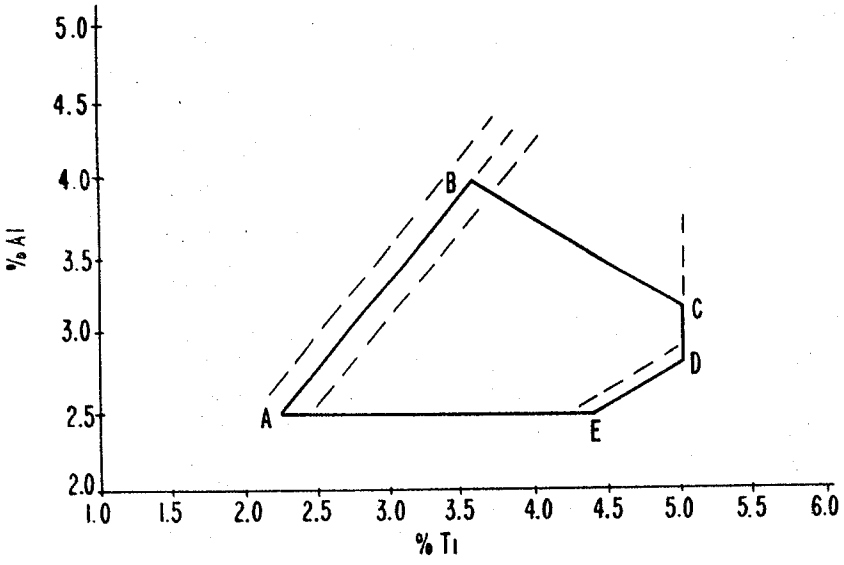
June 29, 1971 C. H. LUND ET AL 3,589,893

