

Oct. 9, 1951

C. G. BIEBER ET AL

2,570,193

HIGH-TEMPERATURE ALLOYS AND ARTICLES

Filed April 9, 1946

4 Sheets-Sheet 1

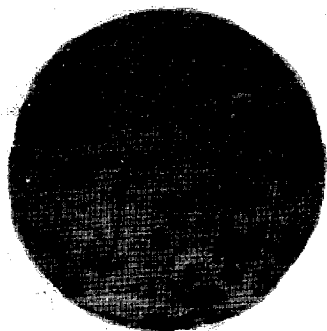


FIG. 1.

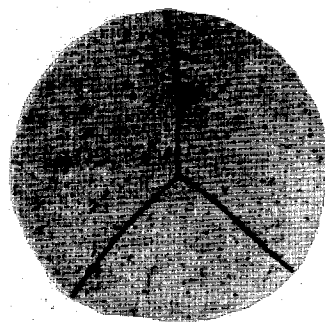


FIG. 2.

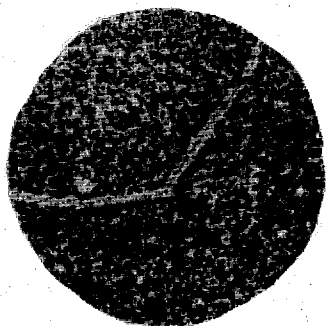


FIG. 3.

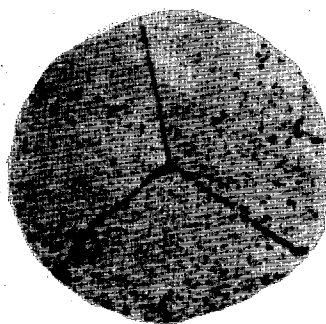


FIG. 4.

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4 Sheets-Sheet 2

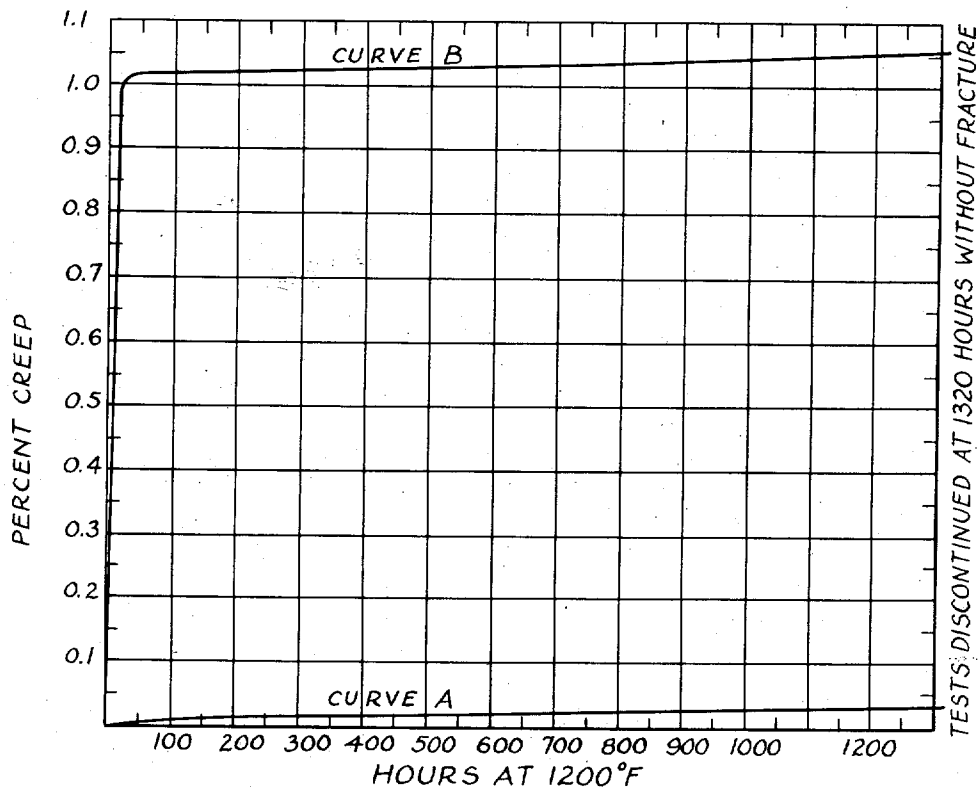


FIG.5.

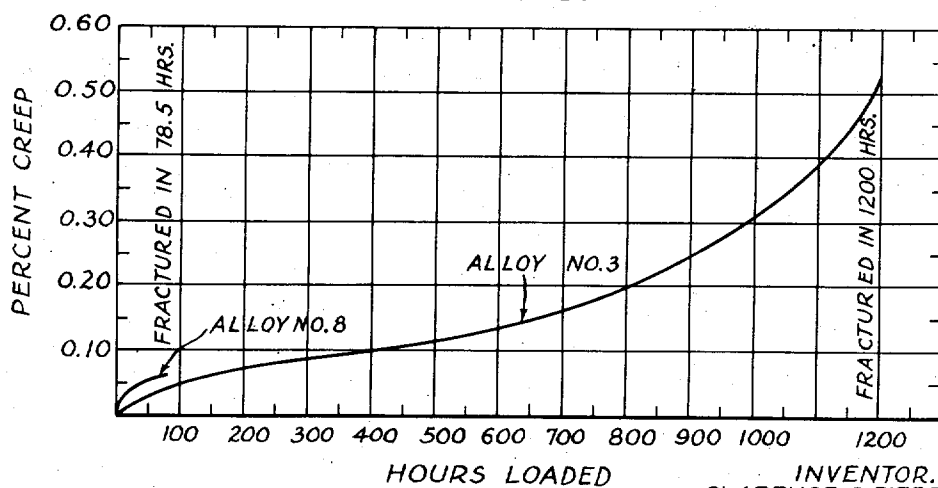


FIG.8.

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HIGH-TEMPERATURE ALLOYS AND ARTICLES

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4 Sheets-Sheet 3

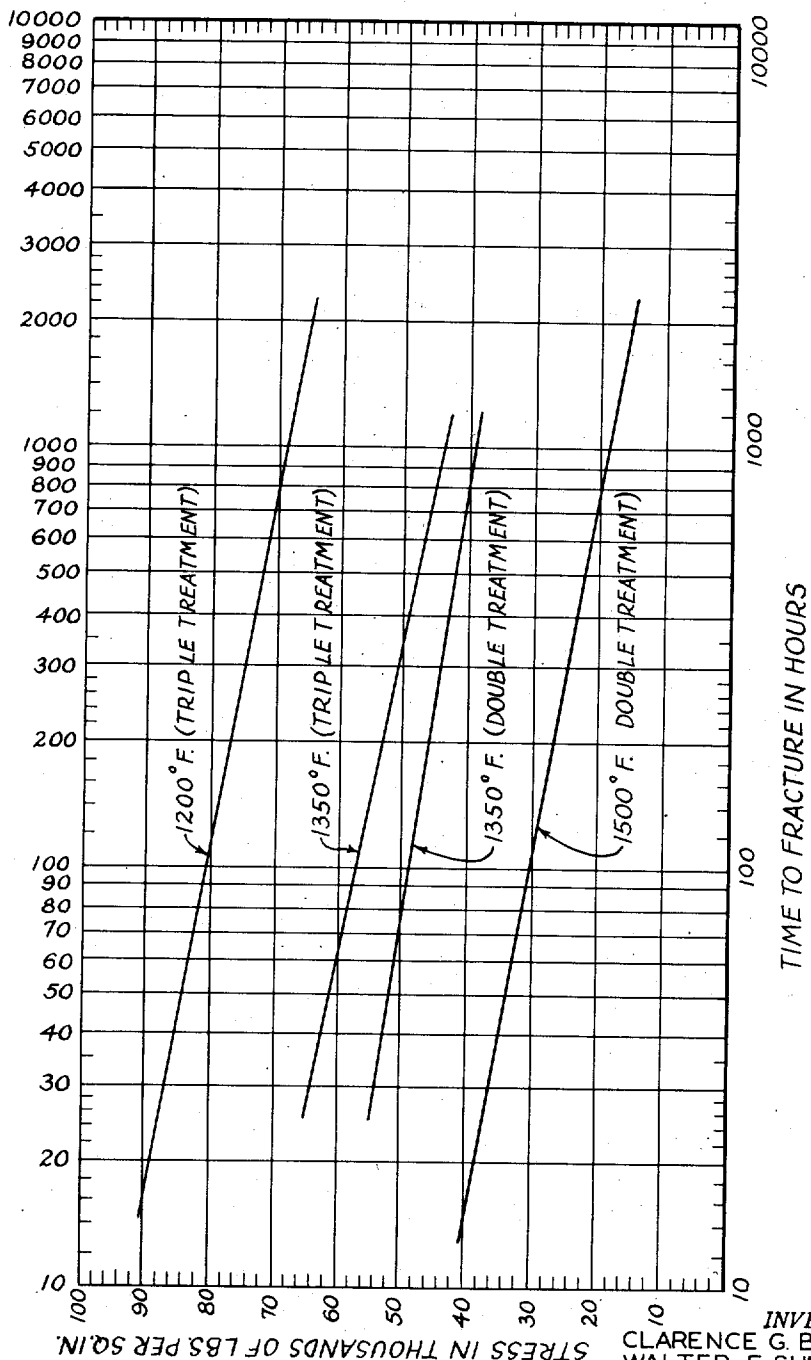


FIG. 6.

