chromium	9.5-11.0
Cobalt	9.0-11.0
Tungsten	8.5-9.5
Aluminum	6.0-6.8
Titanium	0.75-1.25
Columbium	1.2-1.8
Carbon	0.085-0.14
Boron	0.02-0.04
Zirconium	0.07-0.13
Nickel	Substantially the balance

said alloy having an aluminum plus titanium content of from 7.25 to 8.25% and having sufficient nickel present to provide the compound $\text{Ni}_3\text{Al}_x\text{Ti}_y$ where x plus y equals 1, but y is not greater than 0.6, said alloy in the as cast condition having a stress rupture life of at least 100 hours at 1800° F. at an applied stress of 24,000 p.s.i.

4. The alloy of claim 3 in which the microstructure of the alloy in the as cast condition includes dispersed, relatively symmetrical fine particles of said $\text{Ni}_3\text{Al}_x\text{Ti}_y$ in a matrix of a solid solution of tungsten in nickel.

5. An alloy having improved stress rupture properties at high temperatures and consisting essentially of the following analysis:

	Percent
Chromium	9-13
Cobalt	5-15
Tungsten	7-12
Aluminum	5.5-7
Titanium	0.5-2.0
Columbium, up to	2
Carbon	0.05-0.25
Boron	0.01-0.08
Zirconium	0.01-0.20
Nickel	Substantially the balance

said alloy having an aluminum plus titanium content of from 6.5 to 9% and having sufficient nickel present to provide the compound $\text{Ni}_3\text{Al}_x\text{Ti}_y$ where x plus y equals 1, but y is not greater than 0.6, said alloy in the as cast condition having a stress rupture life of at least 100 hours at 1800° F. at an applied stress of 24,000 p.s.i., and an elongation of at least 4% without fracture at room temperature.

6. An alloy having improved stress rupture properties at high temperatures and consisting essentially of the following analysis:

6

	Percent
Chromium	10.3
Cobalt	10.0
Tungsten	9.0
Aluminum	6.3
Titanium	1.0
Columbium	1.5
Carbon	0.11
Boron	0.03
Zirconium	0.10
Nickel	Substantially the balance

said alloy in the as cast condition having a stress rupture life of at least 100 hours at 1800° F. and at an applied stress of 24,000 p.s.i.

7. An alloy having improved stress rupture properties at high temperature and consisting essentially of the following analysis:

	Percent
Chromium	9.5-11.0
Cobalt	9.0-11.0
Tungsten	8.5-9.5
Aluminum	6.0-6.8
Titanium	0.75-1.25
Columbium	1.2-1.8
Carbon	0.085-0.14
Boron	0.02-0.04
Zirconium	0.07-0.13
Nickel	Substantially the balance

said alloy having an aluminum plus titanium content of from 7.25 to 8.25% and having sufficient nickel present to provide the compound $\text{Ni}_3\text{Al}_x\text{Ti}_y$ where x plus y equals 1, but y is not greater than 0.6, said alloy in the as cast condition having dispersed, relatively symmetrical particles of said $\text{Ni}_3\text{Al}_x\text{Ti}_y$ in a matrix of a solid solution of tungsten in nickel, said alloy being capable of an elongation of at least 4% without fracture at room temperature.

8. The alloy of claim 3 having a microstructure as shown in the photomicrograph of FIGURE 1.

References Cited by the Examiner

UNITED STATES PATENTS

2,977,222 3/1961 Bieber 75-171

FOREIGN PATENTS

226,003 5/1958 Australia.
227,261 12/1959 Australia.
1,224,480 2/1960 France.
1,264,111 5/1961 France.

OTHER REFERENCES

Nordheim et al.: "Aging Characteristics of Nickel-Chromium Alloys Hardened with Titanium and Aluminum," February 1954, Journal of Metals, pp. 211-218.

DAVID L. RECK, *Primary Examiner*.

WINSTON A. DOUGLAS, *Examiner*.

C. M. SCHUTZMAN, *Assistant Examiner*.