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3,705,827

NICKEL-IRON BASE ALLOYS AND HEAT TREATMENT THEREFOR

Filed May 12, 1971

2 Sheets-Sheet 1



FIG. 1A



FIG. 2A



FIG. 3A



FIG. 4A

**Dec. 12, 1972**

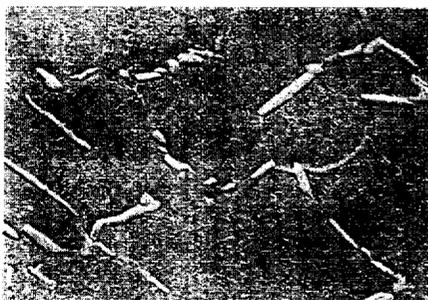
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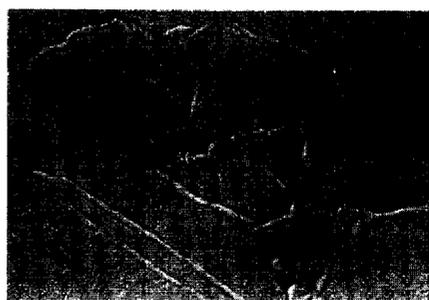
**NICKEL-IRON BASE ALLOYS AND HEAT TREATMENT THEREFOR**

**Filed May 12, 1971**

**2 Sheets-Sheet 2**



**FIG. 1B**



**FIG. 2B**



**FIG. 3B**



**FIG. 4B**

1

2

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**NICKEL-IRON BASE ALLOYS AND HEAT TREATMENT THEREFOR**

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4 Claims

**ABSTRACT OF THE DISCLOSURE**

Precipitation hardened nickel-iron base alloys with or without chromium and cobalt containing columbium, titanium and aluminum are provided by heat treatment with a unique combination of room temperature and elevated temperature properties.

This invention relates to nickel-iron base alloys with or without chromium and cobalt in which columbium, titanium and aluminum take part in the main precipitation hardening and strengthening reaction which is controlled by forming and heat treating so as to provide a unique combination of room temperature and elevated temperature properties.

In the heat treatment of such nickel-iron base alloys and the parts made thereof to prepare them for use in environments where they are to be subjected to repeated temperature cycling to an elevated temperature with or without stress, as for example in gas turbine engines, considerable difficulty has been encountered in achieving minimum desired properties at elevated temperatures, particularly tensile ductility and stress rupture properties. Commonly used heat treatments start with an initial heating period at a high enough temperature and for a long enough period to ensure complete dispersion in solid solution of all the hardening and strengthening elements. Hence the name "solution treatment" for this stage. After more or less rapid quenching, sometimes preceded by a period of slow controlled cooling, there is a further period of heating at a lower temperature for a long enough time for the precipitation hardening reaction to take place during which the strengthening phase or phases appear throughout the matrix of the alloy. This latter step is usually termed "aging." In some instances, a stabilization aging treatment has been used at a temperature intermediate the solution treating temperature and the precipitation aging temperature.

In practice, the results attained in nickel-iron base alloys strengthened by columbium, titanium and aluminum have left much to be desired. In such alloys, the main strengthening effect is provided by an intragranular precipitate Ni<sub>3</sub> (Cb, Ti, Al) the precise composition of which may vary, depending upon process and composition variables. The form of the precipitate is difficult to determine, but may be gamma prime which is a face centered cubic (FCC) structure, gamma double prime which is a body centered tetragonal (BCT) structure or a combination of the two. The precise form is not considered to be as important to the present application as the solvus temperature thereof which can be determined as will be more fully pointed out hereinafter. In addition to the gamma prime and/or gamma double prime intragranular precipitate, additional phases involving the elements nickel, columbium and titanium are also formed not only along the grain boundaries where they are desirable, but also to some extent within the grains where they are definitely not desirable. We believe that the shortcomings of such

prior alloys and the heat treatments for processing them has largely resulted from the fact that in processing such alloys, solution treatment was carried out at a high enough temperature and long enough for most if not all of the precipitates, both those formed intragranularly and those at the grain boundaries exclusive of primary carbides, to be taken into solid solution.