SULFIDATION RESISTANT ALLOYS AND STRUCTURES

Filed Nov. 24, 1967 2 Sheets-Sheet 1

FIG. 1



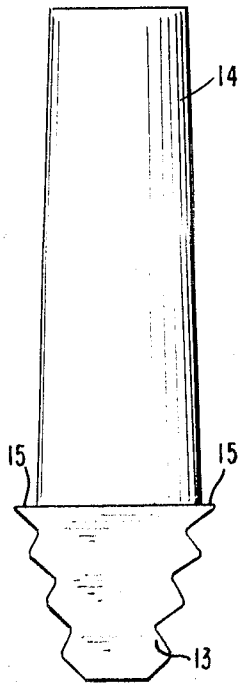


FIG. 3

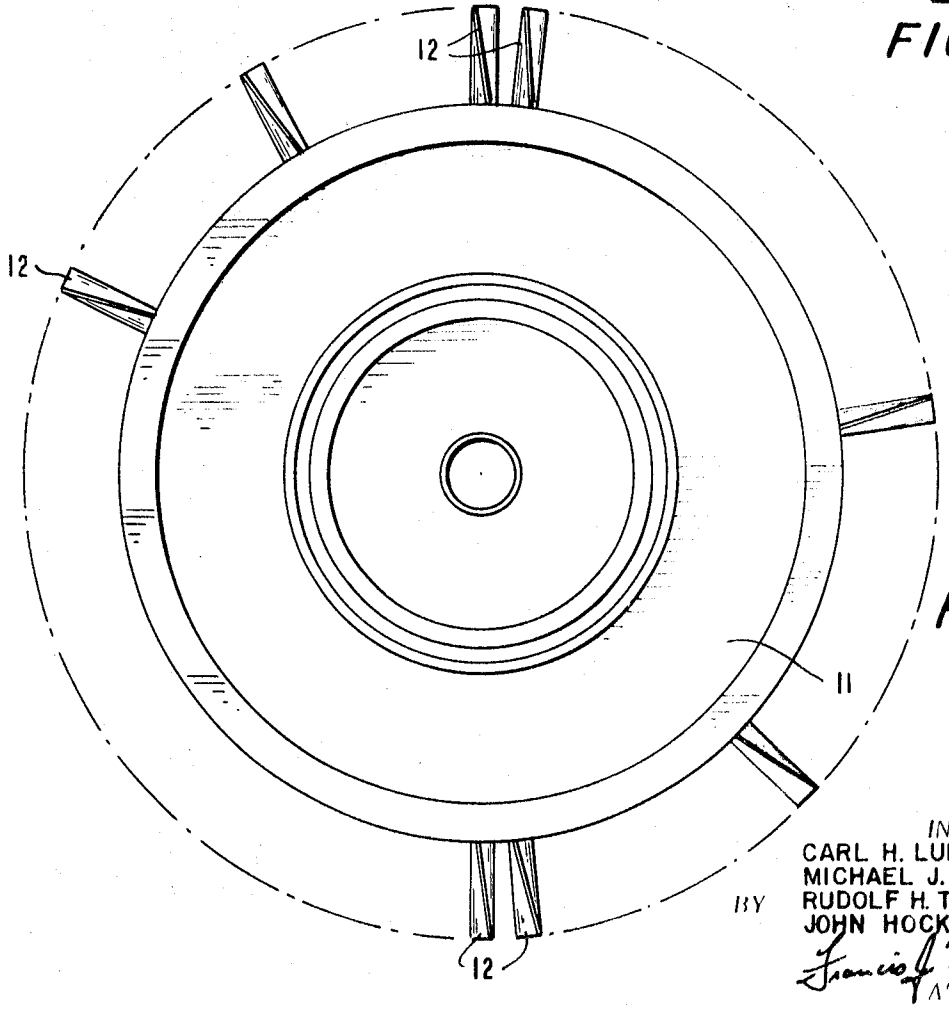


FIG. 2

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SULFIDATION RESISTANT ALLOYS AND STRUCTURES

Filed Nov. 24, 1967 2 Sheets-Sheet 2

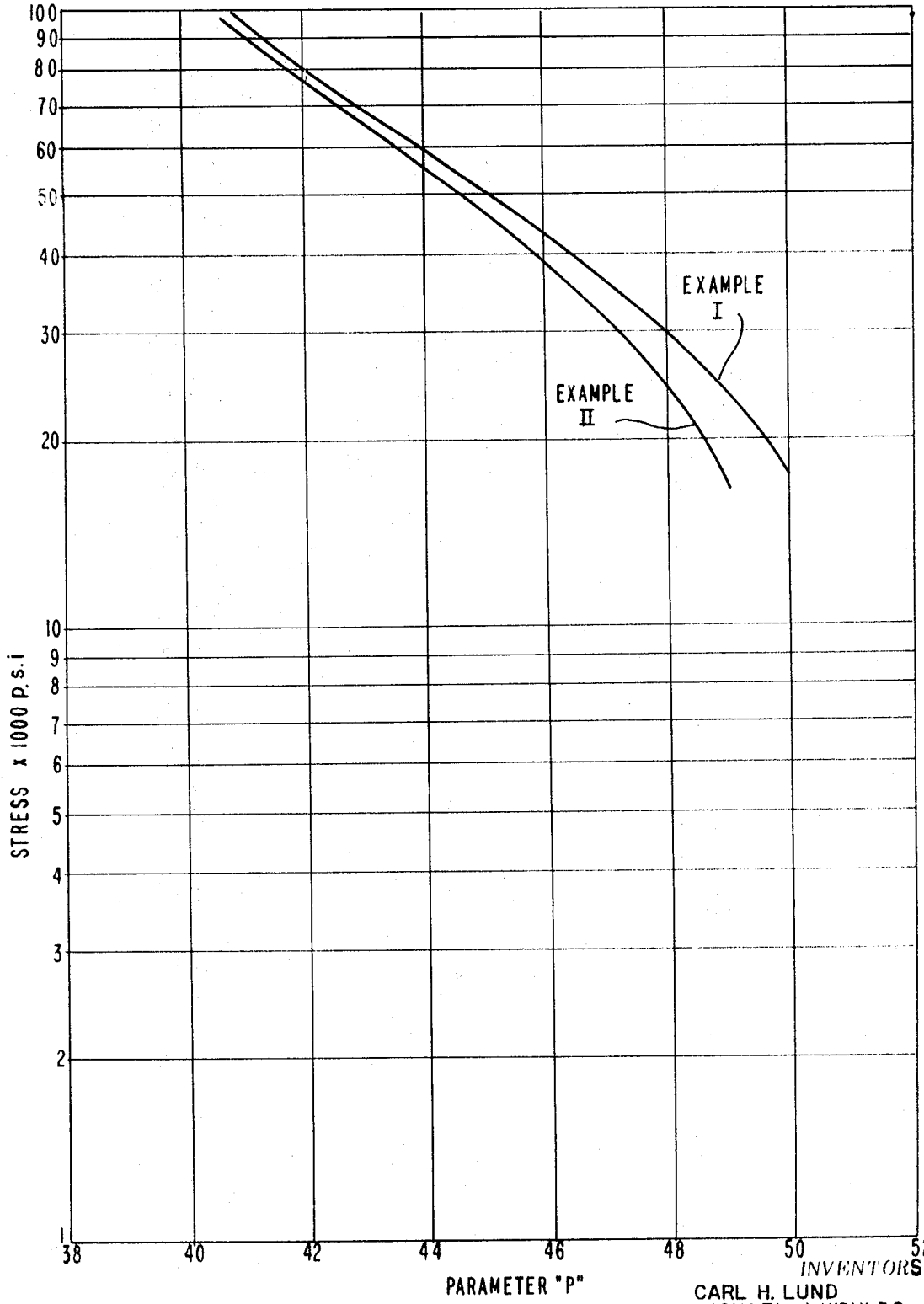


FIG. 4

$P = T(20 + \log t) \times 10^{-3}$

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3,589,893

SULFIDATION RESISTANT ALLOYS AND STRUCTURES

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Int. Cl. C22c 19/00
U.S. Cl. 75—171 14 Claims

ABSTRACT OF THE DISCLOSURE

A nickel-containing alloy and hot stage gas turbine parts made therefrom comprising in weight percent about 16% chromium, about 20% cobalt, a member of the group consisting of molybdenum, tantalum, columbium and mixtures thereof within the range of up to 4% molybdenum, up to 5% tantalum and up to 2.5% columbium (niobium), about 0.25% to about 5% tungsten, about 0.03% to about 0.2% carbon, about 0.005% to about 0.05% boron and about 0.01% to about 0.2% zirconium. The alloy also contains amounts of aluminum and titanium such that the ratio of the atomic percent aluminum to the atomic percent titanium is between about 1 and 2 and the total of the atomic percent titanium and the atomic percent aluminum is less than about 12 with the minimum amount of aluminum being about 2.5% by weight and the maximum amount of titanium being about 5% by weight and the balance of the alloy, except for impurities and incidental elements, being nickel.

