

July 24, 1973

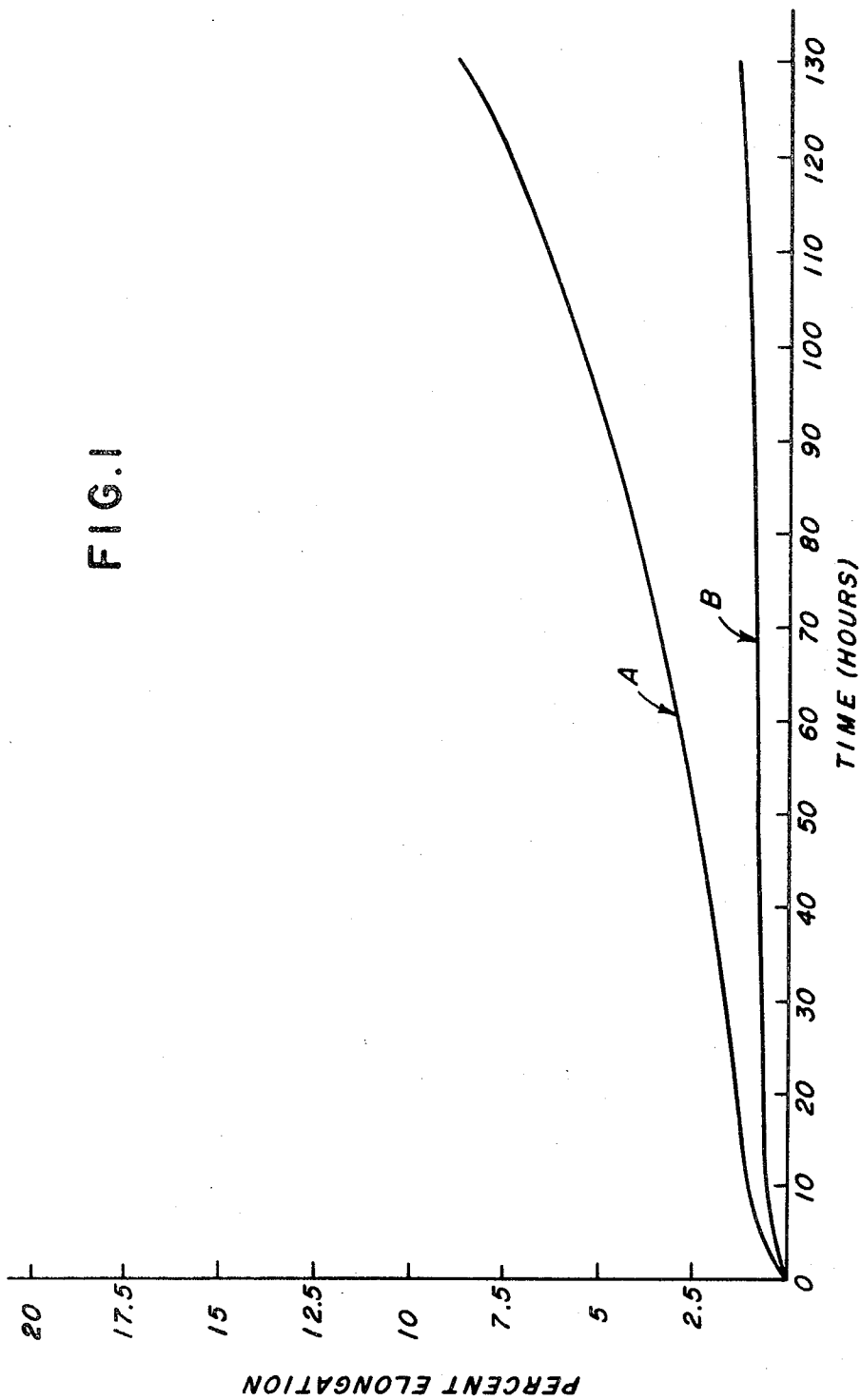
W. J. BOESCH
NICKEL BASE ALLOY

3,748,192

Filed Feb. 1, 1972

3 Sheets-Sheet 1

FIG. 1



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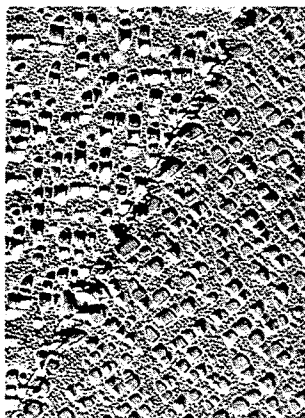


