Dec. 10, 1968 E. W. ROSS 3,415,641

WROUGHT NICKEL BASE ALLOY

Filed Aug. 24, 1966 2 Sheets-Sheet 1

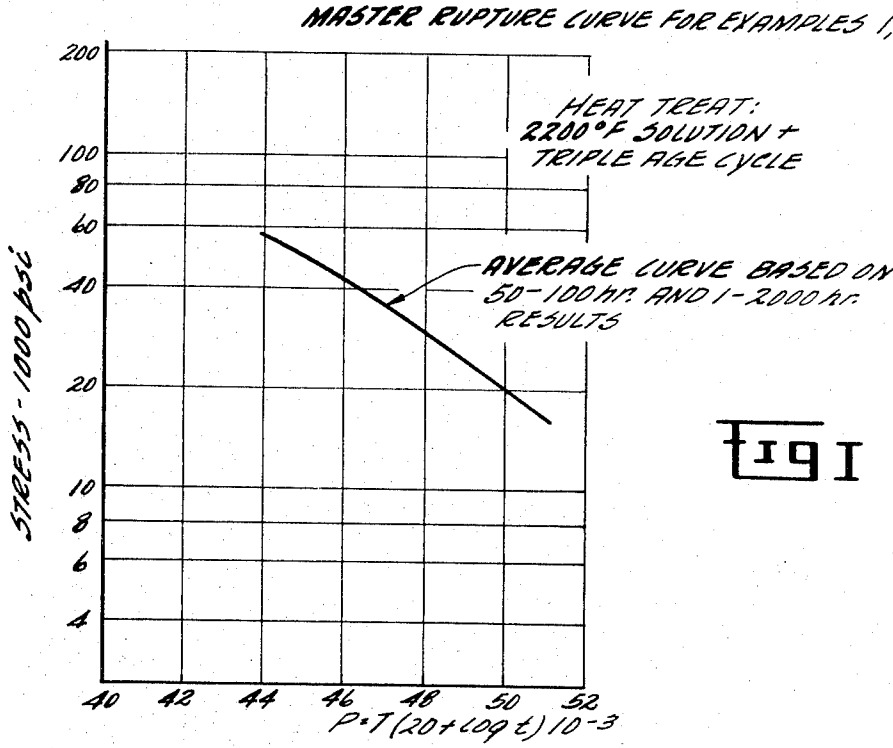

Fig 1

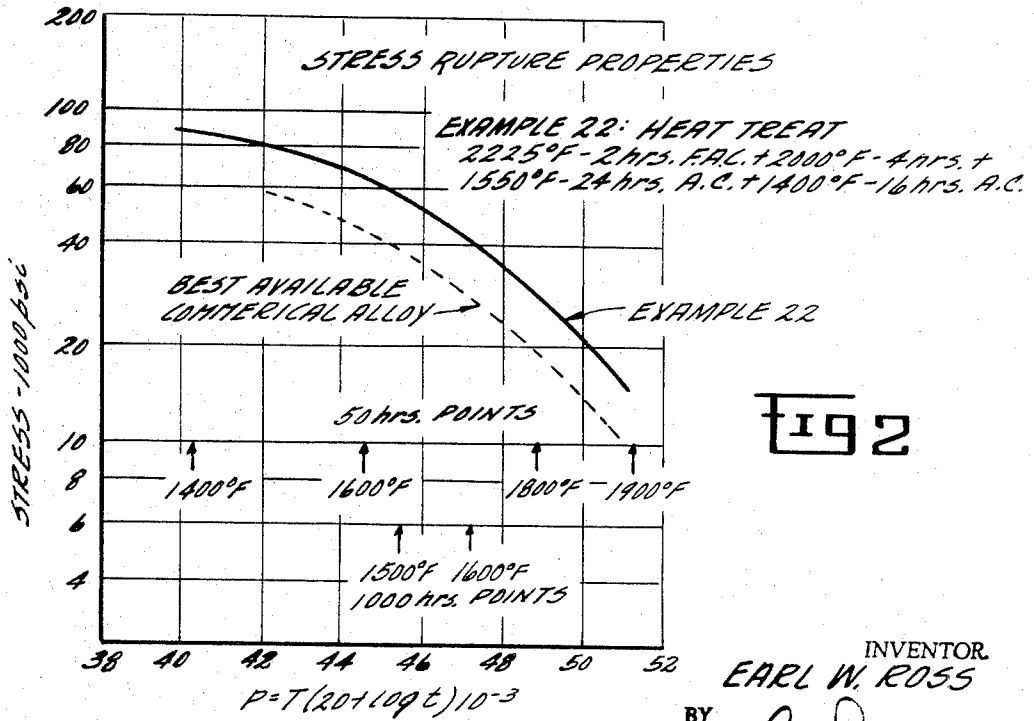