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4 Sheets-Sheet 4

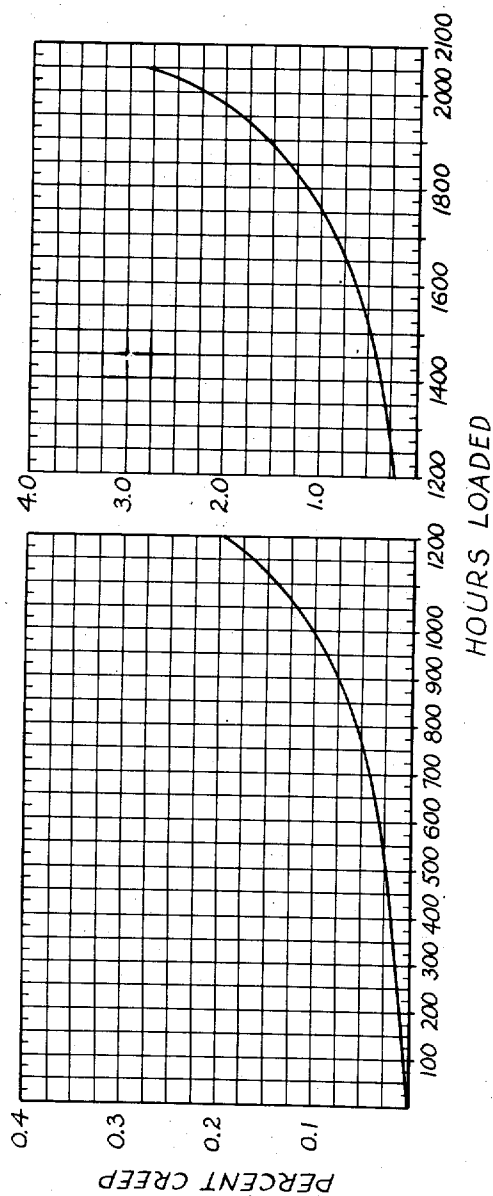


FIG. 7.

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HIGH-TEMPERATURE ALLOYS AND ARTICLES

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Application April 9, 1946, Serial No. 666,748

10 Claims. (Cl. 75-171)

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The present invention relates to alloys particularly suitable for use under load at elevated temperatures, and articles made thereof.

In recent years the art has been earnestly endeavoring to obtain creep resistant alloys having heat resistance and high strength at elevated temperatures, particularly lower creep rates, longer time to rupture under a given stress at given elevated temperatures, i. e., longer fracture life, and/or the ability to withstand higher stresses or loads at a given elevated temperature for a given fracture life, i. e., higher load-carrying capacity. Thus, a major difficulty in extending the use of gas turbines has been the unavailability of materials capable of withstanding high loads or stresses at high temperatures for long periods of time as well as withstanding heat, corrosion, distortion, growth, etc. For example, blades of gas and internal combustion turbines are desired which are capable of withstanding temperatures within the range of about 1200° F. to 1500° F. and even higher, particularly temperatures of 1350° F. and higher, for long intervals of time. The moving blades on the rotors must simultaneously withstand the high stresses set up by the revolving rotors which may operate at speeds from 30,000 to 50,000 revolutions per minute. At such high speeds, accurate dynamic balance of the rotating parts is essential throughout the life of the turbines. This required balance demands that the rotating parts maintain their shape, size and balance and that the parts be made of alloys which are highly resistant to heat, warping, distortion, growth and creep and are capable of withstanding high stresses at the elevated service temperatures for longer periods of time without fracturing or rupturing.

In determining the suitability of an alloy for the manufacture of gas turbine parts and other articles subjected to load at elevated temperatures, rupture or fracture tests are frequently resorted to. In such tests a number of specimens of the same alloy are loaded with stresses calculated to cause fracture within a period of time corresponding to the expected useful life of the part at the temperature at which the part is expected to operate. In the case of gas turbines for airplane superchargers, the expected useful life has been considered to be between 300 and 1000 hours. Other articles may require different lives varying from a short life of only a few hours to a long life of many thousand hours. In conducting rupture tests to determine the suitability of an alloy for gas turbines or other articles, the temperature of test is generally 1200° F., 1350° F. or 1500° F. By these tests the loads or stresses which will cause fracture within the desired time limits at the test temperatures are determined.

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Many alloys have been proposed for use at elevated temperatures, but the properties have not been as high as desired, particularly at temperatures of 1350° F. and higher. Furthermore, it has been found that the properties at elevated temperatures frequently varied considerably and could not be obtained consistently. It was also found that the proposed alloys often tended to be brittle and to lack ductility at the elevated service temperatures. The prior alloys also tended to contain seams, splits, and the like which resulted in a high number of rejections of the finished articles after fabrication or in premature failure in service when these defects were not detected during inspection. Although many attempts were made to provide alloys having more improved properties at elevated temperatures, none, as far as we are aware, was entirely satisfactory when carried into practice.

We have discovered that an improved combination of high temperature properties, including longer fracture life, can be obtained by employing nickel alloys containing a critical combination of chromium, aluminum, titanium, columbium and zirconium, and preferably also containing iron and magnesium.

It is among the objects of our invention to provide cast and wrought nickel alloys having improved properties at elevated temperatures; to provide nickel alloys having good hot malleability or hot working properties combined with improved creep resistance, i. e., improved fracture life, higher load-carrying capacity and/or lower creep rate; to provide improved heat resistant, age hardenable, wrought nickel alloys having enhanced properties under load or stress for longer intervals of time at elevated temperatures, particularly at temperatures of 1200° F. and higher; to provide improved age hardened nickel alloys exhibiting consistently outstanding properties at elevated temperatures, particularly at temperatures of 1350° F. to 1500° F. and higher; to provide age hardened nickel alloys having such improved high temperature properties that at 1200° F. they are capable of withstanding a load of about 60,000 pounds per square inch or more for at least 1000 hours, at 1350° F. they are capable of withstanding a load of about 40,000 pounds per square inch or more for at least 1000 hours, and at 1500° F. they are capable of withstanding a load of about 18,000 pounds per square inch or more for at least 1000 hours; to provide improved articles of manufacture, particularly wrought articles, subjected in use to stress at elevated temperatures made of the age hardened nickel alloys provided by the present invention; to provide improved age hardenable alloys having high mechanical properties; to provide an improved heat treatment, particularly a triple treatment,

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for improving the ductility and increasing the time to fracture at elevated temperatures of the nickel alloys contemplated by the present invention, etc.

Other objects and advantages of the invention will become apparent to those skilled in the art from the following description taken in conjunction with the accompanying drawings in which:

Figs. 1 to 4 are reproductions of photomicrographs taken at 1000 magnifications showing the structure of an alloy contemplated by the invention after various heat treatments;

Fig. 5 containing curves A and B shows the effect of holding time in one step of a triple heat treatment contemplated by the invention;

Fig. 6 depicts curves showing the properties of an alloy within the scope of the invention after various heat treatments;

Fig. 7 is a creep curve of an alloy contemplated by the invention under a load of 15,000 pounds per square inch at 1500° F.; and

Fig. 8 depicts a pair of creep curves comparing an alloy of the invention with another alloy having a composition not in accordance with the invention under a load of 60,000 pounds per square inch at 1200° F.

