

Nov. 3, 1964

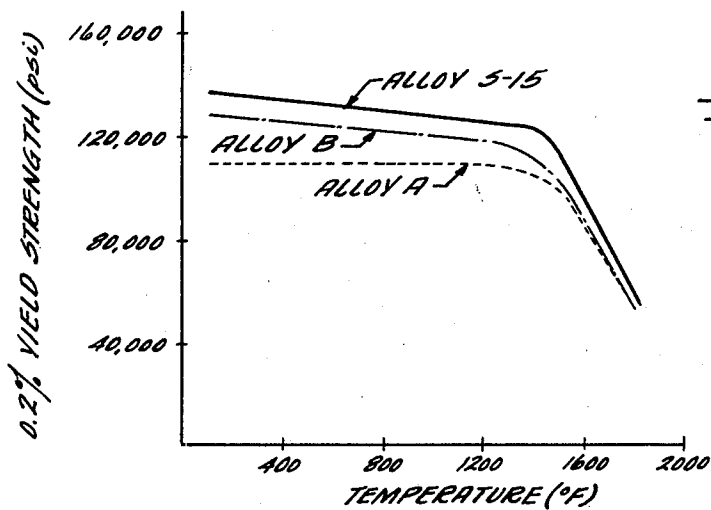
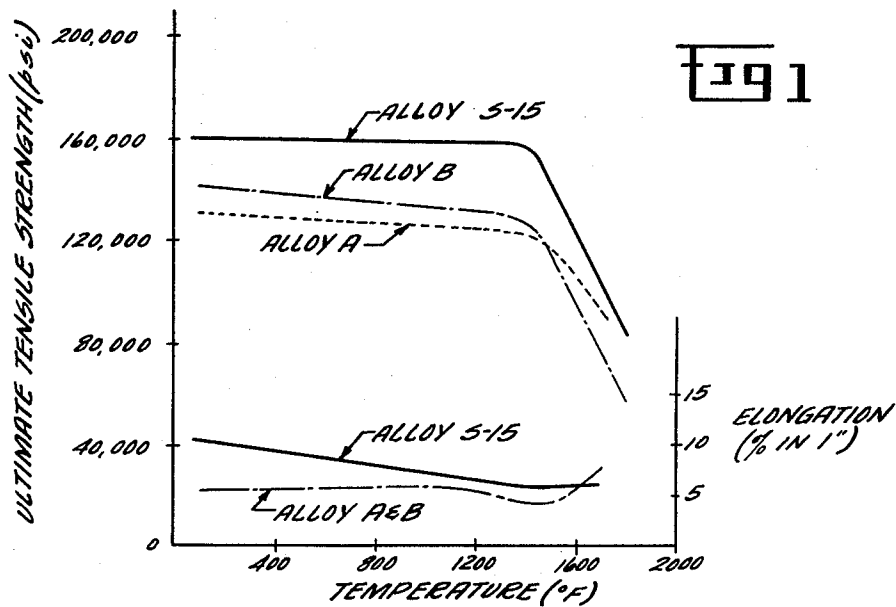
M. KAUFMAN ETAL