The present invention is concerned with an alloy and parts made therefrom particularly adapted to withstand high stress at high temperatures and to be resistant to sulfidation corrosion.

When alloys are employed in hot stages of gas turbine engines, they are subjected in use to environments which include a combination of detrimental factors. When the engine is running, rotating hot stage turbine parts are subjected to high stress at high temperatures in a high velocity sulfur-containing corrosive and erosive atmosphere. When the engine is stopped, the hot stage parts cool. Thus in a gas turbine engine which is stopped and started in sequence, such as is common in aircraft usage, a suitable alloy must be resistant to stress at high temperature; it must be resistant to thermal fatigue and shock; it must be resistant to erosion and corrosion; and it must be stable. Failure in any of these areas can doom an otherwise suitable alloy. In addition to the foregoing, a suitable alloy must not be brittle either when cold or when hot and must be resistant to mechanical shocks occasioned when miscellaneous objects go hurtling into the engine air intake ducts and through the engine.

Of the many aforelisted jet engine, hot stage, alloy criteria and others, one of the more important is resistance to sulfidation corrosion. All practical jet engine fuels contain some organically bound slfur which is next to impossible to remove in refining procedures. The atmospheere itself contains significant amounts of sulfur compounds especially in the vicinity of large metropolitan and industrial centers. Thus the essential element for sulfidation corrosion, sulfur, is always present in the atmosphere rushing through an aircraft turbine rotor

housing. The atmosphere impelling against a turbine rotor not only contains sulfur dioxide and sulphate salts but also contains other deleterious substances all at an effective temperature of up to 2000° F. For example, chlorides such as sodium chloride and the like, can be present in sufficient concentration from atmospheric sources to abet, enhance, and even catalyze sulfidation corrosion of alloys in contact with fuel combustion products. It is known that at high temperatures sulfur dioxide and/or sulphate salts can both oxidize and sulfidize many nickel-base chromium-containing alloys. Under laboratory conditions, sodium chloride contamination can increase the rate of oxidation and sulfidation by a factor of ten or more. Experience has shown that the same holds true for actual jet engine service especially in chloride laden marine atmospheres.

When the gas turbine engine was first being developed (in the modern sense) in England in the 1930's, one of the first series of alloys used in hot stage parts were alloys similar to electric resistance wire alloy containing 80% nickel and 20% chromium. In low power engines, these 80–20 type alloys were substantially satisfactory, although, by today's standards, they are very weak. Gradually, over the years, metallurgical practice has been refined to the extendt that strong alloys, having adequate mechanical strength at temperature of 1800° F. and higher are currently available. In many instances, however, this superior mechanical strength has been gained in part by lowering chromium contents to about 9% at the cost of oxidation and sulfidation resistance. As hot stage temperatures in state of the art engines have crept up from about 1200° F. to 1800° F. and higher, corrosion problems relating to hot stage alloys including oxidation, sulfidation and erosion effects have become more and more severe. As it stands today, the art often is frustrated more by corrosion problems than by the problem of providing adequate strength. Thus the present invention is directed to an alloy having hot strength (including creep resistance) adequate for use in the most advanced gas turbine engines in combination with superior resistance to corrosion particularly sulfidation corrosion. An additional feature of the alloys of the present invention is that in obtaining adequate hot strength and corrosion resistance, we have, at the same time, provided in the same alloy excellent tensile strengths (U.T.S.) and yield strengths (Y.S.) at room temperature.

It is an object of the present invention to provide a novel alloy composition.

Another object of the present invention is to provide hot stage, gas turbine structures including rotors and turbine blades made of a novel alloy composition.

A still further object of the present invention is to provide novel hot stage integral turbine rotors and blades, turbine vanes, and integral nozzle vanes.

Other objects and advantages will become apparent from the following description taken in conjunction with the drawing in which:

FIG. 1 illustrates, in rectangular coordinate graphic form, the advantageous interrelation of the alloying elements aluminum and titanium in accordance with the present invention;

FIG. 2 shows a turbine rotor integral with blades;

FIG. 3 shows a typical turbine blade; and

FIG. 4 is a Larson-Miller parameter curve illustrating, in graphical form, strength characteristics of alloys in accordance with the present invention.

Generally speaking, the present invention contemplates a nickel-containing alloy comprising in weight percent about 16% chromium, about 20% cobalt, a member of the group cosisting of molybdenum, tantalum, columbium and miand mixtures thereof within the range of up to 4% molybdenum, up to 5% tantalum and up to 2.5% columbium, about 0.25% to about 5% tungsten, about 0.03% to about 0.2% carbon, about 0.005% to about 0.05% boron, about 0.01% to about 0.2% zirconium, amounts of aluminum and titanium such that the ratio of the atomic percent aluminum to the atomic percent titanium is between about 1 and 2 and the total of the atomic percent titanium and the atomic percent aluminum is less than about 12 with the minimum amount of aluminum being about 2.5% by weight and the maximum amount of titanium being about 5% by weight and the balance of the alloy, except for impurities and incidental elements being nickel, usually in amounts of about 35% to 58% by weight.