The present invention is based on the discovery made by us that nickel alloys having improved high temperature creep properties can be produced by incorporating in the composition controlled amounts of chromium, aluminum, titanium, columbium and zirconium in combination. The alloys preferably also contain iron which when present in amounts exceeding about 4% to 5% has been found by us to be decidedly beneficial and further to raise the high temperature properties in a marked manner. Silicon is also usually incorporated in the alloys. Optionally, molybdenum may also be present. In general, the alloys provided by the invention contain the aforementioned critical combination of essential elements and other elements within the following ranges:

Element:	Per cent
Chromium	10 to 35
Aluminum	0.1 to 8
Titanium	0.1 to 8
Columbium	0.1 to 8
Zirconium	0.002 to 2
Iron	0.1 to 25
Silicon	0.05 to 8
Molybdenum	0 to 5
Nickel (+cobalt)	Balance

The sum of the aluminum, silicon and titanium contents should be at least about 2% and not over about 10%. The foregoing ranges are particularly suitable for castings. The aluminum and titanium contents in cast alloys preferably do not exceed about 5% of either. When the alloys are to be worked into wrought products, the composition should be maintained within the following ranges:

Element:	Per cent
Chromium	10 to 25
Aluminum	0.2 to 1.5
Titanium	1.5 to 3
Columbium	0.1 to 3
Zirconium	0.002 to 0.2
Iron	0.1 to 20
Silicon	0.05 to 0.8
Molybdenum	0 to 1
Nickel (+cobalt)	Balance

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The sum of the aluminum, titanium and silicon contents of the alloys to be worked should be at least about 2% and not over about 4.5%.

It is an essential feature of the invention that the alloys not only contain titanium and aluminum but also at least a small but effective amount of zirconium and at least 0.10% columbium in order that the improved high temperature properties provided by the present invention be obtained. Tests which have been conducted have established that the slight amount of zirconium is very essential for the improved results of the invention although the minimum amounts required are as small as or even smaller than accurately measurable by conventional methods of analysis. When zirconium is not added, the results of the invention are not obtained. The minimum columbium content is to a considerable extent dependent upon the carbon content and should be increased with increasing carbon content. Thus, 0.10% columbium is a satisfactory minimum when the carbon content is low, e. g., about 0.01%. In general, when the carbon content is increased, the columbium content is preferably at least about ten times the carbon content. Usually, the alloys of the invention contain about 0.02% to 0.06% carbon and at least 0.25% columbium. For good hot workability in combination with good high temperature properties, it is essential that the columbium content not exceed 3%, that the zirconium content not exceed 0.2%, that the aluminum content not exceed about 1.5% and that the sum of the aluminum content, the titanium content and the silicon content be at least about 2% but not over about 4.5%. While small amounts of molybdenum up to about 5% may be beneficial for high temperature properties in castings and where hot workability is not an important factor, molybdenum decreases hot workability and should not exceed about 1% when hot workability is important. About 0.5% molybdenum has been found satisfactory from the viewpoint of workability. Silicon contributes to fluidity and castability and to the high temperature properties of the alloys, but when weldability is an important factor, the silicon content is controlled by the desired combination of high temperature properties and welding properties. In general, about 0.2% to 0.6% silicon gives satisfactory results.

When it is stated that nickel constitutes the balance, it is to be understood that the balance will be substantially all nickel but can contain small amounts of other elements as noted hereinafter. The nickel content of the alloys in all cases will be at least about 40% by weight of the alloys and preferably will be at least 50%. In commercial alloys embodying the present invention, part of the nickel may be replaced by small amounts of other elements, such as metalloids of the sulfur and arsenic group, lead, phosphorus, carbon, manganese, copper, cobalt, magnesium, boron and calcium, in a total amount up to about 5%. As noted, hereinbefore, molybdenum, in amounts up to 5%, preferably not over 1%, may also be present. In addition to being present as an incidental element, cobalt may be added in place of part of the nickel. The content of metalloids of the sulfur and arsenic group and of lead should be as low as possible. Lead should preferably not exceed 0.002%. Sulfur should preferably be below 0.01% and more preferably not in excess of about 0.007%. Phosphorus preferably should not exceed about 0.025%. The alloys may be substantially carbon-free, or carbon may be present up to about 0.25% and pref-

erably is maintained below about 0.10%. Ordinarily, carbon will be present within the range of about 0.02% to 0.06%. Manganese ordinarily will not exceed about 2.5% and preferably will be within the range of about 0.1% to 0.8%, e. g., about 0.5%. The alloys may be substantially copper-free or may contain up to about 2% copper, preferably not over about 0.5%. Ordinarily, any copper present will be as an impurity and will not exceed about 0.15%. Cobalt may be introduced in the alloy along with nickel which often contains small amounts of cobalt up to 1% or 2% or even more. When the extra cost of a cobalt addition can be tolerated, cobalt in amounts up to about 25% may replace nickel. When the alloy is to be worked or used in a wrought form, it is preferred that the cobalt content not exceed about 15%, e. g., about 10% or less. Magnesium and/or calcium is advantageously added to the alloy when it is to be hot worked. Magnesium is preferred because it produces consistently good forgeability and creep and fracture properties. It is preferable that the magnesium content of the alloy not exceed about 0.15% as larger amounts render the alloy very difficult to forge or roll. A very small but effective amount of magnesium, e. g., about 0.002% or less, improves the creep properties, e. g., the creep rate and/or fracture life, and is preferably present. Magnesium in amounts of about 0.01% to about 0.03% is particularly effective, but smaller amounts, e. g., about 0.002% to 0.008%, have given satisfactory results. Alloys containing very small but effective amounts of magnesium, as small as or even smaller than accurately measurable by conventional methods of analysis, have an improved combination of low creep rates, high fracture lives and good workability compared to similar alloys in which magnesium has not been added. In castings, up to about 0.5% magnesium can be used. The addition of a very small amount of calcium has also been found to improve the fracture properties but is not as preferred as magnesium. Three comparable alloys containing chromium, aluminum, titanium, columbium, zirconium, iron, silicon and nickel in approximately the same amounts and within the ranges contemplated by the invention but containing no magnesium, 0.03% magnesium and 0.15% magnesium, respectively, had, after proper heat treatment as set forth hereinafter, fracture lives of 134 hours, 500 hours, and 541 hours, respectively, and had second stage creep rates of 0.004% per hour, 0.0003% per hour and 0.0001% per hour, respectively, under a load of 20,000 pounds per square inch at 1500° F. Another heat treated, similar alloy to which about 0.015% calcium was added instead of magnesium lasted for 437 hours at 1500° F. under a load of 20,000 pounds per square inch.

As noted hereinbefore, iron is very beneficial for improved creep properties. When good hot working properties, e. g., hot malleability, hot forgeability, hot rolling properties, etc., are especially desired in alloys containing 20% or more chromium and at least 60% nickel, the sum of the chromium and iron contents should be less than about 30%, preferably not more than about 26%. Thus, when a nickel-base alloy containing over 60% nickel and having a composition within the ranges contemplated by the invention is made from substantially pure chromium having an iron content of about 1%, the chromium content should not exceed 30%, pref-

erably not over 25%. However, if a standard grade of ferro-chromium containing about 70% chromium and 30% iron is employed in making the alloy, the maximum chromium content is about 21% and preferably is not over 18% when the alloy is to be hot worked. When the nickel content is under 60% and/or the chromium content is not over about 16%, iron and nickel are interchangeable as far as workability or forgeability is concerned. However, for optimum high temperature properties it is preferred that the alloy contain about 4% to 15% iron, 13% to 16% chromium and 64% to 76% nickel in addition to aluminum, titanium, columbium and zirconium and other elements such as magnesium, silicon, manganese, carbon, etc., as set forth herein. Excellent results are obtained with 6% to 8% iron, 14% to 16% chromium and 71% to 75% nickel. The effect of varying the chromium and iron contents in the base composition of the alloys upon the fracture life at 1500° F. under a high load of 20,000 pounds per square inch and upon the workability of the alloys after proper heat treatment, as described hereinafter, is illustrated by the following data, the remainder of the composition being nickel in addition to about 2.3% to 2.5% titanium, 0.5% to 0.7% aluminum, 0.9% to 1.1% columbium, about 0.01% to 0.06% zirconium and the usual small amounts of incidental elements and impurities:

Per Cent Chromium	Per Cent Iron	Fracture Life	Workability
10	5	Hours	
15	1	67.5	workable.
15	7	11.1	Do.
15	15	490	Do.
20	1	306	Do.
20	3	172	Do.
20	10	133	Do.
25	1	116	not workable. difficultly workable.