FIG. 2



FIG. 3

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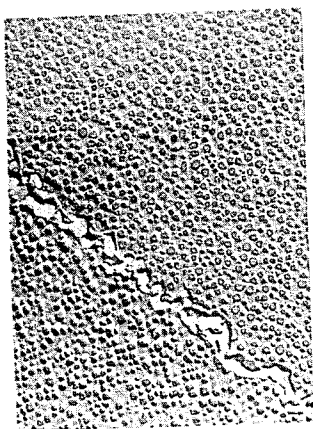


FIG. 4

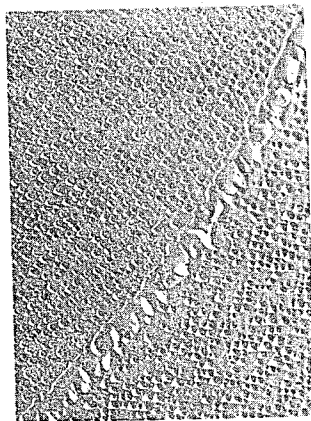


FIG. 5

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2

3,748,192

NICKEL BASE ALLOY

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Continuation-in-part of application Ser. No. 42,412, June 1, 1970. This application Feb. 1, 1972, Ser. No. 222,504 The portion of the term of the patent subsequent to Apr. 4, 1989, has been disclaimed

Int. Cl. C22c 19/00

U.S. Cl. 148—32.5

10 Claims

ABSTRACT OF THE DISCLOSURE

A nickel base alloy consisting essentially of, in weight percent, up to 0.18% carbon, from 14.2 to 20% cobalt, from 13.7 to 16% chromium, from 3.8 to 5.5% molybdenum, from 2.75 to 3.75% titanium, from 3.75 to 4.75% aluminum, up to 4% iron, from 0.005 to 0.035% boron, up to 0.5% zirconium, up to 0.5% hafnium, up to 0.75% columbium, up to 0.5% rhenium, up to 0.75% tantalum, up to 1.0% manganese, up to 3.0% tungsten, up to 0.5% rare earth metals, balance essentially nickel with incidental impurities, and having an average grain size coarser than ASTM No. 4 and a morphology comprised of gamma prime particles which consist essentially of randomly dispersed irregularly shaped particles less than about 0.35 micron in diameter.

This application is a continuation-in-part of copending application Ser. No. 42,412 filed June 1, 1970, now Pat. No. 3,653,987.

The present invention relates to a nickel base alloy and more particularly to a nickel base alloy with improved high temperature properties.

Nickel base alloys have been known and used at elevated temperatures for quite some time. In particular, it is known that nickel base alloys can be markedly improved by employing a precipitation hardening mechanism so that their useful life is not only prolonged, but so the alloy can be used at higher temperatures. Perhaps the best known strengthening precipitate in nickel base alloys is the intermetallic compound known as "gamma prime." Gamma prime is believed to have the general composition M_3 (Al, Ti). As used herein, the "M" portion of the gamma prime composition is regarded as consisting mainly of nickel with some substitution of chromium and molybdenum and is considered to have the approximate atomic proportions, 95 nickel, 3 chromium, and 2 molybdenum.