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NICKEL BASE ALLOY

Filed June 30, 1961

2 Sheets-Sheet 1



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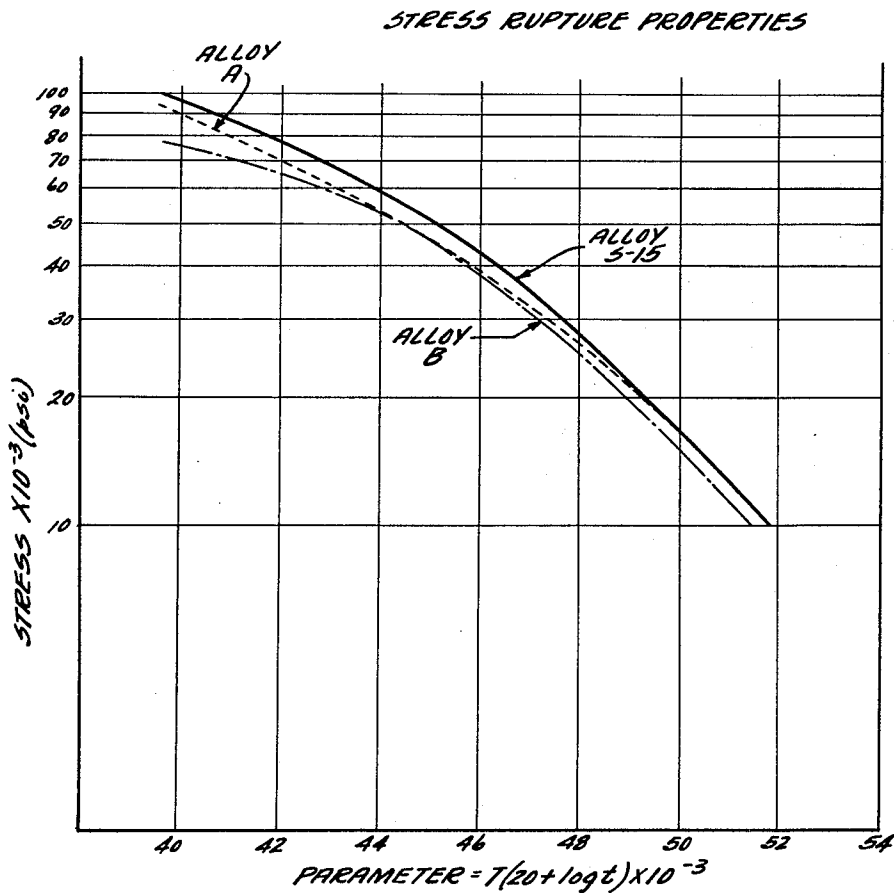
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Fig 3



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## NICKEL BASE ALLOY

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Filed June 30, 1961, Ser. No. 121,144  
3 Claims. (Cl. 75-171)

This invention relates to multiphase nickel base alloys, particularly to one having a unique combination of greatly improved strength below about 1700° F., coupled with high strength at 1700-1800° F.

As the art of metallurgy has improved, a more complete realization of the interdependence of elements and the phases they form has become known. In the development of nickel base alloys, sometimes classed as "super alloys," the elements Ti, Al, Co, Cr, C and Mo have all been added to Ni to form a nickel base alloy. Sometimes elements such as Fe, Cb, Zr, B or W have been used as alloying additions.

In many reported alloying situations and combination of elements, different relationships exist between the elements. Different phases of different physical and mechanical characteristics, solution temperatures and melting points are formed. Nevertheless, despite the large amount of data available concerning nickel base alloys, it is still not possible for a metallurgist to predict accurately the physical and mechanical characteristics of each and every phase formed from every given combination of elements. Thus unexpected results can still be obtained even in an area so widely studied.

It is a principal object of this invention to provide a nickel base alloy having a careful and critical balance of alloying elements to result in an alloy of improved strength below about 1700° F. coupled with strength in the 1700-1800° F. range at least equivalent to known alloys.

These and other objects and advantages will be recognized from the following detailed description, the appended claims and the drawing in which:

FIG. 1 is a graphical comparison of some tensile strength properties of the alloy of this invention, designated as S-15, with the strongest commercially available alloys;

FIG. 2 is a graphical comparison of the 0.2% yield strength properties of the alloy of this invention, designated as S-15, with the strongest commercially available alloys; and

FIG. 3 is a graphical comparison of stress rupture properties of the alloy of this invention, designated as S-15, with the strongest commercially available alloys.

The alloy of this invention, designated as S-15 in the drawing and sometimes referred to as "SEL 15," in one form, consists by weight of 4-7% Al, 1.5-4% Ti, 7-16% Co, 8-16% Cr, 5.5-8% Mo, 0.03-0.1% C, 0.3-1.2% Cb, 0.003-0.4% B, 1-3% W with the balance Ni and incidental impurities including Fe, Mn, Si etc. up to about 2% maximum and with the further provision that the minimum nickel percentage must be 4+6 (percent Al+percent Ti) when the Al/Ti ratio is greater than 2 and 4+5 (percent Al+percent Ti) when the Al/Ti ratio is lower than 2. In some forms up to 0.2% Zr can be included.

The alloying elements and their ranges have been carefully selected to provide an improved alloy of unexpected strength properties particularly in the range below 1700° F. while maintaining a high strength level between 1700-1800° F.

As is shown by the above formulae for the minimum weight percent Ni, a particularly critical relationship exists between the elements Ni, Al and Ti. This relationship coupled with carbon and the carbide formers included

within the range of this alloy are particularly significant in providing the unexpected result.