In carrying the invention into practice, it is preferred to maintain the composition within the ranges set forth in the schedule below, whether the alloy is to be used in a wrought form or as a casting, for example, precision castings made by the process employed in the dental art or modifications of said process. For the production of precision castings, the art frequently demands wrought stock, i. e., bars, rounds, etc., which can be conveniently cut to the desired size to make up a charge, then melted and cast by precision casting methods. The compositions preferably employed in practice are as follows:

Element	Range	Preferred Range	Example
	Per cent	Per cent	Per cent
Chromium	12 to 18	14 to 16	15
Aluminum	0.2 to 1.6	0.4 to 0.8	0.7
Titanium	1.5 to 3	2.25 to 2.65	2.5
Columbium	0.10 to 3	0.4 to 1.2	1.0
Zirconium	0.002 to 0.2	0.01 to 0.08	0.05
Iron	4 to 20	6 to 8	7
Silicon	0.05 to 0.8	0.2 to 0.5	0.3
Magnesium	0.001 to 0.15	0.002 to 0.03	0.03
Nickel	Balance	Balance	Balance

Amounts up to about 1% molybdenum, e. g., about 0.5% molybdenum, are the preferred optional contents that can be incorporated in the foregoing compositions. The term "balance" includes small amounts of other incidental elements and impurities commonly present, as discussed hereinbefore, for example, carbon, manganese, sulfur, copper, etc. Illustrative values

are about 0.05% carbon, about 0.55% manganese, about 0.007% sulfur, about 0.05% copper, etc. The sum of the aluminum, titanium and silicon advantageously does not exceed about 4%, for example, about 3.5%. Cobalt in amounts up to 15%, e. g., about 10%, may replace part of the nickel as noted hereinbefore.

The high temperature properties of the age hardenable alloys embodying the present invention are developed by a high temperature heat treatment followed by an aging treatment at lower temperatures. The high temperature treatment must be conducted at temperatures far exceeding the temperature at which the precipitable phases which impart age hardenability go into complete solution. Said high temperature treatment comprises heating the alloy within the range of about 1950° F. to 2200° F., preferably about 2050° F. to 2150° F., for at least about one hour, more preferably at least about two hours and up to about 24 hours or more, followed by sufficiently rapid cooling to preserve the solid solution of the age hardening precipitable phases. Ordinarily, the alloy is rapidly cooled by quenching in water or oil. However, air cooling is sufficiently rapid, especially when the service temperatures are 1350° F. or lower. When the service temperature is 1500° F., it is preferred to cool large sections of the alloy by quenching. Small sections may be air cooled. In general, the cooling rate should be such that the alloy will cool to about 1300° F. within ten minutes. If desired, the cooling after any treatment may be interrupted at the temperature of the subsequent treatment and held there for the required time, i. e., in heat treating the alloys it is not essential that the alloy be cooled from the temperature of one treatment to room temperature and then reheated to the temperature of the subsequent treatment. The alloys after the high temperature treatment are subjected to an aging treatment which comprises holding the alloy within the range of about 1300° F. to 1500° F. for at least about four hours, preferably about eight hours to 20 hours or more. Longer treating times for the higher temperature treatment and the aging treatment than noted hereinbefore are not detrimental but generally are not necessary. The aging treatment imparts high temperature strength at about 1200° F. and up to at least about 1500° F. to the alloys when preceded by the above-described high temperature treatment. If the high temperature treatment is below about 1950° F., for example, at 1850° F., the subsequent aging treatment at lower temperatures will not impart the high temperature properties at 1200° F. and higher contemplated by the present invention even though the alloys are age hardened. Thus, an alloy (No. 1) made in accordance with the present invention and containing 14.26% chromium, 0.79% aluminum, 2.45% titanium, 0.33% silicon, 1.05% columbium, 0.07% niobium, 6.91% iron, 0.03% carbon, 0.49% manganese, 0.03% copper, 0.007% sulfur and 73.56% nickel ruptured in 99.8 hours under a load of 20,000 pounds per square inch at 1500° F. when given a treatment for four hours at 1850° F. followed by an aging treatment for 20 hours at 1300° F., whereas the same alloy under the same load did not rupture until after 848 hours at 1500° F. when given a high temperature treatment for four hours at the temperature of 2100° F. followed by the same aging treatment. As will be apparent to those skilled in the art, the high temperature treatment may be carried out simultaneously with other opera-

tions. Thus, when the finishing temperature after hot working, e. g., in large forgings, is high and within the ranges set forth herein for the high temperature treatment, it is possible to combine the high temperature treatment with a hot working operation. By accurate control of the finishing temperature in hot working, small articles, e. g., rods, turbine blades, etc., can be produced having good properties, by combining the high temperature treatment with a hot working operation such as rolling or forging, provided the hot working is finished at sufficiently high temperatures, for example, at about 2100° F. However, the smaller the section size the more difficult is the control of the finishing temperature required to produce consistent results.

When good properties at high service temperatures such as about 1500° F. are desired, satisfactory results are obtained by employing a double heat treatment comprising a high temperature treatment at about 2100° F. for about four hours, cooling by quenching in water or oil or by air cooling, followed by an aging treatment at 1300° F. to 1500° F.

We also have found that better properties are obtained at service temperatures of about 1200° F. to 1500° F. when the aging treatment is conducted at a temperature at least as high as the service temperature to which the alloy is to be subjected under load but within the range of about 1300° F. to 1500° F. Aging at the service temperature for about 8 to 20 hours has given excellent results. Thus, an alloy (alloy No. 5 given hereinafter) embodying the present invention exhibited better properties at 1500° F. under a load of 15,000 pounds per square inch when aged at 1500° F. for about eight hours than when aged at 1300° F. for 16 hours after the high temperature treatment. Where the alloy is to be subjected to varying service temperatures, as in gas turbines, the aging temperature is preferably that at which the alloy will operate over the greater portion of its service. For general purposes, about 1300° F. is a satisfactory aging temperature. When good creep and fracture properties at temperatures below 1300° F. are desired, the aging temperature preferably should not be below about 1300° F. Thus, if an alloy is to be employed under load at a service temperature of 1200° F., it is aged at a temperature of 1300° F., say for 16 or 20 or even 40 hours. In other words, it is preferred that the aging temperature not be lower than about 1300° F. even when the service temperature will be lower.

The heat treatment which has been described in the preceding paragraphs may, for convenience, be referred to as a double treatment, i. e., a high temperature treatment followed by a lower temperature aging treatment. This double treatment gives satisfactory results, particularly when the alloy is being treated for use at service temperatures of about 1500° F. and higher or for use at lower temperatures under the same loads as would be used at about 1500° F., for example, up to about 30,000 pounds per square inch. However, when the alloy is to be subjected in use to heavy loads at the lower temperatures of about 1350° F. to 1200° F., for example, 50,000 pounds per square inch or more at 1200° F. or 35,000 pounds per square inch or more at 1350° F., and when longer time to fracture, decreased brittleness and/or higher ductility are consistently desired at the service temperature, particularly at service temperatures of about 1350° F. and lower, e. g., at least down to about 1200° F. and even

down to 1000° F., improved properties are obtained when a triple treatment is employed. This triple heat treatment involves the use between the high temperature treatment and the aging treatment of an intermediate treatment at a temperature above 1450° F. but below 1850° F. The intermediate or pre-aging treatment, when preceded by the high temperature treatment and followed by the aging treatment, markedly improves the ductility and/or the time to fracture under load while retaining high strength properties at the elevated temperatures. Thus, the fracture life of an alloy contemplated by the invention (alloy No. 2 set forth hereinafter) was raised from 85 hours after the double treatment to well over 1320 hours (at which time the test was discontinued without any evidence that the alloy was near the fracture point) after the triple treatment when tested under a load of 54,000 pounds per square inch at 1200° F. The same alloy after the double treatment had a fracture life of 493 hours at 1500° F. under the heavy load for this temperature of 20,000 pounds per square inch.