In order for those skilled in the art to more clearly visualize the amounts of aluminum and titanium contemplated as being included in alloys of the invention, FIG. 1 has been provided. Essentially this figure is a graph using rectangular coordinates on which percent by weight aluminum is plotted against percent by weight titanium. Within limits of graphical accuracy, the area ABCDE represents those combinations of aluminum and titanium contents which are contemplated as being included in alloys of the present invention. Line segment AE represents the minimum content of 25% by weight of aluminum. Line segments AB and ED represent the limits of the atomic percent ratio of aluminum-to-titanium of 1 to 2. Line segment CD represents the maximum of 5% by weight of titanium. Line segment BC represents the maximum summation of atomic percentages of titanium and aluminum, i.e. 12 atomic percent. The exact position of the line BC is not accurately depictable by graph since the atomic percentage of two elements in a complex alloy depends on the relative amounts of the other constituents. However, as depicted in FIG. 1, line segment BC is in a mean position. Whatever the exact position of line segment BC may be, its slope will remain substantially the same as depicted in FIG. 1 and its termini will be on line segments CD and AB or the interrupted extensions thereof. The maximum amount of aluminum in the alloy must, under no circumstances, exceed about 5% by weight. It is not contemplated that the compositional limits depicted in FIG. 1 by the area ABCDEA be considered as precise limitations. For example, line segments AB and ED representing the permisible limits of the atomic percent ratio of aluminum-to-titanium may be shifted laterally somewhat depending upon the exact cobalt content of the alloy. The interrupted lines paralleling line segments AB and ED on the right and left thereof are indicative of the permissible variation which is contemplated in accordance with the present invention. In particular, if the cobalt content of the alloy is as high as 25% by weight, line segment ED will be shifted to the extreme right position as indicated in FIG. 1 of the drawing.

While applicants do not wish to be held to any particular theory with respect to their invention, it is believed that the alloys described hereinbefore involve a number of metallurgical concepts which, in combination, provide advantageous alloy characteristics not fully achieved by the prior art. For example, the relatively high chromium and cobalt contents of the present alloys provide, in combination with the restricted aluminum-to-titanium atomic percent ratios, a combination of stability, corrosion resistance and good mechanical strength. If one lowers the atomic percent ratio as specified hereinbefore, it is possible to increase alloy strength but only at a severe stability price. Likewise, if one were to raise the chromium content above about 18% by weight, corrosion resistance might be improved but only at a penalty in strength and stability. Thus when one produces the alloy of the present invention using chromium contents of about 14% to 18% by weight and cobalt contents of about 15% to 25% by weight, in conjunction with the remainder of the compositional limits set forth hereinbefore, one achieves an expectedly high combination of practical engineering advantages in a single alloy. One of the surprising aspects of the alloys of the present invention is a newly discovered synerigistic effect existing among cobalt, aluminum and titanium. In an effort to improve the already excellent sulfidation resistance of a prior alloy, similar in overall composition to the present alloys except for cobalt content and the atomic percent ratio of aluminum-to-titanium, the cobalt content of that prior art alloy was increased from 10% by weight to 20% by weight. This increase resulted in a substantial lowering of stress rupture life at 1400° F. and 1880° F. A change in the atomic percent ratio of alumium-to-titanium at the prior art 10% by weight cobalt level to within that range of atomic percent ratio specified herein resulted in stability problems. However, when about 20% cobalt is used in association with the range of atomic percent ratio of aluminum-to-titanium as specified herein, the alloys are stable, the stress rupture life at 1400° F. and 1800° F. is equivalent to that of the prior alloy and the sulfidation resistance of the alloy is substantially enhanced. A further surprising and unexpected effect occurs. The low temperature tensile strength of the alloys of the present invention is unexpectedly higher than the low temperature tensile strength of the prior alloy. This unexpected phenomenon is highly useful in that the alloys of the present invention can be used not only for hot stage turbine parts which operate at relatively uniform high temperatures, i.e. turbine blades and guide vanes but also can be used for hot stage turbine parts such as an integral rotor blade unit wherein the hub portion operates under high stress at relatively low temperatures, e.g. up to about 1600° F. and the blade portions operate at somewhat lower stress at relatively high temperatures, e.g. up to about 2000° F. FIG. 2 of the drawing depicts an integral turbine rotor blade unit having hub **11** which operates at relatively low temperatures and blades **12** which operate at relatively high temperatures due to impingement on the surfaces thereof of hot, product-of-combustion gases containing corrosion-inducing amounts of sulfur dioxide and/or sulfate salts. It is to be understood that the novel alloys of the present invention can be used with advantage not only in the manufacture of such integral units but can also be used for turbine blades and guide vanes and other turbine hardware subjected in use to relatively uniform high temperatures through contact with such product-of-combustion gases. FIG. 3 shows a turbine blade of the present invention made of an alloy of the present invention having fir-tree root portion **13**, blade portion **14** having an airfoil shaped cross section, and platform area **15** therebetween.