One manifestation of such practice has been a certain amount of coarsening of the grain structure during heat treatment as compared to the as-forged grain size. In addition, and probably as a direct result, the high temperature properties of the compositions as indicated by tensile ductility and stress rupture tests were low and in the case of the compositions described in U.S. Pat. No. 3,157,495 were so low as to indicate that the composition should be used where low plastic ductility (that is a tendency to fracture rather than deform) was a desirable property as in the case of certain measuring instruments.

It is therefore a principal object of this invention to provide a heat treatment for nickel-iron base alloys strengthened by precipitation hardening in which the elements columbium, titanium and aluminum take part in the strengthening reaction so as to impart improved elevated temperature tensile ductility and stress rupture properties to such compositions.

In said Pat. No. 3,157,495, there is disclosed a controlled expansion alloy having low plastic ductility. We have found that when a small but critical amount of boron is included in such a composition that is processed in accordance with the present invention, it not only retains its desired controlled expansion properties, but also consistently exhibits highly improved stress rupture properties. In addition, certain compositions of the present invention are characterized by improved elevated temperature tensile strength and stress rupture life and ductility.

Thus a further important object of the present invention is to provide a nickel-iron base alloy which responds to the heat treatment of the present invention and which has improved elevated temperature tensile and stress rupture properties.

The foregoing as well as additional objects and advantages of the present invention will be apparent from the following description of preferred embodiments thereof and the accompanying drawing in which

FIGS. 1A and 2A are light micrographs having a magnification of 500X and FIGS. 1B and 2B are electron micrographs having a magnification of 7700X all prepared from specimens formed and heat treated in accordance with the present invention; and

FIGS. 3A/4A and FIGS. 3B/4B are respectively corresponding light and electron micrographs prepared from specimens of the same composition as those shown in FIGS. 1 and 2, and formed and treated in the same way except that they were solution treated at a higher temperature outside the scope of the present invention.

The process of the present invention is applicable to a narrowly defined class of alloys in which the predominant elements are nickel and iron that coact to provide an austenitic or gamma face centered cubic microstructure. Broadly stated, nickel can be present from about 30% to 50% and at least about 30% iron should be present. The strengthening elements columbium, titanium and aluminum react with some of the nickel to form one or more strengthening phases brought out as an intragranular precipitate by age or precipitation hardening. The composition of those phases is generalized as Ni<sub>3</sub>(Cb,Ti,Al) and may be gamma prime which has a face centered cubic structure, gamma double prime which has a body centered tetragonal structure, or both phases may be present. As a

class, the composition of these alloys is such that the  $Ni_3(Cb,Ti,Al)$  intragranular precipitate has a solvus temperature which is considerably below that of the same or similar phase found in commercial nickel base super alloys now in use containing little or no iron. Its solvus temperature is also substantially lower than that of additional precipitated phases formed of the elements Ni, Cb, and Ti designated as eta phase for  $Ni_3Ti$  and delta phase for  $Ni_3Cb$ .  $Ni_3Ti$  in the form of eta phase has a close packed hexagonal crystal structure and is thus distinguishable from the face centered cubic structure typical of the gamma prime form of  $Ni_3Ti$  by means of well known X-ray diffraction techniques. By means of similar techniques, the orthorhombic delta phase formed by  $Ni_3Cb$  as a grain boundary precipitate can be distinguished from the intragranular body centered tetragonal gamma double prime phase of  $Ni_3Cb$  brought out by aging. Hitherto, eta phase and/or delta phase not only appeared along the grain boundaries where they could be beneficial, but also within the grain structure where their presence was not desired. As will be more fully pointed out hereinafter, eta phase and/or delta phase are brought out along the grain boundaries so as to provide improved properties, and no effective amount appears within the grains to detract from the over-all properties.

Thus, in addition to nickel and iron, the only other essential elements in the compositions that respond to the present process are the elements columbium, titanium and a small but necessary amount of aluminum. From about 2.5% to no more than about 6% columbium, from about 1% to no more than about 3% titanium, and from about 0.1% to no more than about 2% aluminum should be present in order to ensure the desired response to the present process. While aluminum is not one of the main strengthening elements, some small amount is necessary, and the minimum amount required should be increased as the columbium content tends toward the lower end of the range stated. Thus, when the amount of columbium present is from about 2.5% to 3%, the minimum amount of aluminum preferably should not be less than about 0.15% and better yet not less than about 0.20%.