Fig 2

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WROUGHT NICKEL BASE ALLOY

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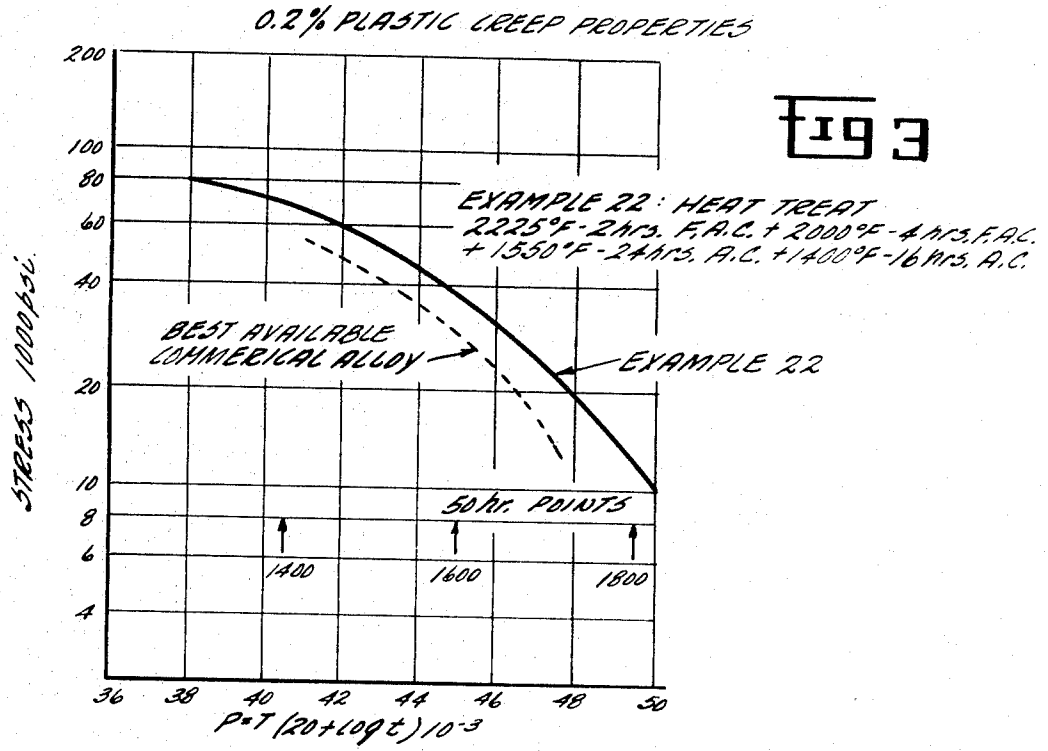