The alloys of the present invention can be processed as forgings or castings but are particularly adapted to be cast to shape by means of the usual state of the art, vacuum, precision casting techniques. Master melts are made by melting the basic alloying ingredients under vacuum, deoxidizing, and adding oxygen sensitive elements with the boron and/or zirconium usually being added last. As is usual with nickel-containing alloys it is necessary to scrupulously avoid contamination by elements such as lead which form low melting and/or embrittling phases. Illustrative amounts in percent by weight of incidental elements which may be present in the alloys of the invention and which, in the amounts specified, do not materially alter the basic and novel characteristics of the invention include up to .35% manganese, up to .35% silicon, up to 1.0% iron, up to .02% sulfur, up to .20% copper and up to .02% phosphorus. Highly advantageous results are obtained when the alloys of the present invention contain relatively large amounts of tungsten, i.e. 2.2% to about 5% by weight. It is equally advantageous when

molybdenum is present in alloys of the present invention to include at least about 1% of metal from the group of tantalum and columbium.

While the alloys of the present invention can be formulated anywhere within the aforestated ranges, it is advantageous to maintain the alloy composition within commercial production limits of the compositions set forth in Table I.

TABLE I

	Composition "A"		Composition "B"	
	Percent by wt.	Atomic percent	Percent by wt.	Atomic percent
Element:				
Al	2.8	5.85	2.8	5.9
B	0.015	0.06	0.015	0.06
C	0.15	0.74	0.15	0.74
Cr	15.5	16.95	15.5	17.04
Co	19.7	19.0	19.7	19.1
Cb	2.0	1.2	2.0	1.2
Mo	2.0	1.2		
Ni	Balance	48.9	Balance	49.23
Ta			2.0	0.63
Ti	4.2	5.05	4.2	5.09
W	3.1	0.96	3.1	0.97
Zr	0.06	0.06	0.06	0.06

It is to be noted from Table I that the compositions A and B set forth therein have total aluminum and titanium atomic percentages of 10.9% and 11.0%, respectively. It is further to be noted that the sum of the atomic percentages of molybdenum, tungsten, tantalum and columbium are 3.36 and 2.80, respectively. It is necessary in order for the alloy to be stable that the sum of the atomic percentages of the four elements—molybdenum, tungsten, tantalum and columbium—be less than a total of about 4.8% (atomic). It is highly advantageous that there be at least about 0.5% by weight of metal from the group of molybdenum, tantalum and columbium in the alloy. If the chromium content of the alloys is relatively low, for example about 13% to 14.5% by weight, it is advantageous for oxidation and sulfidation resistance to maintain the tantalum content at or near 5% by weight, that is approximately 1.5% or 1.6% (atomic percent). Consequently, under such circumstances, the contents of molybdenum, tungsten and columbium in the alloy should be carefully controlled to avoid exceeding the aforesaid total maximum of 4.8 atomic percent. Best results appear evident when at least two of the members of the group consisting of molybdenum, tantalum and columbium are copresent in the alloy in a total amount of at least 3% by weight.

After master heats of the alloy have been made, the alloy can be remelted and cast in vacuum using the method of precision casting. This technique is particularly applicable to the manufacture of integral turbine rotors and blades as depicted in FIG. 2 as well as to the manufacture of other hot stage turbine structures. As is well known in the art, a model in wax or other model material is made of the part to be produced; adequate pouring basins, gates and risers are attached to the model; the model with its accouterments is invested with ceramic; the model is removed from the ceramic shell; and, after the shell has been matured by heat, metal is cast therein, advantageously under high vacuum. Test specimens of all the specific alloy compositions discussed hereinafter were made using such a precision casting technique. In practice, the alloy was superheated to a temperature of 2850° F. and poured into appropriately shaped, preheated, ceramic shell molds held in a vacuum. The well known advantages of precision casting are that complex undercut shapes can be cast, and, in cases such as the integral turbine rotor and blades depicted in FIG. 2, relatively little machining is necessary to produce the final finished article. It is highly advantageous to cast alloys of the present invention in accordance with the teachings of U.S. patent application Ser. No. 684,916 filed Nov. 22, 1967 concurrently herewith in the name of John Hockin entitled "Casting Process" now U.S. Pat. No. 3,552,479, granted Jan. 5, 1971 for "Casting Process Involving Cooling of a Shell Mold Prior to Casting Metal Therein." In accordance with these teachings a ceramic shell mold is permitted to cool, for example from 1900° F. for a short time prior to casting metal therein. Each of the examples of the present invention discussed herein were cast in this manner.

After the casting is cooled, all gates, risers and the like have been removed and any mechanical finishing is completed, it is advantageous to heat treat the casting by holding it at a temperature between about 2000° F. and 2200° F. for about 1 to about 4 hours. Subsequent thereto the casting is held at a temperature of about 1800° F. to 2000° F. for about 1 to about 8 hours, followed by aging at a temperature from 1350° F. to 1700° F. for about 10 to 50 hours. Once the heat treating process is completed the casting is ready for service. An advantageous heat treating schedule comprises 2 hours at 2100° F., 4 hours at 1975° F., and 16 hours at 1400° F. The purpose of holding the casting at the higher temperature is to dissolve the gamma prime compounds, usually designated $Ni_3(Al \cdot Ti)$ in the basic solid solution, along with certain of the carbides existing in the as-cast condition, while holding the casting at the lower temperatures serves to reprecipitate the gamma prime compounds and carbides in the most advantageous places and in the most advantageous sizes.