I have found that the already good high temperature properties of nickel base alloys consisting essentially of, in weight percent, up to 0.18% carbon, from 14.2 to 20% cobalt, from 13.7 to 16% chromium, from 3.8 to 5.5% molybdenum, from 2.75 to 3.75% titanium, from 3.75 to 4.75% aluminum, up to 4% iron, from 0.005 to 0.035% boron, up to 0.5% zirconium, up to 0.5% hafnium, up to 0.75% columbium, up to 0.5% rhenium, up to 0.75% tantalum, up to 1.0% manganese, up to 3.0% tungsten, up to 0.5% rare earth metals; e.g. cerium and/or yttrium and/or lanthanum, balance essentially nickel with incidental impurities, can be materially improved if the alloys are treated to develop a particular gamma prime morphology and an average grain size coarser than ASTM No. 4. The particular morphology is comprised of gamma prime particles which consist essentially of randomly dispersed irregularly shaped particles less than about 0.35 micron in diameter.

In the past nickel base alloys having the composition described in the preceding paragraph often had a morphology comprised of oriented cubic gamma prime particles about 0.5 micron per side. These cubic gamma prime particles adversely affected the alloy's high tem-

perature properties as they tended to agglomerate during prolonged elevated temperature service and form rod-like particles in certain crystallographic planes along which slip rapidly occurs. Formation of these cubic gamma prime particles was due to the high temperatures employed during the second stage of the prior art heat treatments, during which gamma prime precipitation is initiated. The heat treatment described herein avoids the formation of cubic gamma prime by employing a maximum second stage temperature of 1850° F. A particular prior art heat treatment used a second stage temperature of 1975° F. It comprised the steps of: (1) heating at a temperature of 2135° F. for 4 hours and cooling; (2) heating at a temperature of 1975° F. for 4 hours and cooling; (3) heating at a temperature of 1550° F. for 24 hours and cooling; and (4) heating at a temperature of 1400° F. for 16 hours and cooling.

It is accordingly an object of this invention to provide a nickel base alloy with improved high temperature properties.

The foregoing and other objects of this invention will be best understood from the following description, reference being had to the accompanying drawing and photomicrographs wherein:

FIG. 1 is a plot of percent elongation versus time for two samples of a nickel base alloy which underwent different second stage heat treatments at 1975° F. for 4 hours and at 1700° F. for 8 hours;

FIG. 2 is a photomicrograph at 7200X of a nickel base alloy which underwent a second stage heat treatment at 1975° F. for 4 hours,

FIG. 3 is a photomicrograph at 7200X of a nickel base alloy which underwent a second stage heat treatment at 1700° F. for 8 hours;

FIG. 4 is a photomicrograph at 7200X of a nickel base alloy which underwent a second stage heat treatment at 1750° F. for 8 hours; and

FIG. 5 is a photomicrograph at 7200X of a nickel base alloy which underwent a second stage heat treatment at 1750° F. for 24 hours.

The alloys of the present invention have a composition consisting essentially of, in weight percent, up to 0.18% carbon, from 14.2 to 20% cobalt, from 13.7 to 16% chromium, from 3.8 to 5.5% molybdenum, from 2.75 to 3.75% titanium, from 3.75 to 4.75% aluminum, up to 4% iron, from 0.005 to 0.035% boron, up to 0.5% zirconium, up to 0.5% hafnium, up to 0.75% columbium, up to 0.5% rhenium, up to 0.75% tantalum up to 1.0% manganese, up to 3% tungsten, up to 0.5% rare earth metals, e.g., cerium and/or yttrium and/or lanthanum, balance essentially nickel with incidental impurities and a morphology comprised of gamma prime particles which consist essentially of randomly dispersed irregularly shaped particles less than about 0.35 micron, preferably 0.25 micron, in diameter. In addition the alloys can have other precipitates such as an $M_{23}C_6$ precipitate (M is generally chromium) which improves grain boundary ductility. Alloys are respectively considered to be within the scope of the invention and within the preferred embodiment of the invention even if they have occasional gamma prime particles (gamma prime particles which constitute less than five volume percent) in excess of 0.35 and 0.25 micron. In most instances, the gamma prime particles of the preferred embodiment range between 0.1 and 0.25 micron. The average grain size of the alloys is coarser than ASTM No. 4 and generally coarser than ASTM No. 3. As a general rule, coarse grain alloys have a greater strength at elevated temperatures; e.g. 1800° F. than do fine grain alloys.