In carrying out the triple treatment, the alloy is subjected to the high temperature treatment described hereinbefore; cooled sufficiently rapidly, for example, by quenching in water or oil or by air cooling, etc., as described hereinbefore; given the intermediate treatment at temperatures between about 1800° F. and 1500° F., preferably within the range of 1500° F. to 1700° F., for at least about one-half hour, preferably at least one hour and up to about 24 hours or more; cooled rapidly, for example, by quenching; and then given the aging treatment described hereinbefore. Treating times of 1 hour, 4 hours, 16 hours, 24 hours and 168 hours in the intermediate treatment have all given improved results. A suitable triple treatment comprises treating the alloy at 2100° F. for about four hours, quenching or air cooling, treating for about 24 hours at 1550° F., 1600° F. or 1650° F., quenching or air cooling, and treating at a lower aging temperature but preferably not below about 1300° F. for about 16 to 20 hours, e. g., at 1350° F. if that is the service temperature or at 1300° F. if the service temperature is 1200° F. For general purposes, and particularly when optimum ductility at the service temperature is desired, treatment for about four hours at about 1550° F. is satisfactory as an intermediate treatment. When low second stage creep rate is more important than ductility, a higher temperature, e. g., 1650° F., may be desirable. When a substantial amount of plastic flow in the initial stage is desired or can be tolerated, long holding times, e. g., 168 hours, may be employed in the intermediate treatment. Such a long-time intermediate treatment can be useful in some applications where it is desired to cold work the alloy after heat treatment, e. g., in forming turbine blades by cold striking. As in the case of the double treatment, it is not essential in the triple treatment that the alloy be cooled to room temperature between treatments. The alloy can be cooled from the temperature of one treatment directly to that of the next treatment.

The triple treatment contemplated by the invention will produce the optimum combination of fracture life and creep resistance under heavy loads for service at temperatures in the range of about 1000° F. to 1350° F. However, in some applications where a fine grain size and higher ductility are more to be desired than high load-carrying capacity, the high temperature treatment may be omitted and the material merely

given the intermediate treatment, e. g., within the range of about 1550° F. to 1750° F., and then aged. Thus, when alloy No. 1 was hot rolled and then given an intermediate treatment for 24 hours at 1650° F. and an aging treatment for 20 hours at 1300° F. and then tested under a load of 60,000 pounds per square inch at 1200° F., it had a fracture life of 200 hours with an elongation of 6.5% in six inches and a reduction of area of 6.2%. This kind of treatment can be satisfactory for some applications where the design calls for loads of the order of only 30,000 or 40,000 pounds per square inch and where fine grain size and higher ductility are considered to be desirable. Examples of such applications are extrusion dies which in order to resist spalling require sufficient ductility to withstand the severe thermal stresses encountered in service. Extrusion dies given the foregoing heat treatment without a prior high temperature treatment have performed satisfactorily in use. Another example of when the high temperature treatment may be omitted is in the case of hot worked articles, such as large forgings, where the finishing temperature after hot working is so controlled that a high finishing temperature within the ranges of the high temperature treatment is obtained. In this manner, the high temperature treatment is in effect accomplished from the residual temperature after hot working. Such a heat treatment can be employed, for example, in producing a 30-inch gas turbine rotor by finishing the hot forging at a high temperature, e. g., at 2100° F., and then conducting the intermediate and aging treatments. Even smaller articles, such as rods or turbine blades, which are finished at a high enough temperature after hot rolling or forging can develop good properties by accurate control of the finishing temperature, but, as noted hereinbefore, such control is very difficult and it is preferred not to combine the hot working operation with the high temperature treatment, particularly when articles of small section size are being produced.

The intermediate treatment is conducted above the temperature at which age hardening occurs. In fact, the treatment is generally accomplished by a decrease in hardness. The intermediate treatment initiates the profuse precipitation of a relatively coarse constituent, which precipitation does not have a hardening effect. Thus, after the intermediate treatment the hardness is of the order of about 160 Brinell hardness number, e. g., about 140 to 180, whereas after the subsequent aging treatment at lower temperatures the hardness is about 350 to 400 Brinell hardness number. The precipitation initiated by the intermediate treatment of the triple treatment can be illustrated by reference to Figs. 1 to 4 which depict reproductions of photomicrographs taken at 1000 magnifications showing the structure of an alloy (alloy No. 2) after various heat treatments. Fig. 1 shows the microstructure of the wrought alloy after a high temperature treatment at 2100° F. for four hours followed by rapid cooling. Fig. 2 shows the microstructure of the same alloy after an embodiment of the double treatment contemplated by the invention, i. e., after the aforementioned high temperature treatment followed by quenching and aging at 1300° F. for 16 hours. Fig. 3 shows the microstructure of the alloy after an embodiment of the triple treatment contemplated by the invention, i. e., after the aforementioned high temperature treatment followed by quenching, then an intermediate treatment at 1650° F. for 168 hours followed by quenching and an aging treatment at

1300° F. for 16 hours. Fig. 4 shows the microstructure obtained when too high a temperature is employed in the intermediate treatment. The difference between the structure of Fig. 2, illustrative of the double treatment, and that of Fig. 3, illustrative of the precipitation initiated by the triple treatment, is marked. In Fig. 2 moderate amounts of a very fine dispersed constituent are obtained. In Fig. 3 profuse precipitation of a coarser nature has taken place. In addition, "clean" bands free of visible precipitate are adjacent the grain boundaries. The improved fracture life and ductility exhibited by the alloys subjected to the triple treatment are attributed to the unusual structure initiated or developed by this treatment. When the intermediate treatment is of shorter duration, e. g., 16 or 20 hours, the unusual structure is not as distinct but is initiated and becomes more evident when the treatment is prolonged. As shown in Fig. 4, the unusual structure of Fig. 3 is no longer obtained when too high a temperature is employed in the intermediate treatment, the structure in that case being similar to that of Fig. 2.

The triple treatment contemplated by the invention improves the properties of the alloys provided by the invention but does not improve the properties of similar alloys devoid of columbium and zirconium. Thus, alloy No. 8 given herein-after had a fracture life of 312 hours under a load of 54,000 pounds per square inch at 1200° F. after a double treatment and had a fracture life of only 300 hours under the same test conditions after a triple treatment. The same alloy containing both columbium and zirconium in accordance with the invention would have lasted for thousands of hours under the same test conditions after the same triple heat treatment. While the theoretical explanation of the effects obtained by the use of the intermediate treatment contemplated by the invention is not fully understood, a possible explanation mentioned hereinbefore in describing Figs. 1 to 4 is that the intermediate treatment initiates the precipitation of a phase in a controlled manner which produces better properties and that when the intermediate treatment is omitted the precipitation is uncontrolled at lower temperatures during the aging treatment and/or in use. The microstructures of the alloys and the structures shown in the photomicrographs of the drawings are in harmony with such an explanation. Whatever the correct explanation, the facts are that the intermediate treatment produces improved properties as described herein.

Under the microscope the precipitate of Fig. 3 appears light-colored, i. e., pale grey in color, and because of the light color of the matrix or background, i. e., white, the precipitate is difficult to photograph because of the absence of contrast between the precipitate and the matrix or background. By careful polishing, etching and photomicrographic technique, including the use of photographic plates, films and papers which develop contrast, the precipitate can be photographed. A method which we have found satisfactory, and which was employed in obtaining Fig. 3, comprises carefully polishing the alloy and then etching the same with a solution containing about 95% concentrated nitric acid and about 5% of hydrofluoric acid by volume.

The improved ductility and fracture life obtained by the triple treatment are illustrated by data based on rolled alloy No. 1 described here-

inbefore. One portion of the rolled alloy was given a double treatment comprising a high temperature treatment at 2100° F. followed by an aging treatment at 1300° F. Another portion of the same alloy was given a triple treatment comprising an intermediate treatment at 1550° F. for 24 hours in addition to a prior high temperature treatment and a subsequent aging treatment at the same temperatures as employed in the double treatment. The thus-treated portions were then subjected to fracture tests at 1350° F. under a high load of 45,000 pounds per square inch. The following schedule sets forth the results of the tests and demonstrates the marked improvement in fracture life and ductility that can be obtained by the triple treatment:

Treatment	Fracture Life	Per Cent Elongation
	Hours	
Double.....	218	0.23
Triple.....	832	3.7

The per cent elongation is a measure of the ductility and represents the amount of elongation when fracture occurred compared to the original dimensions of the test specimens which were 0.500 inch in diameter at each end and were 0.30 inch in diameter in the minimum section at the center portion of the test piece where fracture occurs. This minimum section was six inches in length and the per cent elongation is the percentage increase in dimension which occurred during the fracture test over the six-inch length. As is well known to those skilled in the art, the per cent elongation will vary with the length over which it is measured, and the same alloy will have higher elongation if determined from a specimen having only a one-inch minimum-section length than when determined over a six-inch or four-inch minimum-section length. From available data, it might be said that, in general, the elongation measured on a one-inch minimum-section specimen will be at least 1.5 to 2 times as large as when measured on a six-inch or four-inch minimum-section specimen.

The high properties obtained by the invention under high loads at 1350° F. and the improvement in fracture life obtained by the triple treatment are illustrated by the following data from tests at 1350° F. on alloy No. 1 after a double treatment and after a triple treatment:

Treatment	Load, p. s. i.	Fracture Life, Hours
Double.....	40,000	901
Do.....	45,000	218
Do.....	55,000	36
Triple.....	45,000	832
Do.....	55,000	146

Data obtained at 1200° F. have shown that the triple treatment similarly develops notably improved properties at that temperature.