While the process of the present invention can impart stress rupture ductility to the class of alloys thus far defined, a small but critical amount of boron is also necessary if the composition is consistently to have the improved properties characteristic of the present invention. Therefore, a minimum of 0.001% boron or preferably a minimum of 0.003% boron should be present. As much as 0.03%, preferably no more than about 0.020%, boron can be beneficially used as for example in compositions containing little or no chromium while when significant amounts of chromium are present, then preferably boron is limited to no more than about 0.01% and better yet to no more than about 0.006%.

Optional elements that can be present include up to about 20% chromium to impart stainless properties, up to about 20% cobalt which may be used in addition to or in place of some of the nickel particularly in controlled expansion-type alloys. When desired, up to about 1% vanadium may be used to beneficially affect hot workability of a particular analysis, up to about 0.1% zirconium may be included for its beneficial effect on ductility, and up to 2% hafnium may be included as a solid solution strengthener and as a carbide former. When desired, such solid solution strengtheners as up to about 3% molybdenum and up to about 3% tungsten may also be present.

In keeping with good commercial metallurgical practice, up to about 0.1% carbon, up to about 1%, preferably no more than 0.50% manganese, and up to about 0.50% silicon may be present in the nickel-iron base alloys with which the present invention is concerned. Usually the expensive involved in keeping carbon below a few hundredths of a percent is not warranted and in some instances about 0.01% to 0.05% carbon can be beneficial.

Phosphorus and sulfur are not desirable additions, and preferably each does not exceed about 0.020%.

Such alloys are readily melted and cast as ingots using conventional techniques: however, for best results, a multiple melting practice is preferred. For example, a heat can be first melted and cast as an ingot under vacuum in an induction furnace, and that ingot is then used as a consumable electrode and remelted under vacuum.

In the forming and heat treating compositions in accordance with the present invention, hot working is preferably carried out so as to provide a fine grain structure of at least A.S.T.M. 4 or finer. In practice, forging from a furnace temperature of about 2000° F. to 2100° F. to at least about 60% reduction in cross-sectional area is adequate, but reductions of as much as 80% to 90% provide better results. For optimum results, it is preferred that the final forging operations be carried out at least in part within about 100° F., above or below, of the effective solvus temperature of the eta and delta phases of the composition. This ensures the desired grain structure of no coarser than A.S.T.M. 4. The starting grain structure for heat treatment which has been found to give best results is at least as fine as A.S.T.M. 8 or finer.

The solution treatment of the present process serves several functions including the usual one of putting back into solution the intragranular strengthening gamma prime and double prime phases brought out during hot working. This is to avoid banding or other non-uniform distributions of the phases which, as a practical matter, usually cannot be avoided during hot working. Another and important function of the solution treatment of the present invention is the formation of the eta phase and/or delta phase precipitate along the grain boundaries. The solution treatment is carried out at a temperature and for time long enough to provide the amount and also the distribution of the eta and delta phases which favors the attainment of elevated temperature tensile and stress rupture ductility.

For any given composition of such nickel-iron base alloys, the solution-treating temperature is readily determined empirically using the following guidelines. Hot worked specimens are heated at about 25° F. increments from about 1400° F. up to determine the solvus temperature of the intragranular gamma prime and double prime precipitates. Further testing is carried out in the 25° F. increments above the solvus temperature of the gamma prime and double prime precipitates to the temperature at which the eta phase and delta phase effective solvus temperature is found. That is the temperature at which enough of the eta and delta phases have been put back into solution so that what remains is no longer effective to prevent grain growth and other objectionable effects. The effective solvus temperature is somewhat below the equilibrium solvus temperature, the latter being the temperature at which those phases are entirely taken into solution. The effective solvus temperature is readily identified by examining the microstructure of the solution treated specimens because of the grain growth from the as-forged condition which occurs as soon as the solution-treating temperature used is above the effective solvus temperature. The best solution-treating temperature for use can be readily verified by aging tensile and stress rupture specimens in the usual way, that is, below the gamma prime/gamma double prime solvus and observing the effect of the various solution-treating temperatures on the elevated temperature tensile and stress rupture properties.