FIG 3

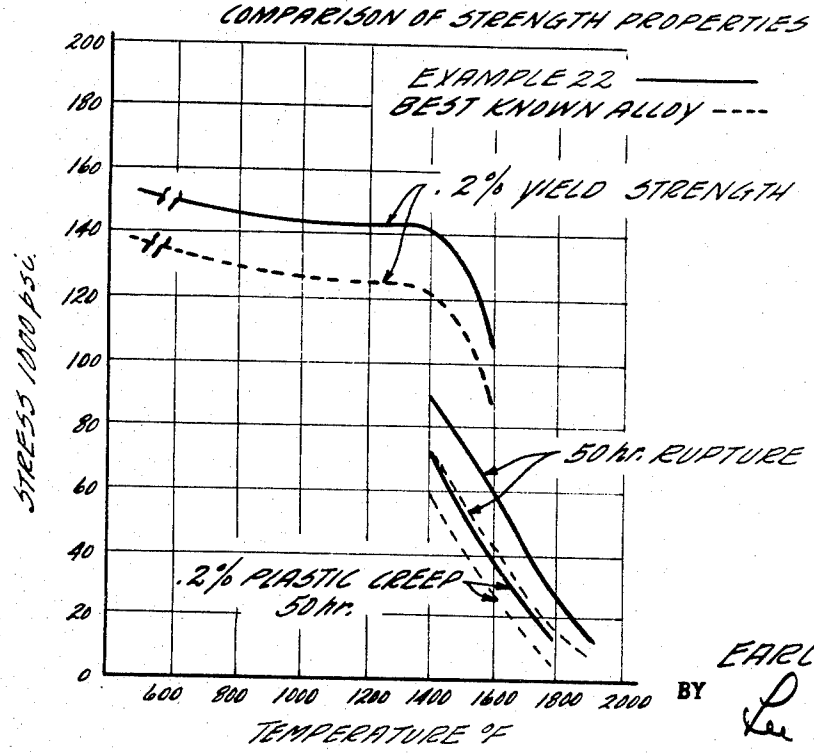

FIG 4

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WROUGHT NICKEL BASE ALLOY

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5 Claims. (Cl. 75—171)

This invention relates to nickel base alloys suitable for use at elevated temperatures. More particularly, it relates to a wrought nickel base alloy having stability for long times at temperatures up to about 1900° F. and having improved stress rupture and creep properties.

Many years of careful study of the nickel base superalloys have led to the identification of various structural phases affecting properties of the alloys or of articles made from the alloys. While some of the phases are beneficial, some have been shown to be undesirable. One of the phases more recently reported as very detrimental to high temperature and long time stability is known to metallurgists as sigma phase.

A typical article including some known alloys and earlier references regarding sigma phase is "Preventing Sigma Phase Embrittlement in Nickel Base Superalloys" by Boesch and Slaney in Metal Progress, July 1964, pp. 109–111.

Sigma phase has been identified in some nickel base superalloys as a direct function of the quantities of certain strengthening elements. Thus as the nickel base superalloy technology has developed and as strengthening elements such as the precipitation hardeners aluminum and titanium and the solution strengtheners tungsten, molybdenum and chromium have been added in increasing amounts, the frequency and amount of sigma phase formation has increased. This has been true particularly during long time exposure at elevated temperatures.

Because the formation of sigma phase is a function of the alloy content, sigma phase will recur when the alloy is subjected to certain temperatures for periods of time even though sigma phase may be removed temporarily by heat treatment. Thus it has been recognized that presently the formation of sigma phase can only be inhibited by a careful adjustment of the composition of the alloy. Unfortunately, studies prior to the discovery of the alloy of the present invention have shown that reduction of the hardening elements in nickel base superalloys result in a similar reduction in certain strength properties.

Therefore, it is an object of the present invention to provide an improved wrought nickel base alloy having a particular grouping of elements in ranges which inhibit the formation of sigma phase thus providing long time stability at elevated temperatures, such as up to about 1900° F., with little or no sacrifice of strength and oxidation resistance properties.

Another object is to provide a nickel base alloy having improved long time stability, increased stress rupture life ann improved creep properties.

Still another object is to provide for a gas turbine engine a wrought turbine blade capable of being used at elevated temperatures for long periods of time while at the same time maintaining improved strength and corrosion resistance characteristics.

These and other objects and advantages will be more clearly understood from the following detailed description, representative examples and the drawing in which:

FIG. 1 is a graphical presentation of the average stress rupture properties of Examples 1–3 within the scope of the present invention; and

FIGS. 2, 3 and 4 are graphical presentations of the rupture creep and yield strength properties of specimens of the alloy of the present invention taken from forged turbine blades compared with the best commercially available wrought turbine blade alloy.