In order to obtain maximum strength characteristics in a nickel base alloy including the elements Ti and Al, it would be desirable to include as much Al and Ti as possible to form Ni<sub>3</sub>(Al, Ti). However there is a composition limitation. In order to obtain high temperature strength between 1700-1800° F. without regard to other properties in other ranges, the Al ordinarily should be about 2 to 3½ times the Ti content. If the Ti is increased at the expense of Al, lower temperature strength is gained but at a loss of higher temperature strength. This was recognized by noting that the solution temperature of Ni<sub>3</sub>(Al, Ti) was higher with higher Al/Ti ratios. Also it has been recognized that if the Ti content is below 1.5%, lower temperature strength is lost. For example, referring to FIGS. 1 and 2, the alloy indicated as Alloy S-15 is the alloy of this invention and Alloy A is a nickel base alloy consisting, by weight, of 5.5-6.5% Al, 0.25-1.25% Ti, 11-14% Cr, 3.5-5.5% Mo, 0.05-0.20% C, 1-3% Cb, 0.05-0.2% Zr, 0.005-0.02% B with the balance essentially nickel. Note that the Al/Ti ratio is high. It is also to be noted how the low temperature strength is less than the alloy of this invention. The same reduction in properties can be seen in the stress rupture comparison of FIG. 3. Both effects are due to the high Al/Ti ratios in Alloy A.

In FIG. 3, the stress rupture strengths are represented by the comparison of stress with a time-temperature parameter shown at the horizontal coordinate. This parameter, known as the Larson-Miller Parameter, has been calculated from the formula  $P = T(20 + \log t) + 10^{-3}$  in which P equals the time-temperature parameter, T equals absolute temperature in degrees Rankine and t equals the time in hours.

Therefore in order to obtain the same or better properties at 1700-1800° F. and greatly improve the strength properties at 1700° F. or below, it has been found that an optimum amount of Ni<sub>3</sub>(Al, Ti) is required in the careful and critical balance of the elements of the alloy of this invention. The formulae listed above are important features of this invention in view of the fact that the Ti level is maintained within the range of 1.5+4%. If the nickel content is less than that given by the formulae, the phase NiAl may be formed in preference to Ni<sub>3</sub>(Al, Ti) with a consequent great loss in medium and elevated temperature properties.

The element cobalt, which aids in ductility, has been added within the range of 7-16 weight percent. It would be desirable to include a higher percentage of cobalt from a ductility point of view. However, in order to maintain the proper balance of elements, the range has been set at 7-16 weight percent. A higher percentage would be included at a sacrifice of the nickel content thus to form less Ni<sub>3</sub>(Al, Ti) for precipitation hardening; a lower percentage does not have a significant effect on ductility. At Al and Ti levels lower than that of the alloy of this invention an addition of higher percentages of cobalt is possible, but the unique characteristics of this alloy is lost.

The chromium included in the alloy has its principal effect as an aid to oxidation resistance. It has been found that a minimum of 8 weight percent is required to improve the oxidation resistance. However if chromium is increased to too high a level, for example as high as 20 weight percent or more, the chromium is added at the expense of nickel and it drops the nickel below the minimum essential in the above listed formula. Therefore it is essential to balance the chromium and cobalt content with the required amount of nickel. Because more cobalt is required for ductility purposes, the chromium content is maintained as low as possible in order to be able to allow the addition of more cobalt without detracting from the nickel content. In addition, high levels of chromium

favor formation of sigma phase which causes great loss of ductility.

It is preferred to have as little iron as possible in the alloy of this invention because it does not benefit and can actually detract from the properties of the alloy. The alloy of this invention can tolerate up to about 0.5 weight percent Fe in order to allow columbium to be added as ferro columbium, a less expensive type of columbium addition. The inclusion of higher percentages of iron, for example above 0.5% will decrease ductility.

In addition to the careful balance between the elements Ni, Ti and Al to form  $Ni_3(Al, Ti)$  and the critical relationship between Ni, Co and Cr content, a significant feature of the alloy of this invention is adjustment of the levels of carbon and the carbide formers to form the proper carbides. The carbide forming elements are specifically selected to form higher solution temperature phases and to preferentially form carbides to protect other alloying additions added for other purposes.