It is to be understood that by the term "hot working" it is not intended to exclude "warm working," which includes working the metal while it is below its recrystallization temperature, or other thermo-mechanical procedures. For the nickel-iron base alloys of the present application, the effective solvus temperature of the eta and delta phases is the recrystallization temperature of the alloy for most practical purposes but in some in-

stances following extreme warm working the recrystallization temperature can be lower.

## EXAMPLE 1

As an example of a preferred embodiment of the present invention, an experimental vacuum induction heat was prepared of a hitherto known composition falling within an intermediate range of up to about 0.06%, preferably about 0.01% to 0.05% carbon, up to about 0.35% manganese, up to about 0.35% silicon, no more than 0.020% phosphorus or sulfur, about 14.5% to 17.5% chromium, about 39% to 44% nickel, up to about 1% molybdenum, up to about 1% cobalt, about 2.5% to 3.3% columbium, about 1.5% to 2% titanium, about 0.15% to 0.40% aluminum, about 0.001% to 0.01%, preferably 0.001% to 0.006% boron and the balance iron plus incidental impurities. Example 1 had the following analysis in weight percent:

|                  |        |
|------------------|--------|
| Carbon .....     | 0.027  |
| Manganese .....  | 0.08   |
| Silicon .....    | 0.10   |
| Phosphorus ..... | 0.001  |
| Sulfur .....     | 0.005  |
| Chromium .....   | 15.81  |
| Nickel .....     | 39.89  |
| Columbium .....  | 2.83   |
| Titanium .....   | 1.61   |
| Aluminum .....   | 0.30   |
| Boron .....      | 0.0041 |

specimens solution treated at 1800° F., 4 different stabilization treatments were used and are identified by suffixes A-D appended to the 1800° F. solution treating temperature. Thus, 1800° F.-A indicates solution treatment for 1 hour at 1800° F. followed by a stabilization treatment at 1550° F. for 3 hours before aging. The 1800° F.-B solution treatment plus stabilization treatment was the same except that the stabilization treatment was carried out at 1650° F. for 1 hour. 1800° F.-C indicates the same solution treatment followed by a stabilization treatment at 1650° F. for 4 hours, and 1800° F.-D indicates that a stabilization treatment at 1650° F. for 8 hours was used. The effect of different aging treatments is also indicated. In each case, the specimen after being solution treated as indicated and subjected to a stabilization treatment, if one was used, was then heated for 8 hours at one of 4 primary aging temperatures ranging from 1325° F. to 1400° F. in 25° F. increments. This was followed by cooling at the rate of 100° F./hr. to a final aging temperature of either 1150° F. or 1200° F. at which the specimen was held for 8 hours and then air cooled. The primary and final aging temperatures for each specimen are as indicated in Table I.

The grain size of the heat treated specimens is also indicated in Table I. In the case of the specimen of Test No. 7, an occasional coarser grain about A.S.T.M. 1-2 was noted while in the case of Tests No. 9 and No. 12, an occasional grain of about A.S.T.M. 3 was seen.