The effect on fracture life of varying the temperature and/or time of the intermediate treatment in the triple treatment is illustrated by the following data obtained in fracture tests at 1200° F. under a load of 60,000 pounds per square inch

on alloy No. 3 having the composition given hereinafter:

Treatment			Fracture Life
High Temperature	Intermediate	Aging	
4 hrs. at 2,100° F.	24 hrs. at 1,450° F.	20 hrs. at 1,300° F.	Hours
Do.	24 hrs. at 1,550° F.	do.	80
Do.	1 hr. at 1,650° F.	do.	1,200
Do.	24 hrs. at 1,680° F.	do.	1,572
Do.	24 hrs. at 1,720° F.	do.	1,605
Do.	24 hrs. at 1,780° F.	do.	1,101
Do.	24 hrs. at 1,880° F.	do.	360

For service temperatures of about 1500° F. the double treatment is sufficient, and may even be desirable, although the triple treatment can be employed. Thus, wrought alloy No. 1 when given a double treatment (4 hours at 2100° F. and 20 hours at 1300° F.) had a fracture life of 290 hours under a load of 25,000 pounds per square inch at 1500° F. where as when given a triple treatment, involving an intermediate treatment for 24 hours at 1550° F. in addition to the same high temperature and aging treatments as employed in the double treatment, the alloy had a fracture life of 212 hours under the same conditions of test.

The short- and long-time intermediate treatments are compared in Fig. 5 wherein curve A is the creep curve for alloy No. 2, set forth herein-after, tested under a load of 54,000 pounds per square inch at 1200° F. after a high temperature treatment at 2100° F. for 24 hours followed by a short-time intermediate treatment at 1650° F. for 24 hours and an aging treatment at 1300° F. for 16 hours. Curve B is the creep curve for the same alloy tested under the same load at 1200° F. after a heat treatment comprising the same high temperature and aging treatments but a long-time intermediate treatment at 1650° F. for 168 hours. Curve B demonstrates the ability to load the heat treated alloy far above its yield point and still have the alloy come to an equilibrium where it exhibits good creep rate in the second stage of creep. It will be observed that the alloys in the conditions of both curve A and curve B were still in the second stage of creep with low creep rates, about 0.015% and 0.20% per 1000 hours, respectively, when the test was discontinued after 1320 hours. After cold striking a heat treated alloy having a creep curve such as curve B, the curve for the cold struck alloy would tend to be displaced downward to that of curve A. An alloy exhibiting a creep curve like that of curve B provides a safety factor in the event of an unexpected overload. In general, and particularly when low initial stage creep rate or plastic flow is desired, it is preferable to employ shorter holding times up to about 24 hours for the intermediate treatment.

When the alloys of the invention are to be used below 1200° F., for example, at temperatures of 1000° F. and down to room temperature, the high temperature treatment and the intermediate treatment are not essential and may even be undesirable. Thus, the alloy may be hot rolled and then simply given the aging treatment, e. g., treated 20 hours at 1300° F. and then air cooled. By omitting the aforesaid treatments, advantage can be taken of the effect of hot rolling to increase the tensile strength, etc., of the alloy.

The heat treatments contemplated by the invention also impart other high properties to the alloys of the invention, e. g., tensile strength,

fatigue or endurance limit, etc., at elevated temperatures. Thus, alloy No. 1 after a double treat-

ment exhibited a tensile strength of 76,500 pounds per square inch at 1500° F. A similar alloy (No. 8) devoid of zirconium and columbium and containing 15% chromium, 0.5% aluminum, 2.4% titanium, 0.5% silicon, 6.7% iron, 0.04% carbon, 0.7% manganese, 0.07% copper, 0.007% sulfur and the balance nickel had a tensile strength of 45,400 pounds per square inch at 1500° F. after having been given a double treatment. Likewise, hot rolled alloy No. 1 has an endurance limit for one hundred million cycles at 1500° F. of about 34,000 pounds per square inch after a triple treatment comprising four hours at 2100° F., 24 hours at 1650° F. and 20 hours at 1300° F. At 1200° F. the endurance limit for one hundred million cycles, after a triple treatment, is approximately 65,000 pounds per square inch.

The recrystallization behavior of the alloys of the present invention containing columbium and zirconium is different from that of similar alloys devoid of columbium and zirconium. The alloys of the present invention recrystallize at about 1850° F. to a medium grain size of about No. 6 according to the A. S. T. M. standard grain size classification for steels, and the grain size becomes gradually larger at successively higher temperatures. The alloys devoid of columbium and zirconium recrystallize at about 1950° F. to a large exaggerated grain size of about No. 3 according to the A. S. T. M. standard grain size classification for steels.

The fracture of the alloys of the present invention is also different from that of similar alloys devoid of columbium and zirconium. The alloys of the invention containing zirconium and columbium tend in general to break with a transcrystalline fracture, whereas the alloys devoid of columbium and zirconium break with a coarse intergranular fracture. As pointed out hereinbefore, the response to the triple treatment of the alloys devoid of columbium and zirconium is very different from that of the alloys of the invention containing these elements.

The co-presence of columbium and zirconium in combination with chromium, aluminum and titanium in the proportions provided by the present invention increases the fracture life five to ten times that of similar compositions free from columbium and zirconium under most conditions of load and temperature within the range employed in high temperature applications, for example, in gas turbine design. The co-presence of columbium and zirconium also increases the load-carrying capacity of the alloy at temperatures in the order of 1350° F. to 1500° F. as much as twice that of a similar alloy free from columbium and zirconium.

The necessity for, and the improved results obtained by the present invention when the composition contains, the required amounts of aluminum, titanium, columbium and zirconium are

illustrated by data obtained on the following alloys:

Element, per cent	Alloy Composition						
	1	2	3	4	5	6	7
Cr.....	14.26	14.52	14.76	14.35	14.62	14.95	20.58
Al.....	0.79	0.67	0.63	0.71	0.67	0.70	0.60
Ti.....	2.45	2.36	2.46	2.50	2.46	2.46	2.36
Cb.....	1.05	1.17	1.06	0.57	1.12	1.02	1.05
Zr.....	0.07	0.05	0.04	0.04	0.05	0.05	0.04
Fe.....	6.91	7.06	6.61	7.85	7.23	6.76	1.01
Si.....	0.33	0.27	0.36	0.35	0.30	0.32	0.74
Mo.....	none	none	none	none	0.52	none	none
C.....	0.03	0.04	0.05	0.04	0.04	0.05	0.05
Mn.....	0.49	0.50	0.67	0.48	0.48	0.45	0.68
Co.....	s. a.	s. a.	s. a.	s. a.	s. a.	10.0	s. a.
Ni.....	73.56	73.31	73.30	73.04	72.50	63.19	72.72

Element, per cent	Alloy Composition						
	8	9	10	11	12	13	
Cr.....	15.02	14.40	14.99	15.56	14.89	19.84	
Al.....	0.49	0.63	0.74	0.46	0.19	0.58	
Ti.....	2.42	2.77	2.53	2.37	0.26	2.26	
Cb.....	none	none	1.18	none	1.94	none	
Zr.....	none	none	none	0.05	0.02	none	
Fe.....	6.70	6.17	7.82	6.89	7.21	0.48	
Si.....	0.52	0.52	0.63	0.51	0.50	0.52	
Mo.....	none	none	1.81	none	none	none	
C.....	0.04	0.03	0.05	0.04	0.05	0.02	
Mn.....	0.73	0.53	0.53	0.71	0.46	0.47	
Co.....	s. a.	s. a.	s. a.	s. a.	s. a.	s. a.	
Ni.....	73.98	74.82	69.65	73.35	74.39	75.76	

s. a. = usual small amount, included as nickel.