Fulfillment of the above objects can be achieved for a wrought nickel base superalloy by maintaining the carbon level in the range of 0.2–0.3 weight percent and reducing the chromium content to the range of 9–12 weight percent, while at the same time carefully adjusting the strengthening elements Al, Ti, Mo and W in a nickel base including cobalt, boron and optionally zirconium. It was uexpectedly discovered that by reducing the chromium content for such alloys to the range of 9–12 weight percent, certain larger amounts of the strengthening elements aluminum and titanium could be added without causing sigma phase formation. This change did not reduce the alloy's oxidation resistance up to about 1900° F. while inhibiting the formation of the detrimental sigma phase. The sum of the precipitation strengthening elements aluminum and titanium must be controlled within the range of 8–9 weight percent with the aluminum included in the range of 4.5–6 weight percent and the titanium in the range of 3–4 weight percent. Broadly, the composition of the alloy of the present invention consists essentially of, by weight, 0.2–0.3% C; 0.005–0.002% B; 14–16% Co; 9–12% Cr; 3–4% Mo; 4.5–6% Al; 3–4% Ti; 5–6% W; up to about 0.05% Zr with the balance essentially nickel and incidental impurities, the sum of the Al and Ti being in the range of 8–9%.

Certain known nickel base superalloys which were considered for manufacture into turbine blades for advanced gas turbine apparatus for use up to about 1900° F. either are too weak in the wronght form or do not have sufficient ductility, fatigue strength or stability in the cast form for such application. Attempts to increase the strength of such wrought nickel base superalloys through the addition of precipitation strengtheners as Al, Ti and Cb as well as solution strengtheners as W and Mo along with Cr have resulted in heavy precipitation of sigma phase after elevated temperature exposure. Sigma phase formation can occur in a short period of time or can take thousands of hours depending on the variation in alloy chemistry and the temperature and stress applied. In any event, significant amounts of sigma phase formation results in loss of rupture life and causes low temperature brittleness.

In attempting to improve the strength of wrought nickel base superalloys, one logical approach is to increase the amount of aluminum and titanium which together with nickel form the complex phase Ni_3 (Al, Ti). Although reported studies prior to the present invention have specified the inclusion of Al and Ti in larger amounts, for example a total of more than 9 weight percent, the present invention has identified that in the presence of larger amounts of carbon in the range of 0.2–0.3 weight percent, the sum of aluminum and titanium must be maintained at 9 weight percent or less. As will be shown in detail in the examples, the reduction of the chromium level to the range of about 9–12 weight percent allows the use of the sum of aluminum and titanium up to about 9% for precipitation strengthening and, at the same time, inhibits sigma phase formation.

The solution strengthening elements molybdenum and tungsten are other elements in addition to the aluminum, titanium and chromium which along with carbon affect the long time stability of the alloy. As will be shown in detail later in connection with the examples, tungsten and molybdenum are included in particular ranges and are not interchangeable one with the other as is indicated to be possible in some prior work.

The present invention will be more fully understood from the following detailed examples which are typical

of but are not meant to be limitations on the scope of this invention.

Typical of the alloys melted, cast, reduced and tested in the evaluation of the present invention are those listed in the following Table I. These alloy forms, as well as the other alloys shown in other tables, were vacuum cast into 5" diameter 50 pound cropped ingots. They were then extruded to a 3" diameter size after which they were either flattened or further extruded for test purposes.

TABLE I

[Weight percent, Bal. Ni and impurities]

Ex.	C	B	Co	Cr	Mo	Al	Ti	W	Cb	Al+Ti
1	.28	.017	15.1	11.1	3.5	5.3	3.0	5.3	-------	8.3
2	.28	.017	15.1	11.3	3.6	5.0	3.5	5.5	-------	8.5
3	.28	.016	15.1	11.3	3.6	5.3	3.3	5.4	-------	8.6
4	.24	.019	13.7	9.1	3.0	4.7	2.8	4.9	-------	7.5
5	.27	.017	15.1	11.3	3.8	5.2	3.3	5.7	1.1	8.5
6	.28	.015	15.0	11.1	3.7	5.2	3.2	5.5	0.8	8.4