From consideration of the carbides, it is required that at least 5.5 weight percent Mo be added with the carbon level between 0.03-0.1 weight percent in order to form  $M_6C$  type carbide instead of the  $M_{23}C_6$  type carbide.  $M_6C$  carbide is a high molybdenum carbide stable to higher temperatures and is not dissolved until about 2150° F. The low molybdenum  $M_{23}C_6$  carbide is soluble in the 1900-1950° F. temperature range and would be formed with lower molybdenum and higher chromium. It is the intention of the alloy of this invention to form the higher molybdenum, lower chromium  $M_6C$  carbide.

Below about 5.5 weight percent Mo the undesirable  $M_{23}C_6$  carbide begins to form. Above about 8 weight percent molybdenum, the molybdenum is added at the expense of nickel. No real advantage has been found in adding higher molybdenum percentages although some strengthening is achieved from higher percentages of molybdenum in some solution hardening type of alloys. The solution hardening value of molybdenum reaches the maximum at about 4-5 weight percent; however it is the intention of this alloy to include molybdenum at higher levels to assure the formation of  $M_6C$  carbide. With the previously mentioned Alloy A,  $M_{23}C_6$  may form (less than 5.5% Mo) the same as in Alloy B shown in the drawing and having a nominal composition, by weight, of 4.5% Al, 3.5% Ti, 18% Co, 15% Cr, 4.5% Mo, 0.12% C, 0.01% B, balance Ni. Although some prior alloys report a broad molybdenum range, the significance of the range 5.5-8 weight percent Mo in an alloy such as the alloy of this invention has been unrecognized heretofore, in view of the relationship between Mo and C in the proper carbon range.

Although it is the intention of the alloy of this invention to cause formation of  $M_6C$  carbide in preference to  $M_{23}C_6$ , it is important to keep all the carbides to a relatively low level. Probably more important than the lower solution temperature of the  $M_{23}C_6$  carbide, is that such carbide is to be avoided in the alloy of the type of this invention because  $M_{23}C_6$  carbide precipitates in the normal aging and operation ranges at the grain boundaries and usually is an embrittler.  $M_6C$  carbide will not precipitate in the grain boundaries excessively. When it does, it precipitates in the form of spherical particles which do not harm ductility.

The carbides formed give a small amount of strengthening insofar as the high temperature stress rupture properties are concerned. They also act to block grain growth in wrought materials, especially the  $M_6C$  carbide. It has been found that the carbon level must be kept within the range of 0.03-0.1 weight percent particularly with the level of chromium and molybdenum described above and in view of the carbide former columbium which will be described in more detail later. Above 0.1 weight percent carbon excessive carbides formed, which in wrought material form carbides stringers which cause material to split and peel. Another reason for keeping the carbon

level below 0.1 weight percent is that the formation of a large amount of carbide, even though they may be titanium carbide or columbium carbide rather than  $M_{23}C_6$ , can group in excessive quantities to form what corresponds to a grain boundary network.

Tungsten has been included in the alloy of this invention within the range of 1-3 weight percent because it has been recognized that the properties of nickel base material can be increased by such an addition. However below 1% no appreciable improvement was recognized. Although the elements W and Mo are sometimes considered equivalent from a solution hardening point of view, the substitution of 1-3 weight percent molybdenum for the 1-3 weight percent tungsten does not have the same effect on the alloy of this invention as does the tungsten inclusion. Molybdenum and tungsten act individually in this case, as would be expected on a theoretical basis. Over 3 weight percent W does not further improve properties, but merely decreases ductility.

Columbium is included in the alloy of this invention, because in addition to being a solution hardener, it is a more successful carbide former than titanium. This means that columbium rather than titanium will selectively form carbides with the carbon thus the titanium is free for the more important action in the  $Ni_3(Al, Ti)$ . Thus the alloy of this invention obtains a double benefit from the inclusion of columbium. The inclusion of above 2 weight percent columbium within the range of the alloy of this invention begins to embrittle the alloy by too much solution hardening. In addition, columbium may also form an  $Ni_3Cb$  precipitation hardening phase which has a lower solution temperature than does the  $Ni_3(Al, Ti)$ . Therefore the columbium range for the alloy of this invention is maintained below 2% to avoid displacement of Al and Ti from the  $Ni_3(Al, Ti)$ .

Although the element boron has been included in nickel base alloys of this type, a particular and critical minimum amount has been recognized. At least 0.003 weight percent boron must be included in wrought materials to help prevent carbide precipitation in the grain boundary by performing relatively low melting phases in the grain boundary. Somewhat more, about 0.006 weight percent boron is required in cast alloys. However, above about 0.4 weight percent there is too great an amount of low melting phase formed in the grain boundary which results in a weak material.