In order to give those skilled in the art a greater appreciation of the advantages of the invention, the following examples are given:

EXAMPLE I

An alloy having a specific composition within commercial tolerances of composition "B" set forth in Table I was made and was analyzed. The alloy contained (in percent by weight) 2.87% aluminum, 0.016% boron, 0.15% carbon, 15.4% chromium, 20.0% cobalt, 1.95% columbium, 2.0% tantalum, 4.48% titanium, 2.94% tungsten, 0.14% zirconium, with the balance being essentially nickel. Test specimens were cast from this alloy by precision casting techniques. Mechanical characteristics of this alloy determined on specimens which were heat treated after casting by being held for two hours at 2100° F., followed by holding for four hours at 1975° F., followed by holding for 16 hours at 1400° F. are set forth in Table II.

TABLE II

Room temperature U.T.S.	[1] 187.9K s.i.
Room temperature Y.S.[2]	146.6K s.i.
Elongation	7 percent.
Reduction in area	9.2 percent.
14–85 life-to-rupture [3]	212.5 hours (5% elongation).
18–22 life-to-rupture [4]	59.2 hours (10% elongation).

[1] K.s.i.=thousands of pounds per square inch.
[2] 0.2% offset.
[3] 14–85%=tested at a temperature of 1400° F. with a load of 85 K. s.i.
[4] 18–22=tested at a temperature of 1800° F. with a load of 22 K. s.i.

Table II shows that castings made from the alloy of the present invention exhibit excellent room temperature strength and ductility in combination with adequate or more than adequate stress rupture strengths and ductility at 1400° F. and 1800° F. The alloy of Example I, in common with all the alloys of the present invention, is stable. Thus all of the alloys of the present invention resist the formation of plate-like phases, e.g. sigma phase and laves phase, particularly when subjected to temperatures of about 1300° F. to 1800° F. for substantial periods of time. It is well known that such plate-like phases decrease the ductility of nickel-containing alloys during service and lead to premature failures. Alloys of the present invention have been found to be free of detrimental phases after being held for 3000 hours at 1550° F. All of the alloys of the present invention are highly resistant to sulfidation corrosion. A laboratory test simu-

lating the conditions of sulfidation corrosion generally accepted by turbine engine manufacturers comprising immersing a weighed alloy sample half way in a liquid in a Vycor crucible, the liquid consisting of a molten mixture of 9.5 parts by weight of sodium sulfate and 0.5 part by weight of sodium chloride. The crucibles are positioned in an Inconel metal tray and placed in a furnace maintained at 1700° F. for 24 hours. After heating is completed, the salts are dissolved off in boiling water and the samples sandblasted clean and reweighed. The weight loss per unit of surface area is calculated and attack has heretofore been deemed severe if the loss exceeds 30 milligrams per square centimeter (mg./cm.^{2}). Alloys having weight losses less than 10 mg./cm.^{2} have heretofore been considered to have good sulfidation resistance. Under these test conditions, alloys of the present invention exhibit maximum weight losses of about 3 mg./cm.^{2} thus indicating the extraordinary resistance of the present alloys to sulfidation corrosion. The alloy of Example I exhibited a weight loss of only 0.83 mg./cm.^{2}.

EXAMPLE II

An alloy within commercial tolerance of composition "A" of Table I was made and analyzed. The alloy contained in percent by weight 2.79% aluminum, .015% boron, .11% carbon, 15.3% chromium, 19.7% cobalt, 1.99% columbium, 1.98% molybdenum, 4.15% titanium, 3.1% tungsten, .06% zirconium, with the balance being essentially nickel. After the same heat treatment as specified in Example I, the alloy exhibited the mechanical characteristics set forth in Table III.

TABLE III

Room temperature tensile strength	181.9K. s.i.
Room temperature yield strength	145K. s.i.
Elongation	10 percent.
Reduction in area	7.9 percent.
14–85 life-to-rupture	148.6 hours (7.5% elongation).
18–22 life-to-rupture	23 hours (14.5% elongation).

The data in Table III shows that the alloy of Example II has only slightly less advantageous mechanical characteristics at elevated temperatures than the alloy of Example I, the mechanical characteristics of the alloy of Example II being quite adequate for the intended usages. By virtue of the substitution of 2% by weight of molybdenum for 2% by weight of tantalum, the alloy of Example II can offer a slight price advantage over the alloy of Example I while substantially retaining the excellent stability and sulfidation corrosion resistance of the slightly more expensive alloy. Specifically, the alloy of Example II showed no detrimental phases after being held for 3000 hours at 1550° F. and showed a weight loss of 2.5 mg./cm.^{2} in the aforedescribed sulfidation corrosion test. The alloy of Example II exhibits slightly improved elongation which can be of advantage in applications such as integral turbine wheels.

Additional examples of alloys of the present invention are set forth in Table IV. All of the alloys in Table IV are stable and exhibit extraordinarily low rates of sulfidation corrosion.

TABLE IV

	Percent by weight	
Example No.	3	4
Element:		
Al	2.8	3.45
B	0.015	0.017
C	0.15	0.12
Cr	15.5	15.4
Co	19.7	19.8
Cb	----	2.07
Mo	2.0	1.98
Ni	Balance	----
Ta	3.8	----
Ti	4.2	3.11
W	3.1	3.39
Zr	0.06	0.06

In comparison to the alloys of the present invention and their advantageous combination of significant engineering characteristics, alloys outside the present invention are set forth in Table V. All of the alloys of Table V are stable with the exception of alloys A and B, but lack one or more of the advantageous features exhibited in combination by the alloys of the present invention.