Of the alloy forms in Table I, Examples 1, 2 and 3 fall within the scope of the present invention having a composition consisting essentially of, by weight, 0.2–0.3% C; 0.005–0.02% B; 14–16% Co; 9–12% Cr; 3–4% Mo; 4.5–6% Al; 3–4% Ti; 5–6% W with the balance essentially nickel and incidental impurities, the sum of the Al and Ti being in the range of 8–9%. Examples 4 through 6 of Table I are outside the scope of the invention because in Example 4 the sum of the Al and Ti is too low with respect to the 8–9% range or because in Examples 5 and 6 the alloy includes the element columbium. As will be shown in the following Table II, these differences though numerically small are significantly great as they relate to long time stress rupture properties and as they relate to the formation of the detrimental sigma phase which affects the stability of the alloy. The properties of the various alloy forms including the same elements as those within the scope of the present invention as well as Examples 5 and 6 including columbium are shown in the following Table II.

TABLE II

[Long Time Stress Rupture Properties]

Ex.	Condition	Life (hrs.)	El. (percent)	R.A. (percent)	Grain Size	Sigma Phase
1	1,600° F. 35 Ks.i	1,131	6.3	10.1	3-4	None.
2	1,600° F./35 Ks.i	1,312	10.3	12.1	3-4	Do.
3	1,600° F./35 Ks.i	973	15.2	15.6	3-4	None to slight.
4	1,600° F./35 Ks.i	544	9.1	8.5	4	None.
5	1,600° F./35 Ks.i	520	15.3	20.8	3-4	Heavy.
6	1,600° F./35 Ks.i	837	17.2	23.1	4-5	Medium.
1	1,500° F./45 Ks.i	2,394	7.0	9.3	3-4	None to slight.
2	1,500° F./45 Ks.i	2,325	6.0	6.8	3-4	Do.
3	1,500° F./45 Ks.i	2,803	10.8	11.3	3-4	Do.
4	1,500° F./45 Ks.i	1,110	5.3	5.3	3-4	None.
5	1,500° F./45 Ks.i	1,075	20.7	10.7	2-3	Heavy.
6	1,500° F./45 Ks.i	1,648	7.1	7.7	3-4	Medium.

The master stress rupture curve for Examples 1–3 is shown in FIG. 1 presented in the well known Larson-Miller Parameter form more fully described in Example 4, although the aluminum is in the proper range, the titanium at 2.8 weight percent is too low. The lower combination of aluminum and titanium in Example 4 eliminated the formation of sigma phase. However, as was stated above, such reduction has resulted in a significant decrease in properties such as long time stress rupture strength.

As was mentioned above, Examples 1, 2 and 3 fall within the scope of the present invention whereas Examples 4 through 6 are outside the scope. By comparing Examples 1, 2 and 3 with Examples 4 through 6 under the two conditions listed in Table II for long time stress rupture properties, it is easily seen that significant differences both in phase structure and strength properties exist. For instance, Examples 1 through 3 have stress rupture lives of 973–1312 hours with good ductility and little, if any, sigma phase formation when tested at 1600° F. under a stress of 35,000 p.s.i. When tested under the same conditions, Examples 4 through 6 either were too weak to be considered as an improved structural material or had significant amounts of sigma phase formation or both. Although reduction in the sum of aluminum and titanium in Example 4 eliminated the formation of the detrimental sigma phase, the strength properties were significantly reduced to less than half of that of the alloy of the present invention.

In Example 4, the primary difference is that the sum of the aluminum and titanium content is below the range of this invention. For such a small numerical difference, note the great difference in strength, the detrimental effect of higher content, particularly of Ti, is shown in detail later with respect to Table III compositions. Thus, it can be seen that the effect of the sum of the aluminum and titanium on sigma phase formation is critical. The data shown in Table II as it relates to testing at 1500° F. and 45,000 p.s.i. of the examples of Table I shows the same significant strength property differences based on metal structure differences though the chemistry may appear numerically to be relatively close.