Alloys Nos. 1 to 7, inclusive, have compositions in accordance with the invention, and alloys Nos. 1 to 6 contain amounts of chromium and iron within the preferred ranges for these elements. Alloys Nos. 8 to 13, inclusive, have compositions outside the scope of the invention and are included for comparison purposes. Alloys Nos. 8 to 12 can be compared with alloys Nos. 1 to 6 while alloy No. 13 can be compared with alloy No. 7. All the alloys were heat treated within the temperature ranges set forth hereinbefore and were then subjected to fracture or rupture tests. The results of the tests are summarized in the following schedule and illustrate the improved properties obtained with the alloy compositions of the invention which contain columbium and zirconium in addition to at least about 2% of titanium plus aluminum:

Alloy No.	Temperature, °F.	Load, p. s. i.	Life to Rupture, Hours
8	1,200	48,000	425
8	1,200	54,000	312
8	1,200	60,000	78.5
11	1,200	60,000	502
3	1,200	60,000	1,806
1	1,200	70,000	785
1	1,200	80,000	120
11	1,350	35,000	175
2	1,350	35,000	over 1,878
1	1,350	45,000	832
1	1,350	50,000	296
1	1,350	55,000	146
12	1,500	10,000	225
9	1,500	10,000	710
9	1,500	15,000	56
10	1,500	15,000	574
5	1,500	15,000	2,200
1	1,500	20,000	848
4	1,500	20,000	497
6	1,500	20,000	582
1	1,500	25,000	290
1	1,500	30,000	112
13	1,500	15,000	64
13	1,500	20,000	22
7	1,500	20,000	173

1 Test discontinued at 1,878 hours.

When the composition is in accordance with the invention, as illustrated by alloys Nos. 1 to 7, the alloys exhibit much longer fracture or rupture lives for a given load and withstand much higher loads for a given life than alloys of similar base composition which do not contain the combination of special elements in the amounts set forth hereinbefore.

The fracture properties that can be obtained by the invention at 1200° F., 1350° F. and 1500° F. under various loads are illustrated graphically in Fig. 6 which depicts curves based on data obtained on alloy No. 1. The various heat treatments employed in obtaining the data for these curves were as follows:

Temperature, °F.	Heat Treatment
1,200.....	4 hrs. at 2,100° F., air cooled, 24 hrs. at 1,550° F., 20 hrs. at 1,300° F.
1,350.....	1. 4 hrs. at 2,100° F., 24 hrs. at 1,550° F. to 1,650° F., 20 hrs. at 1,300° F. 2. 24 hrs. at 2,100° F., 16 to 20 hrs. at 1,300° F.
1,500.....	4 hrs. at 2,100° F., air cooled, 20 hrs. at 1,300° F.

The improvement obtained by the triple treatment of the invention is well illustrated by the two curves at 1350° F. comparing the same alloy after a triple treatment (1) and a double treatment (2).

The present invention provides alloys, and articles made thereof, which exhibit low second stage creep rates. The following are illustrative of the creep rates obtained by the invention:

Alloy No.	Load, p. s. i.	Temperature, °F.	Second Stage Creep Rate, Per Cent Per Hour
2.....	54,000	1,200	0.000015
3.....	60,000	1,200	0.00015
3.....	30,000	1,350	0.00032
3.....	35,000	1,350	0.00036
1.....	40,000	1,350	0.00010
5.....	15,000	1,500	0.00005
2.....	20,000	1,500	0.0005
14.....	20,000	1,500	0.0001

Alloy No. 14 contained about 16.1% chromium, 0.7% aluminum, 2.5% titanium, 1% columbium, 0.045% zirconium, 7.3% iron, 0.4% silicon, 0.05% carbon, 0.6% manganese and 71.2% nickel. In comparison, heat treated alloys having compositions devoid of columbium and/or zirconium or containing insufficient amounts of titanium plus aluminum exhibited the following second stage creep rates:

Alloy No.	Load, p. s. i.	Temperature, °F.	Second Stage Creep Rate, Per Cent Per Hour
11.....	55,000	1,200	0.00026
8.....	60,000	1,200	0.00040
9.....	10,000	1,500	0.00034
12.....	10,000	1,500	0.0093
10.....	15,000	1,500	0.00013
8.....	20,000	1,500	0.0056

The creep curve of alloy No. 5 under a load of 15,000 pounds per square inch at 1500° F. is shown in Fig. 7. The alloy was heat treated for 24 hours at 2100° F. and then for eight hours at 1500° F. In Fig. 8 the creep curve for alloy No. 3 under a load of 60,000 pounds per square inch at 1200° F. is compared under the same conditions with the curve for an alloy (No. 8) outside the scope of this invention.

The high load-carrying capacity of the alloys and articles provided by the invention is indicated in the following schedule:

Temperature, °F.	Stress for—	
	1,000 hr. Life	100 hr. Life
900	130,000	150,000
1,200	60,000	80,000
1,350	44,000	57,000
1,500	19,000	30,000

As pointed out hereinbefore, for service at temperatures of about 1000° F. or lower, the alloys may simply be aged without previous treatment at higher temperatures. For many purposes, such a treatment is preferred as it produces higher properties. The alloys of the invention do not require a high temperature treatment or even a conventional solution treatment prior to the aging treatment to develop age hardening and can be aged without prior heat treatment. This is illustrated by the data in the following schedules showing the high mechanical properties obtained by the invention in short-time tests at 900° F. and also at room temperature. The data at 900° F. were obtained on alloy No. 15 containing about 15.74% chromium, 0.66% aluminum, 2.40% titanium, 1.06% columbium, 0.045% zirconium, 7.22% iron, 0.45% silicon, 0.04% carbon, 0.59% manganese and 71.74% nickel.

	Condition
A.....	Hot rolled and then aged at 1,300° F. for 24 hrs.
B.....	Hot rolled, treated at 2,100° F. for 4 hrs. and at 1,300° F. for 24 hrs.
C.....	Hot rolled and then aged at 1,300° F. for 16 to 20 hrs.
D.....	Hot rolled, treated at 2,100° F. for 24 hrs. and at 1,300° F. for 16 to 20 hrs.

Alloy No.	Temp., °F.	Condition	T. S., p. s. i.	Y. S., p. s. i.	El., Per Cent	R. A., Per Cent	VHN
15	900	A	176,800	-----	21.6	45.2	-----
15	900	B	143,700	-----	25.8	37.6	-----
1	room	C	199,000	139,500	25.7	43.7	343
1	room	D	163,000	108,000	17.8	20.0	404

T. S. = tensile strength.
Y. S. = yield strength (0.2% offset).
El. = elongation in 2 inches.
R. A. = reduction in area.
VHN = Vickers hardness number.

The alloys provided by the present invention have exhibited good fracture lives at 900° F. under heavy loads. Thus, a hot rolled and aged alloy having a composition similar to those of alloys No. 1 to No. 3 was loaded to 130,000 pounds per square inch at 900° F. and was still under test after 1200 hours without showing any indications of fracture.

In addition to their exceptional high temperature properties, the alloys of the invention also possess exceptionally high physical properties at room temperature. For example, some wire (0.070 inch in diameter) made of an alloy similar to alloys No. 1 to No. 3 exhibited the following properties after being cold drawn 75% and then subsequently aged at 1250° F. for four hours:

Property	Cold Drawn	Cold Drawn and Aged
Tensile strength, p. s. i.	262,000	302,000
Yield strength, p. s. i.	266,000	286,000
Per Cent Elongation (in 2 inch)	4.0	5.0
Per Cent Reduction in area	33.3	13.0

The wire in the "as drawn" condition was capable of wrapping around its own diameter indefinitely without breaking. This is the highest tensile strength we are aware of in a nickel-base alloy which is capable of withstanding this test. These high properties render the alloy suitable for various applications, including armature binding wire, bicycle spoke wire, etc., where such an optimum combination of high properties is required. The high properties at room temperature exhibited by the alloys of the invention make them useful for numerous room temperature and atmospheric temperature applications. The alloys attain a higher level of hardness after aging than similar alloys devoid of zirconium and columbium. The hardenability of alloy No. 1 made in accordance with the invention is compared with the hardenability of a similar alloy (No. 16) devoid of zirconium and columbium in the following schedule after aging hot rolled rods made thereof for various periods of time at 1300° F.:

Aging Time at 1,300° F.	Vickers Hardness Number	
	Alloy No. 1	Alloy No. 16
as hot rolled	235	235
2 hrs.	341	330
4 hrs.	373	348
8 hrs.	383	357
17 hrs.	398	360
32 hrs.	410	363
40 hrs.	414	367

Alloy No. 16 contained about 14.45% chromium, 0.69% aluminum, 2.54% titanium, 6.28% iron, 0.43% silicon, 0.05% carbon, 0.68% manganese and 74.81% nickel.