Table V shows that alloys B through F exhibit relatively poor resistance to sulfidation corrosion. None of the listed alloys for which data is available exhibits as good resistance to sulfidation corrosion as the alloys of the present invention. The room temperature tensile strengths of all the alloys A through H are very low when compared to the room temperature tensile strengths of alloys of the present invention. With the exception of alloy H an even more spectacular difference between the alloys of Table V and the alloys of the present invention appears when the life-to-rupture at 1400° F. and 85,000 p.s.i. is considered. Most of the alloys of Table V exhibit lives-to-rupture at 1400° F. under a load of 85,000 p.s.i. of less than 100 hours. In this regard, the alloys of the present in-

TABLE V.—ALLOY IDENTIFICATION

[Elemental amounts in percent by weight]

	713C A	713C B	21A4 C	21G D	21C E	21D F	21A3 G	21D4 H	I	J
Element:										
Al	6.0	6.0	4.1	4.9	4.4	4.5	6.0	4.25	----	
B	0.012	0.010	0.018	0.011	0.016	0.018	0.012	0.015	----	
C	0.12	0.14	0.18	0.16	0.18	0.18	0.13	0.15	----	
Cr	13	14.5	19.2	15.8	15.7	15.7	15.9	15.5	----	
Co	----	1.0	18.8	10.1	10.2	10.0	----	10.0	----	
Cb	2.0	1.8	----	----	----	2.2	1.9	1.75	----	
Mo	4.5	4.1	4.3	4.1	----	2.1	----	1.75	----	
Ni	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.		
Ta	----	----	----	2.0	4.3	----	1.2	----	----	
Ti	0.75	0.77	3.2	2.1	1.8	2.1	1.0	1.75	----	
W	----	----	----	----	4.5	3.8	4.8	3.5	----	
Zr	0.1	0.11	0.058	0.56	0.049	0.054	0.039	0.05	----	
Characteristics	X	X	X	X	X	X	X	X	----	
R.T.U.T.S., K s.i.	123	129	111	127	138	130	140	154	----	
R.T.Y.S. (0.2%), K s.i.	107	120	101	110	119	120	128	134	----	
Elongation, percent	8	2	2.5	5.0	5.0	4.0	3.0	4.5	----	
Red. in area, percent	12	4.7	3.0	6.1	7.0	5.2	6.0	5.7	----	
14–85 L.T. rupt.[1]	80h-6	22.4h-2	4.8h-7.0	13.5h-4.0	26.h-20	57.7h-4.5	12.6h-1.5	143.4h-5	----	
Sulfid. cor. in mg./cm.^{2}	----	132	242	535	27	27	4	5	----	

[1] The first figure is hours and the second figure is the value of the percent elongation.

substantially superior to the remainder of the alloys in Table V. The alloys of the present invention are unexpectedly superior to alloy H in resistance to sulfidation corrosion and in room temperature tensile characteristics. Directly comparable data for comparison of stress rupture characteristics at 1800° F. of alloys A to H and the alloys of the present invention is not currently available and thus has not been included herein. However, extrapolation of currently available data indicates that the relative merit of the alloys in stress rupture tests at 1400° F. is substantially the same at 1800° F. with the exception that at 1800° F. alloy A exhibits substantially the same life-to-rupture as do alloy H and the alloys of the present invention.

FIG. 4 of the drawing has been provided to provide a clearer understanding of the advantages of alloys of the present invention. This figure is a conventional Larson-Miller parameter graph showing curves for the alloys of Examples I and II, respectively, and, being directed to those skilled in the art, needs no further explanation.

As mentioned hereinbefore, an important aspect of the present invention is providing novel structures for use in the hot stages of gas turbines. Such structures include turbine blades, guide vanes, integral rotors and blades and other parts. The high room temperature tensile characteristics of the alloys of the present invention make possible the precision casting of parts which have strengths at low temperature substantially equivalent to forged parts. In addition to hot stage turbine structures, the alloys of the present invention can be used to make high strength structural parts which require resistance to corrosion at room temperature or elevated temperatures. The presently disclosed alloys are useful applications where alloys such as 410 stainless steel or 17–4 pH stainless steel are currently being used.

While the present invention has been described in conjunction with advantageous embodiments, those skilled in the art will recognize that modifications and variations may be resorted to without departing from the spirit and scope of the invention. Such modifications and variations are considered to be within the purview and scope of the invention .

We claim:

1. A nickel-containing alloy consisting essentially of in weight percent about 16% chromium, about 20% cobalt, a member of the group consisting of molybdenum, tantalum, columbium and mixtures thereof within the range of up to 4% molybdenum, up to 5% tantalum and up to 2.5% columbium, about 0.25% to about 5% tungsten, about 0.03% to about 0.2% carbon, about 0.005% to about 0.05% boron, about 0.01% to about 0.2% zirconium, amounts of aluminum and titanium such that the ratio of the atomic percent aluminum to the atomic percent titanium is between about 1 and 2 and the total of the atomic percent titanium and the atomic percent aluminum is less than about 12 atomic percent with the minimum amount of aluminum being about 2.5% by weight and the maximum amount of titanium being about 5% by weight and the balance of the alloy, except for impurities and incidental elements, being nickel.