Columbium is sometimes included in other nickel base alloys as a precipitation hardener. However, the effect of columbium on long time stress rupture strength and sigma phase formation is easily seen from the data of Table II by the medium-heavy sigma phase formation. Therefore, the elements aluminum and titanium have a different effect on the alloy of the present invention than does the element columbium in the presence of higher carbon within the range of the present invention. Similarly, alloying additions greater than the composition of the present invention tend to cause sigma phase formation and are to be avoided.

In heat treatment studies to determine the best heat treatment for the type of alloy to which the present invention relates, it was found that a solution heat treatment followed by triple aging resulted in better overall properties. Consequently, the alloy forms tested in Table II were solution heat treated at about 2200° F. for 2 hours followed by furnace air cooling. Then they were heated to 2000° F. for 4 hours after which they were furnace air cooled at 1550° F. for 24 hours, air cooled and then heated to 1400° F. for 16 hours followed by air cooling. The specimens were machined from bar stock which had received this optimum heat treatment.

Tensile testing of the alloy forms of Table I both at room temperature and at 1300° F. showed the tensile properties to be approximately the same. For example, at room temperature the ultimate tensile strength varied between 166,000–185,000 p.s.i., the 0.2 yield strength varied between 147,000–157,000 p.s.i. and the percent elongation ranged between about 5–9% except for Example 4 which had slightly higher ultimate strength and lower yield strength and much greater elongation. At 1300° F. the ultimate tensile strength was in the range of 174,000–185,000 p.s.i. with the 0.2% yield strength being in the range of 128,000–147,000 p.s.i. The elongation ranged between 10–18%.

The principal significant differences between alloy forms within the scope of the present invention and those outside the scope lie in the long time stress rupture properties, which are a measure of stability, and in the formation of a different kind of phase—the sigma phase—which is detrimental to long time properties. In addition, although the ultimate tensile and yield strengths were not

affected significantly as between the various alloy forms in Table I, it was recognized that the excessive formation of sigma phase will result in low temperature brittleness.

Although aluminum and titanium play a significant part in controlling the formation of sigma phase, the elements W, Mo and Cr also affect the formation of sigma phase in combination with aluminum and titanium when the carbon range is about 0.2–0.3 weight percent. Some of these differences are shown by the alloy forms of the following Table III representing alloys which were melted, cast, reduced and tested in the manner discussed above.

TABLE III

[Wt. Percent, Balance Ni and Impurities]

Ex.	C	B	Co	Cr	Mo	Al	Ti	W	Zr	V	Al+Ti
7	.16	.014	15.0	12.1	3.9	6.2	4.0	5.0	.04	-----	10.2
8	.26	.017	14.9	11.8	4.0	5.1	4.2	5.2	.03	-----	9.3
9	.24	.012	15.5	10.6	4.1	6.1	4.5	5.5	.03	-----	10.6
10	.15	.015	15.7	10.7	4.0	5.3	4.3	5.5	.03	.79	9.6
11	.28	.018	15.6	15.0	3.9	5.0	4.4	-----	.03	.76	9.4
12	.05	.016	15.4	14.6	3.7	6.2	3.9	-----	.04	.77	10.1
13	.19	.015	15.5	15.4	3.8	6.2	4.0	-----	.03	.69	10.2
14	.28	.015	15.4	15.3	4.0	6.2	4.1	-----	.03	.77	10.3
15	.27	.012	15.0	12.0	3.8	6.0	4.0	-----	.03	.73	10.0

Although all of the alloys of Table III are outside the scope of the present invention, comparisons of the effect of various elements can be made. One known approach to improved oxidation and sulfidation resistance with carbon in the range of 0.05–0.2% is to maintain the Cr level at about 15 weight percent. Table III represents a comparison between high and low carbon with particular variations in higher chromium at about 15 weight percent, higher aluminum at about 6.2 weight percent and higher titanium which, as was pointed out above, is a critical contributor to formation of sigma phase. In addition, tungsten was eliminated from Examples 11 through 15 whereas the effect of vanadium was tested in Examples 10 through 15.

The tensile ductility of the group of Examples 7 and 12 through 14 were very low, being in the range of 3–6% reduction in area. Consequently, long time stress rupture tests were not conducted on these alloy forms. Example 7 was selected as a representative one of that group for testing because its variation from the alloy of the present invention existed in a lower carbon content, higher aluminum content and higher sum of the aluminum and titanium precipitation hardeners. The long time stress rupture properties of Examples 7 through 11 are shown in the following Table IV.