As representative of the alloy of this invention, a series of alloys within the preferred range, by weight, 4.9-6% Al, 2-3% Ti, 13-16% Co, 9-13% Cr, 6-7.2% Mo, 0.04-0.10% C, 0.2-0.7% Cb, 0.01-0.02% B, a maximum of .5% Fe, with the balance essentially nickel and impurities of Mn, Si, S and Cu were melted and cast into test bars of about 0.250" diameter size to a maximum grain size of about  $\frac{1}{8}$ ". The specimens were aged for 2-4 hours at 1400° F. and air cooled before testing. The following table shows the average and maximum tensile data for such preferred form of the alloy of this invention.

Tensile Data

| Temperature (° F.) | Ultimate Strength<br>(K p.s.i.) |       | 0.2% Yield Strength<br>(K p.s.i.) |       |
|--------------------|---------------------------------|-------|-----------------------------------|-------|
|                    | Avg.                            | Max.  | Avg.                              | Max.  |
| Room.....          | 158                             | 169.4 | 131                               | 158.8 |
| 1,200.....         | 160                             | 165.4 | 126                               | 132.3 |
| 1,300.....         | 168                             | 180.5 | 138                               | 141.2 |
| 1,400.....         | 158                             | 170.3 | 118                               | 131.8 |
| 1,500.....         | 154                             | 158.0 | 120                               | 124.2 |
| 1,600.....         | 123                             | 131.8 | 94                                | 96.9  |
| 1,700.....         | 102                             | 105.4 | 71                                | 77.0  |
| 1,800.....         | 82                              | 83.5  | -----                             | 56.5  |

Through the careful balance of the elements in the alloy of this invention, there has been provided a nickel base alloy of improved low temperature strength up to about 1700° F. compared with the best available commer-

cial alloys. In addition the alloy of this invention has at least the same high temperature stress rupture properties available in alloys of this type.

Although this invention has been described in connection with specific examples, it is to be understood that these are exemplary of rather than limitations on this invention. It will be understood by those skilled in the metallurgical arts the modifications and variations of which this invention is capable.

What is claimed is:

1. An improved nickel base alloy which inhibits the formation of embrittling precipitate phases through a balance of carbon, the carbide formers, the solution strengtheners and chromium, consisting essentially of, by weight, 4-7% Al; 1.5-4% Ti; 7-16% Co; 8-16% Cr; 5.5-8% Mo; 0.03-0.1% C; 0.3-1.2% Cb; 0.003-0.4% B; 1-3% W up to 0.2% Zr with the balance nickel and impurities, to form preferentially the  $M_6C$  type carbide rather than the  $M_{23}C_6$  type carbide, the minimum weight percentage of nickel when the Al/Ti ratio is greater than 2 being calculated from the formula  $4+6$  (percent Al+percent Ti) and when the Al/Ti ratio is less than 2 being calculated from the formula  $4+5$  (percent Al+percent Ti).

2. An improved nickel base alloy which inhibits the formation of embrittling precipitate phases through a balance of carbon, the carbide formers, the solution strengtheners and chromium, consisting essentially of, by weight, 5-6% Al; 2-3% Ti; 13-16% Co; 9-13% Cr; 6-7% Mo; 0.04-0.10% C; 0.2-0.7% Cb; 0.01-0.02% B and 1-2% W; up to 0.2% Zr with the balance nickel and impurities,

to form preferentially the  $M_6C$  type carbide rather than the  $M_{23}C_6$  type carbide, the minimum weight percentage of nickel when the Al/Ti ratio is greater than 2 being calculated from the formula  $4+6$  (percent Al+percent Ti) and when the Al/Ti ratio is less than 2 being calculated from the formula  $4+5$  (percent Al+percent Ti).

3. An improved nickel base alloy which inhibits the formation of embrittling precipitate phases through a balance of carbon, the carbide formers, the solution strengtheners and chromium, consisting essentially of, by weight, 5.5% Al; 2.5% Ti; 14.5% Co; 11.5% Cr; 6.5% Mo; 0.07% C; 0.5% Cb; 0.015% B; 1.5% W with the balance nickel and impurities, to form preferentially the  $M_6C$  type carbide rather than the  $M_{23}C_6$  type carbide.

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