To illustrate the nickel base alloy of the present invention, reference is directed to Table I which describes

specific ranges for nickel base alloys of the present invention.

TABLE I

Element:	Specific range (weight percent)		
	I	II	III
C-----	0.03-0.10	0.03-0.09	0.05-0.09
Co-----	17-20	16-18	14.25-16.25
Cr-----	14-16	14-16	14-15.25
Mo-----	4.5-5.5	4.5-5.5	3.9-4.9
Ti-----	2.75-3.75	2.35-3.65	3.0-3.7
Al-----	3.75-4.75	3.85-4.15	4-4.6
Fe-----	1.4	1.0.5	1.0.5
B-----	0.025-0.035	0.02-0.03	0.012-0.02
Zr-----	1.0.06	1.0.10	1.0.06
Mn-----	1.0.15	1.0.15	1.0.15
Ni-----	Balance	Balance	Balance

¹ Maximum.

A heat treatment for producing the particular grain size and morphology for the alloy of the present invention is described in the following paragraphs. It is a two and preferably three stage treatment; i.e. two or three heatings each followed by cooling.

The first stage of the heat treatment is designed to put sufficient coarse gamma prime particles which form during alloy production, e.g., during casting and working, into solution. Particles begin to go into solution at a temperature of about 2000° F. (give or take about 25° F., depending upon furnace accuracy) and solutioning is complete at about 2125° F. The particular solutioning temperature employed depends upon the ultimate use for the alloys. For alloys to be used at service temperatures in excess of 1800° F. it is preferable to use a solutioning temperature in excess of 2125° F. as it is desirable to put substantially all the coarse gamma prime particles which do not contribute strength to the alloy into solution. For alloys to be used at a service temperature below 1800° F., e.g. 1400° F., it is sometimes desirable to use a partial solutioning temperature of from 2000° F. to 2125° F. as the lower solutioning temperature will produce an alloy with a finer grain size. In any event, the first stage must be controlled so as to produce an alloy having an average grain size coarser than ASTM No. 4.

The second stage of the heat treatment is designed to initiate the formation of and form the randomly dispersed irregularly shaped fine gamma prime particles and to form a grain boundary precipitate, $M_{23}C_6$ (M is generally chromium) which improves grain boundary ductility. It is a time and temperature dependent process. At lower temperatures longer times are involved and at higher temperatures shorter times. A lower temperature limit of 1500° F. is imposed as it would be commercially impractical to operate at lower temperatures when the time involved is considered. An upper temperature limit of 1850° F. is imposed as $M_{23}C_6$ begins to go into solution at this temperature and since the formation of cubic gamma prime particles is accelerated at higher temperatures. A preferred temperature range is from about 1600° F. to about 1800° F. No range can be placed upon the time period as it depends upon too many variables such as the temperature and thickness of the material being treated.

The third stage of the heat treatment is preferable and not necessary. It is designed to precipitate additional $M_{23}C_6$ particles and is performed at a temperature low enough to preclude detrimental gamma prime particle growth. The temperature range for this stage of the heat treatment is 1350-1450° F.

The following examples are illustrative of the invention.

Several samples (Samples A, B, C and D) were melted, heat treated, and photomicrographed. In addition, Samples A and B were tested for creep at 1800° F. under a stress of 16 k.s.i. The samples had a composition consisting essentially of, in weight percent, 0.88% carbon, 16.9% cobalt, 15.1% chromium, 5.0% molybdenum, 3.47% titanium, 4.0% aluminum, 0.027% boron, balance essen-