TABLE IV

[Long Time Stress Rupture Properties 1,600° F./35,000 p.s.i.]

Ex.	Life (hrs.)	El (percent)	R.A. (percent)	Sigma Phase
7	94	9.6	19.1	Heavy.
8	841	12.3	17.0	Very slight.
9	256	19.0	33.6	Heavy.
10	329	5.7	26.4	None.
11	340	8.6	11.1	Very slight

The alloy of Example 7 shows that the combination of high aluminum and the high sum of aluminum and titanium, coupled with lower carbon in the range of about 0.16%, results in very low stress rupture life and a heavy sigma phase formation. This is a significant structural difference between the alloy of Example 7 and that of the present invention. Although the alloy of Example 8 is significantly better than the other alloy forms in Table III, nevertheless comparing it with Examples 1, 2 and 3 in Table II it can be seen that there is a significant difference between the stress rupture life of the alloy of Example 8 and those within the scope of the present invention. The alloy of Example 9, with the proper carbon range of this invention, shows a significantly reduced long time stress rupture life at the higher aluminum and titanium levels and a heavy formation of the detrimental sigma phase.

Comparison of the various alloys including vanadium showed no particular improvement because of the inclusion of that element. The structure of Examples 12, 13 and 14 were studied in detail for the effect of variations in chromium at about the 15 weight percent level and aluminum at about 6.2 weight percent with variations in carbon between about 0.05, 0.2 and 0.3 with the other elements held relatively constant. All three of these alloys were very weak in stress rupture at 1600 and 1900° F. and had low tensile ductility. The microstructure revealed that there was formed a dark etching phase associated with gamma prime and that acicular plates had formed during the aging cycles. The formation of both the dark etching phase and the acicular plates duplicates previous work which had been conducted at 15 weight percent chromium levels resulting in weak and brittle alloys. The higher Cr-bearing alloys show that with a level of 15 weight percent chromium, the alloy system cannot tolerate larger amounts of the hardeners aluminum and titanium without forming detrimental phases.

Other alloy forms tested at the lower chromium range of 9–12 weight percent with variations in the solution strengthening elements molybdenum and tungsten are shown in the following Table V.

TABLE V

Composition, Wt. Percent

Base: .012-.016B; 14.9-15.5 Co; 9.8-12.0 Cr; .02-.03 Zr; Bal. Ni and impurities

Ex.	C	Mo	W	Al	Ti	V	Al+Ti	Stress Rupture Life (hrs.) 1,600° F. at 55,000 p.s.i.
16	.07	-----	8.6	5.2	4.0	-----	9.2	27
17	.13	-----	8.7	5.0	3.9	-----	8.9	23
18	.12	3.5	5.1	4.9	3.8	-----	8.7	117
19	.24	3.5	-----	5.1	3.8	.72	8.9	40
20	.15	3.5	-----	6.0	3.8	-----	9.8	65
21	.13	3.5	-----	6.0	3.8	.70	9.8	22

It is to be noted that on an atomic basis, all of the alloys of Examples 16 through 21 have approximately the same amounts of the solution strengtheners molybdenum and tungsten. Nevertheless, significant differences can be recognized from the stress rupture data shown in Table V. For example, in Examples 17 and 19 in which, on an atomic basis, approximately the same amounts of such solution strengtheners are included, the stress rupture life is relatively low. However, when the combination of molybdenum and tungsten are included with substantially the same other elements, a drastic improvement in stress rupture life occurred. Thus the inclusion of molybdenum alone or tungsten alone does not result in the same properties as the proper combination of molydenum and tungsten together. Therefore, these elements are not interchangeable as has been indicated to be true in certain other known alloys.

Throughout all of the evalutions of the alloy of the present invention, the range of cobalt has been maintained at a level of about 14–16 weight percent because of widely documented and published work that the range of about 14–16 weight percent cobalt in an alloy of a type to which the present invention relates results in improved workability. Similarly, boron can be included in the range of 0.005–0.02% and in some instances zirconium up to about 0.05 weight percent can be included.