Other physical properties of the alloys provided

by the invention which are useful in designing articles made of the alloys are as follows:

Modulus of Elasticity (p. s. i.)	In tension	
	In tension	In torsion
at 75° F.	31×10 ⁶	11×10 ⁶
at 300° F.	29.8×10 ⁶	10.6×10 ⁶
at 500° F.	28.7×10 ⁶	10.2×10 ⁶
at 700° F.	27.4×10 ⁶	9.7×10 ⁶
at 900° F.	25.9×10 ⁶	9.2×10 ⁶
at 1,050° F.	24.6×10 ⁶	8.7×10 ⁶
at 1,200° F.	23×10 ⁶	8.1×10 ⁶
at 1,500° F.	18×10 ⁶	-----
Coefficient of Expansion (inch/inch/°F.)	Instantaneous	
	Instantaneous	mean
at room temp.	7.4×10 ⁻⁶	7.4×10 ⁻⁶
500° F.	7.7×10 ⁻⁶	7.4×10 ⁻⁶
700° F.	8.0×10 ⁻⁶	7.6×10 ⁻⁶
900° F.	8.3×10 ⁻⁶	7.7×10 ⁻⁶
1,000° F.	8.6×10 ⁻⁶	7.8×10 ⁻⁶
1,200° F.	9.7×10 ⁻⁶	8.1×10 ⁻⁶
1,350° F.	10.8×10 ⁻⁶	8.3×10 ⁻⁶
1,500° F.	12.0×10 ⁻⁶	8.6×10 ⁻⁶

¹ Coefficient at indicated temperature.

² Mean coefficient from room to indicated temperature.

The high temperature properties of the heat treated alloys provided by the present invention have been described with reference to particular temperatures and conditions, but it is to be understood that the alloys in general exhibit improved properties at high temperatures, and at lower temperatures down to atmospheric temperatures, and are not limited to the particular representative temperatures and/or conditions of stress or loading, etc., mentioned only for illustrative purposes. In general, the improved fracture life and load-carrying capacity of the alloys at high temperatures are notable.

The alloys contemplated by the invention combine high properties, as indicated hereinbefore, with the high corrosion and oxidation resistance which characterize nickel-base alloys of nickel and chromium, with or without iron. Thus, the alloys exhibit outstanding resistance to oxidation at the elevated service temperatures as well as resistance to atmospheric corrosion or tarnishing. The latter property combined with the ability to take a high polish makes the alloys suitable as metallic mirrors and reflectors in marine atmospheres and the like, for example, as reflectors in large searchlights, etc., which operate at rather high temperatures. Thus, large searchlight reflectors have to withstand the heat which accompanies the generation of millions of candle power and become quite hot in service. The high room temperature and elevated temperature strength properties make the alloys well suited for springs operating at atmospheric temperatures and/or elevated temperatures.

The alloys of the invention may be employed as cast alloys or castings but are especially useful as wrought products, having suitable hot and cold workability when maintained within the ranges of composition and in the proportions described hereinbefore. In forging or otherwise hot working the alloys, they should be worked within the range of about 2225° F. down to about 1800° F., preferably not below about 1900° F.

The combination of high properties obtainable by the invention makes the alloys suitable for a wide variety of articles subjected in use to load at elevated temperatures and/or at atmospheric temperatures. Such articles include plates, sheets, strips, rods, wires, bars, tubing, forgings, stampings, extrusions, castings, etc., and products manufactured therefrom. Specific examples of such manufactured products include parts of steam turbines, gas turbines (including superchargers), jet propulsion engines, etc., such as moving or stationary turbine blades, buckets and nozzles (including precision cast buckets, etc.), turbine rotors, turbine wheels, turbine bolts, combustion chambers or flame tubes, shrouding, bellows, etc.; parts of internal combustion engines, such as valves, valve seats, valve springs, etc.; parts of machines and apparatus operating at elevated temperatures, such as springs, extrusion dies, mandrels, piercer points, dummies (for extrusion presses), dies and anvils for forging and drop forging, cutters for hot metal, furnace parts, large searchlight reflectors, etc.; supports and elements in radio tubes, incandescent lamps, electronic tubes, etc.; springs operating at elevated temperatures and/or atmospheric temperatures, including valve springs, springs in automatic rifles, springs in torpedoes, springs in measuring and indicating instruments, etc.; bolts; music wire, armature binding wire, bicycle spokes and other wire products; metallic mirrors and reflectors; etc.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such variations and modifications are considered to be within the purview and scope of the invention and the appended claims.

We claim:

1. An article subjected in use to stress at elevated temperatures made of an age hardened alloy containing 10% to 25% chromium, 0.2% to 1.5% aluminum, 1.5% to 3% titanium, up to 0.25% carbon, 0.1% to 3% columbium with the columbium content being at least ten times the carbon content, a small but effective amount up to 0.2% zirconium, 0.1% to 20% iron, 0.05% to 0.8% silicon, and the balance essentially nickel, the sum of the aluminum, titanium and silicon contents being 2% to 4.5% of the alloy.

2. An age hardenable alloy containing 14% to 16% chromium, 0.4% to 0.8% aluminum, 2.25% to 2.65% titanium, up to 0.1% carbon, 0.4% to 1.2% columbium with the columbium content being at least ten times the carbon content, 0.01% to 0.8% zirconium, 6% to 8% iron, 0.2% to 0.5% silicon, 0.002% to 0.03% magnesium and the balance essentially nickel.

3. An age hardenable alloy containing 14% to 16% chromium, 0.4% to 0.8% aluminum, 2.25% to 2.65% titanium, up to 0.1% carbon, 0.4% to 1.2% columbium with the columbium content being at least ten times the carbon content, 0.01% to 0.08% zirconium, 6% to 8% iron, 0.2% to 0.5% silicon and the balance essentially nickel.

4. An age hardenable alloy containing 13% to 16% chromium, 0.4% to 0.8% aluminum, 2.25% to 2.65% titanium, up to 0.1% carbon, 0.4% to 1.2% columbium with the columbium content being at least ten times the carbon content, a small but effective amount up to 0.08% zirconium, 4% to 15% iron, 0.2% to 0.5% silicon and the balance essentially nickel.

5. An age hardenable alloy containing 12% to 18% chromium, 0.2% to 1.5% aluminum, 1.5% to 3% titanium, up to 0.25% carbon, 0.25% to 3% columbium with the columbium content being at least ten times the carbon content, 0.002% to 0.2% zirconium, 4% to 20% iron, 0.05% to 0.8% silicon, the sum of the aluminum, titanium and silicon contents being 2% to 4.5% of the alloy, a small but effective amount up to 0.15% magnesium and the balance essentially nickel.

6. An age hardenable alloy containing 10% to 25% chromium, 0.2% to 1.5% aluminum, 1.5% to 3% titanium, up to 0.25% carbon, 0.25% to 3% columbium with the columbium content being at least ten times the carbon content, 0.002% to 0.2% zirconium, 4% to 20% iron, 0.05% to 0.8% silicon, up to 0.15% magnesium, and the balance essentially nickel, the sum of the aluminum, titanium and silicon contents being 2% to 4.5% of the alloy.

7. An age hardenable alloy containing 10% to 35% chromium, 0.1% to 5% aluminum, 0.1% to 5% titanium, 0.05% to 8% silicon, 0.002% to 2% zirconium, up to 0.25% carbon, 0.25% to 3% columbium with the columbium content being at least ten times the carbon content, 0.1% to 25% iron, up to 0.5% magnesium, and the balance essentially nickel, the sum of the aluminum, titanium and silicon being 2% to 10% of the alloy and the nickel content being at least 40% of the alloy.

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8. An age hardenable alloy containing 10% to 35% chromium, up to 25% iron, 0.1% to 8% aluminum, 0.1% to 8% titanium, up to 8% silicon, a small but effective amount up to 2% zirconium, up to 0.25% carbon, 0.1% to 5% columbium with the columbium content being at least ten times the carbon content, up to 5% molybdenum, up to 2.5% manganese, up to 2% copper, up to 25% cobalt, and the balance essentially nickel, the sum of the aluminum, titanium and silicon being 2% to 10% of the alloy and the nickel content being at least 40% of the alloy.

9. The alloy specified in claim 8 in which magnesium is present in a small amount up to 0.5% of the alloy.

10. An age hardenable alloy containing 10% to 25% chromium, up to 25% cobalt, 1.5% to 3% titanium, 0.1% to 1.5% aluminum, up to 0.25% carbon, 0.1% to 3% columbium with the columbium content being at least ten times the carbon content, up to 0.8% silicon, 0.002% to 0.2% zirconium, up to 20% iron, up to 2.5% manganese, up to 1% molybdenum, up to 0.03% of metal from the group consisting of magnesium and calcium, and the balance essentially nickel, the sum of titanium, aluminum and silicon being at least 2% of the alloy and the nickel content being at least 40% of the alloy.

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