tially nickel with incidental impurities. Sample A was given a heat treatment which comprised the steps of: (1) heating at a temperature of 2135° F. for 4 hours and air cooling; (2) heating at a temperature of 1975° F. for 4 hours and air cooling; (3) heating at a temperature of 1550° F. for 24 hours and air cooling; and (4) heating at a temperature of 1400° F. for 16 hours and air cooling. Sample B was given a heat treatment which comprised the steps of: (1) heating at a temperature of 2135° F. for 4 hours and air cooling; (2) heating at a temperature of 1700° F. for 8 hours and air cooling; and (3) heating at a temperature of 1400° F. for 16 hours and air cooling. Sample C was heat treated in the same manner as Sample B with the exception that the intermediate heating, i.e., the second stage heating, was at a temperature of 1750° F. Sample D was heat treated in the same manner as Sample B with the exception that the intermediate heating was at a temperature of 1750° F. for a 24-hour period.

The results of the creep tests for Samples A and B are shown in FIG. 1 wherein percent elongation is plotted versus time. A study of the results reveals that Sample B, which was given a heat treatment within the scope of this invention, had a lower second stage creep rate, i.e., the substantially constant creep rate commonly used for design purposes, than did Sample A which was given a conventional prior art heat treatment. Samples B and A had respective second stage creep rates of 0.006%/hour and 0.04%/hour. A part with a specification of 1% maximum creep at 1800° F. under a stress of 16 k.s.i. would have a useful life of about 10 hours with the conventional heat treatment given Sample A and a useful life of about 110 hours with the improved heat treatment given Sample B. Sample B, therefore, shows an 11 to 1 improvement over Sample A.

Photomicrographs at 7200 \times show the different morphologies of Samples A and B. FIG. 2, which is the photomicrograph of Sample A, is comprised of oriented cubic gamma prime particles about 0.5 micron per side (some of the gamma prime particles have a triangular or trapezoidal appearance due to the grain orientation and surface intersection) and FIG. 3, which is the photomicrograph of Sample B, is comprised of gamma prime particles which consist essentially of randomly dispersed irregularly shaped gamma prime particles which are less than about 0.25 micron in diameter. The photomicrographs clearly show that the lower second stage creep rate of Sample B is due to its particular morphology which results from the particular heat treatment of this invention.

The photomicrographs of FIGS. 4 and 5 show how the time and temperature of the second stage of the heat treatment of this invention affects the size of the gamma prime particles. Sample C, which was treated in the same manner as Sample B with the exception that the intermediate heating was at a temperature of 1750° F. instead of 1700° F., had gamma prime particles larger in size than the gamma prime particles of Sample B and Sample D which was treated in the same manner as Sample C with the exception that the intermediate heating was for 24 hours instead of 8 hours, had gamma prime particles larger in size than the gamma prime particles of Sample C. Samples C and D are respectively shown at 7200 \times in FIGS. 4 and 5.

Several additional samples (Samples E, F, G and H) were melted, heat treated, and stress rupture tested at 1650° F. under a stress of 35 k.s.i. The samples had a composition consisting essentially of, in weight percent, 0.05% carbon, 17.5% cobalt, 14.5% chromium, 4.5% molybdenum, 3.19% titanium, 4.20% aluminum, 0.028% boron, balance essentially nickel with incidental impurities. Sample E was given a heat treatment which comprised the steps of: (1) heating at a temperature of 2135° F. for 4 hours and air cooling; (2) heating at a temperature of 1975° F. for 4 hours and air cooling; (3) heating at a temperature of 1550° F. for 24 hours and air cooling; and (4) heating at a temperature of 1400° F. for 16 hours

and air cooling. Sample F was given a heat treatment which comprised the steps of: (1) heating at a temperature of 2135° F. for 4 hours and air cooling; (2) heating at a temperature of 1700° F. for 4 hours and air cooling; and (3) heating at a temperature of 1400° F. for 16 hours and air cooling. Samples G and H were heat treated in the same manner as Sample F with the exception that the intermediate heatings were for respective periods of 8 and 16 hours.

The results of the stress rupture tests for Samples E, F, G and H are reproduced below in Table II.