In order to evaluate the alloy of the present invention on a large size heat basis, a 400 lb. heat was vacuum melted of the following composition, by weight: 0.26% C; 0.016% B; 15.1% Co; 9.7% Cr; 3.2% Mo; 5.6% Al; 3.3% Ti; 5.5% W; 0.016% Zr, with the balance nickel and incidental impurities, the sum of the Al and Ti being 8.9%. This will be referred to in the drawing as Example 22. After melting, this 400 lb. heat was cast into 55 lb. molds for further processing. Both wet and spectrographic analysis of the ingots resulted in the above average chemical composition.

Four of the seven ingots were extruded to 3" diameter bars. Some bars were cut into 4" lengths and then flattened to 1½" thick specimens. These "forge downs" were evaluated metallographically as well as for strength properties.

The metallographic study showed the proper solution temperature to be 2225° F. for 2 hours to completely solution the gamma prime. This solution temperature as before was used with the triple age of 2000° F./4 hr. F.A.C.+1550/24 hr. A.C.+1400° F./16 hr. A.C. in the preparation of samples for strength property testing. Representative of such testing is the data shown in Table VI.

TABLE VI

Test Temp. (° F.)	Tensile strength				Rupture Strength			
	Ultimate (K s.i.)	0.2 Yield (K s.i.)	Percent El.	Percent R. A.	Stress (K s.i.)	Life (hrs.)	Percent El	Percent R. A.
Room	191	153	13	16				
1,300	172	142	13	20				
1,600					35	1,706	9	8
1,900					15	44	3	4

In addition to this specimen testing which showed the same fine results as before, the remaining three of the seven ingots were recast into turbine blade precast forms. Also, some of the bar stock was forged into blades by the well known process including upsetting blocking and finish forging. Tensile and rupture strength data for the forged blades were consistent with previous test data shown for the alloy of the present invention. The improved rupture properties are again shown in the rupture curve of FIG. 2.

In FIG. 2, comparison is made with the best available wrought alloy consisting essentially of, by weight, 17% Co, 15% Cr, 15% Mo, 4.3% Al, 3.3% Ti, .015% B, .03% Zr, balance nickel.

Creep measurements conducted on specimens from the forged blades at 1400–1800° F. confirmed that the alloy of the present invention has better creep resistance than any commercially available wrought alloy of this general type. A comparison of 0.2% plastic creep properties between the alloy of the present invention and the above identified commercially available alloy is illustrated in FIG. 3.

This long time rupture stability data again indicates good stability. Metallographic examination of the specimens showed no evidence of the detrimental signal phase.

One meaningful comparison between the alloy of the present invention and the known alloy identified above is shown in FIG. 4. The significant advantages in yield rupture and creep strength over the best commercially available wrought turbine blade alloy is easily seen.

The alloy of the present invention, by avoiding the forming of sigma phase through a specially controlled composition, provides the turbine designer with a significantly improved wrought alloy. Although the alloy has been described in connection with specific examples, it will be understood by those skilled in the metallurgical art, the variations and modifications of which this invention is capable. It is intended by the appended claims to cover all such variations and modifications.

What is claimed is:

1. An improved wrought nickel base alloy having a stress rupture life of greater than 900 hours at 1600° F. and 35,000 p.s.i. stress and virtually no sigma phase formation during such time, the alloy consisting essentially of, by weight:

0.2–0.3% C
0.005–0.2% B
about 14–16% Co
9–12% Cr
3–4% Mo
4.5–6% Al
3–4% Ti
5–6% W
up to about 0.05% Zr
8–9% Al+Ti
with the balance Ni and incidental impurities.

2. The alloy of claim **1** in which:
C is 0.25–.30%
B is 0.01–0.02%
Al is 5–5.5% and
Ti is 3–3.5%.

3. The alloy of claim **2** in which the Zr is 0.02–0.04%.

4. A wrought article made from the alloy of claim **1**.

5. The article of claim **4** in the form of a turbine blade.

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U.S. Cl. X.R.

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