2. An alloy as in claim **1** containing at least about 2.2% by weight of tungsten.

3. A precision cast alloy object made of the alloy of claim **1.**

4. A precision cast hot stage gas turbine structure made of the alloy of claim **1.**

5. A nickel-containing alloy consisting essentially of in weight percent about 13% to about 18% chromium, about 20% cobalt, at least two members of the group consisting of molybdenum, tantalum and columbium within the range of up to 4% molybdenum, up to 5% tantalum and up to 2.5% columbium with the total of said at least two members being at least about 3%, about 0.25% to about 5% tungsten, about 0.03% to about 0.2% carbon, about 0.005% to about 0.05% boron, about 0.01% to about 0.2% zirconium, amounts of aluminum and titanium such that the ratio of atomic percent aluminum to the atomic percent titanium is between about 1 and 2 and the total of the atomic percent aluminum and the atomic percent titanium is less than about 12 atomic percent with the minimum amount of aluminum being about 2.5% by weight and the maximum amount of titanium being about 5% by weight and the balance of the alloy, except for impurities and incidental elements, being nickel, said elements in said alloy being correlated such that the sum of the atomic percentages of molybdenum, tungsten, tantalum and columbium is less than about 4.8 atomic percent.

6. A precision cast alloy object made of the alloy of claim **5.**

7. A precision cast hot stage gas turbine structure made of the alloy of claim **5.**

8. An alloy as in claim **5** containing at least about 2.2% by weight of tungsten.

9. A nickel-containing alloy consisting essentially of in percent by weight about 2.8% aluminum, about 0.015% boron, about 0.15% carbon, about 15.5% chromium, about 19.7% cobalt, about 2.0% columbium, about 2.0% molybdenum, about 4.2% titanium, about 3.1% tungsten, about 0.06% zirconium, with the balance of the alloy, except for impurities and incidental elements, being nickel.

10. A nickel-containing alloy consisting essentially of in percent by weight about 2.8% aluminum, about 0.015% boron, about 0.15% carbon, about 15.5% chromium, about 19.7% cobalt, about 2.0% columbium, about 2.0% tantalum, about 4.2% titanium, about 3.1% tungsten, about 0.06% zirconium, with the balance of the alloy, except for impurities and incidental elements, being nickel.

11. A nickel-containing alloy consisting essentially of in weight percent about 2.8% aluminum, about 0.015% boron, about 0.15% carbon, about 15.5% chromium, about 19.7% cobalt, about 4% total of at least two members of the group of columbium, molybdenum and tantalum, about 4.2% titanium, about 3.1% tungsten, about 0.06% zirconium with the balance of the alloy, except for impurities and incidental elements, being nickel.

12. An article of manufacture for use in a hot stage of a gas turbine having at least one surface adapted to resist hot corrosion, induced when in use, by contact with hot product-of-combustion gas containing a corrosion inducing amount of oxidation products of sulfur impinging against said at least one surface, said article being made of a nickel-containing alloy consisting essentially of in weight percent about 16% chromium, about 20% cobalt, a member of the group consisting of molybdenum, tantalum, columbium and mixtures thereof within the range of up to 4% molybdenum, up to 5% tantalum and up to 2.5% columbium weight of said group is present in the alloy, about 0.25% to about 5% tungsten, about 0.03% to about 0.2% carbon, about 0.005% to about 0.05% boron, about 0.01% to about 0.2% zirconium, amounts of aluminum and titanium such that the ratio of the atomic percent aluminum to the atomic percent titanium is between about 1 and 2 and the total of the atomic percent titanium and the atomic percent aluminum is less than about 12 with the minimum amount of aluminum being about 2.5% by weight and the maximum amount of titanium being about 5% by weight and the balance of the alloy, except for impurities and incidental elements, being nickel.

13. An article of manufacture as in claim **12** having a hub area adapted to operate at relatively low temperatures and blade areas integral therewith and radially extending outwardly therefrom adapted to operate at high temperatures in contact with hot product-of-combustion

gases containing a corrosion inducing amount of oxidation products of sulfur.

14. An article of manufacture as in claim **12** wherein the alloy contains

(A) at least about 2.2% by weight tungsten, and

(B) at least two of the elements molybdenum, tantalum and columbium

and wherein the sum of the atomic percentages of tungsten, molybdenum, tantalum and columbium is less than about 4.8 atomic percent.

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RICHARD O. DEAN, Primary Examiner

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148—32.5, 162

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,589,893 Dated June 29, 1971

Inventor(s) Carl H. Lund et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 25, "extendt" should be -- extent --.

Column 3, line 5, "miand" should not be in before "mixtures".

Column 3, line 30, "25%" should be -- 2.5% --.

Column 4, line 9, "synerigistic" should be -- synergistic --.

Column 4, line 17, "1880°F." should be -- 1800°F. --.

Column 5, line 48, before "3%" the word -- about -- was left out.

Columns 7 and 8 - in TABLE V under Column "21G -D" - twelfth line down in table - "0.56" should be -- 0.056 --.

Column 9, line 1, before "substantially" the following was left out: -- vention are equal to, if not better than, alloy H and are --.

Column 10, line 1, the following was inserted by mistake and should be cancelled: "vention are equal to, if not better than, alloy H and are".

Signed and sealed this 28th day of December 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patents

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