TABLE II

Sample:	(Life hrs.) ¹
E -----	110.5
F -----	115.1
G -----	141.7
H -----	126.2

¹ Average of two specimens.

The data in Table II reveals that Samples F, G and H, which were given heat treatments within the scope of this invention, had a longer life than did Sample E which was given a conventional prior art heat treatment. Sample G had an average life of 141.7 hours at 1650° F. under a stress of 35 k.s.i. with the heat treatment of this invention in comparison to an average life of 110.5 hours for Sample E which had a prior art heat treatment.

It will be apparent to those skilled in the art that the novel principles of the invention disclosed herein in connection with specific examples thereof will suggest various other modifications and applications of the same. It is accordingly desired that in construing the breadth of the appended claims they shall not be limited to the specific examples of the invention described herein.

I claim:

1. A nickel base alloy having improved high temperature properties; said alloy consisting essentially of, in weight percent, up to 0.18% carbon, from 14.2 to 20% cobalt, from 13.7 to 16% chromium, from 3.8 to 5.5% molybdenum, from 2.75 to 3.75% titanium, from 3.75 to 4.75% aluminum, up to 4% iron, from 0.005 to 0.035% boron, up to 0.5% zirconium, up to 0.5% hafnium, up to 0.75% columbium, up to 0.5% rhenium, up to 0.75% tantalum, up to 1.0% manganese, up to 3% tungsten, up to 0.5% rare earth metals, balance essentially nickel with incidental impurities; said alloy having an average grain size coarser than ASTM No. 4 and a morphology comprised of gamma prime particles which consist essentially of randomly dispersed irregularly shaped particles less than about 0.35 micron in diameter.

2. A nickel base alloy according to claim 1 wherein said randomly dispersed irregularly shaped gamma prime particles are less than about 0.25 micron in diameter.

3. A nickel base alloy according to claim 1 wherein said randomly dispersed irregularly shaped gamma prime particles are from about 0.1 to 0.25 micron in diameter.

4. A nickel base alloy according to claim 1 which consists essentially of, in weight percent, from 0.03 to 0.10% carbon, from 17 to 20% cobalt, from 14 to 16% chromium; from 4.5 to 5.5% molybdenum, from 2.75 to 3.75% titanium, from 3.75 to 4.75% aluminum, up to 4% iron, from 0.025 to 0.035% boron, up to 0.06% zirconium, up to 0.15% manganese, balance nickel with incidental impurities.

5. A nickel base alloy according to claim 4 wherein said randomly dispersed irregularly shaped gamma prime particles are less than about 0.25 micron in diameter.

6. A nickel base alloy according to claim 1 which consists essentially of, in weight percent, from 0.03 to 0.09% carbon, from 16 to 18% cobalt, from 14 to 16% chromium, from 4.5 to 5.5% molybdenum, from 3.35 to 3.65% titanium, from 3.85 to 4.15% aluminum, up to 0.5% maximum iron, from 0.02 to 0.03% boron, up to 0.10% zirconium, up to 0.15% manganese, balance nickel with incidental impurities.

7. A nickel base alloy according to claim 6 wherein said randomly dispersed irregularly shaped gamma prime particles are less than about 0.25 micron in diameter.

8. A nickel base alloy according to claim 1 which consists essentially of, in weight percent, from 0.05 to 0.09% carbon, from 14.25 to 16.25% cobalt, from 14 to 15.25% chromium, from 3.9 to 4.9% molybdenum, from 3.0 to 3.7% titanium, from 4 to 4.6% aluminum, up to 0.5% iron, from 0.012 to 0.02% boron, up to 0.06% zirconium up to 0.15% manganese, balance nickel with incidental impurities.

9. A nickel base alloy according to claim 8 wherein said randomly dispersed irregularly shaped gamma prime particles are less than about 0.25 micron in diameter.

10. A nickel base alloy according to claim 2 wherein said average grain size is coarser than ASTM No. 3.

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RICHARD O. DEAN, Primary Examiner

U.S. Cl. X.R.

50 75—171; 148—162