TABLE I

| Test No.: | Heat treatment        |                    | Grain size (ASTM) | Rupture life (hrs.) | El. (percent) | R.A. (percent) |       |
|-----------|-----------------------|--------------------|-------------------|---------------------|---------------|----------------|-------|
|           | Solution temp. (° F.) | Aging temp. (° F.) |                   |                     |               |                |       |
|           |                       | Primary            |                   |                     |               |                | Final |
| 1.....    | 1,725                 | 1,400              | 1,200             | 6-8                 | 52            | 4              | 7     |
| 2.....    | 1,725                 | 1,375              | 1,200             | 7-8                 | 95            | 3              | 7     |
| 3.....    | 1,700                 | 1,400              | 1,200             | 7                   | 81            | 3              | 11    |
| 4.....    | 1,700                 | 1,375              | 1,200             | 7-8                 | 108           | 4              | 13    |
| 5.....    | 1,675                 | 1,400              | 1,200             | 9-10                | 52            | 19             | 55    |
| 6.....    | 1,675                 | 1,400              | 1,200             | 9-10                | 17            | 17             | 46    |
| 7.....    | 1,675                 | 1,375              | 1,200             | 9-10                | 97            | 23             | 57    |
| 8.....    | 1,675                 | 1,375              | 1,200             | -----               | 95            | 19             | 57    |
| 9.....    | 1,675                 | 1,375              | 1,150             | 9                   | 114           | 20             | 58    |
| 10.....   | 1,675                 | 1,350              | 1,150             | 60% 10, 40% 1-2     | 161           | 14             | 55    |
| 11.....   | 1,675                 | 1,325              | 1,150             | 60% 9-10, 40% 2     | 264           | 17             | 59    |
| 12.....   | 1,650                 | 1,400              | 1,200             | 9                   | 76            | 18             | 56    |
| 13.....   | 1,650                 | 1,375              | 1,200             | 9                   | 114           | 20             | 56    |
| 14.....   | 1,625                 | 1,375              | 1,200             | 50% 10, 50% 1-3     | 109           | 17             | 52    |
| 15.....   | 1,600                 | 1,375              | 1,200             | 70% 10, 30% 1-2     | 47            | 19             | 61    |
| 16.....   | 1,800-A               | 1,325              | 1,150             | 5-6                 | 71            | 4              | 8     |
| 17.....   | 1,800-B               | 1,325              | 1,150             | 5-6                 | 26            | 2              | 3     |
| 18.....   | 1,800-C               | 1,325              | 1,150             | 5-6                 | 59            | 8              | 17    |
| 19.....   | 1,800-D               | 1,325              | 1,150             | 5-6                 | 71            | 27             | 61    |

The balance of the alloy was iron except for incidental impurities. The 2¾ inch square ingot was homogenized and then forged from a temperature of 2000° F. to 2 in. sq., reheated to 2000° F. and forged to 1½ in. sq., reheated to 2000° F. for 1 hour and forged to 7/8 in. sq., reheated to 2000° F. for 1 hour and then forged to 7/8 in. sq. The as-forged grain structure was A.S.T.M. 9-10 Blanks for forming test specimens were cut from the thus forged bar stock which were heat treated and then machined and tested.

The combination smooth/notch stress-rupture specimens utilized were standard A.S.T.M. specimens having a 0.178-in. diameter, a 0.712-in. long smooth gage section and a notch stress concentration factor ( $K_t$ ) of 3.8. Stress rupture tests at 1200° F. under a load of 100,000 p.s.i. (100 k.s.i.) were carried out, and the stress rupture life in hours (R.L., hrs.) the percent elongation (% El.) and the percent reduction in area (percent R.A.) are indicated in Table I below.

The test specimens were subjected to various heat treatments including solution treatment for 1 hour at temperatures ranging in 25° F. increments from 1600° F. to 1800° F. In each instance, solution treatment was for 1 hour followed by cooling in air. In the case of the

The optical micrographs, 500× magnification, of FIGS. 1A, 2A, 3A and 4A and the corresponding electron micrographs, 7700× magnification, were prepared from the tested stress rupture specimens of Test No. 13, No. 7, No. 4 and No. 2 respectively, with the area shown extending longitudinally with respect to the test specimen axes. Inasmuch as the primary and final aging temperatures for these four tests were the same, the results can be directly compared to show the critical effect of variations of the solution-treating temperature from 1650° F. and 1675° F., both of which are below the effective solvus temperature of the eta and delta phases and, on the other hand, 1700° F. which is at or just above the effective solvus temperature. The desirable globular form of the grain boundary precipitate is clearly seen in FIGS. 1B and 2B prepared from the specimens of Tests No. 13 and No. 7 respectively while the very much finer gamma prime and double prime can be seen distributed within the grains. On the other hand, an increase in grain size is clearly evident in FIGS. 3A and 3B (Test No. 4) although some but less than an effective amount of the globular eta and delta phases remain. Solution treatment at 1725° F. is clearly seen to be above the equilibrium solvus temperature for the eta and delta phases which have been sub-

stantially entirely been taken back into solid solution. The structures apparent in FIG. 4B extending upward toward the center of the micrograph from the bottom edge just to the right of the vertical center line are believed to be some form of carbide which was brought out. The enlarged size of the grains is clearly apparent.

While the specimens shown in FIGS. 1-4 were aged at a primary aging temperature of 1375° F. and a final aging temperature of 1200° F. which provided good results, the best properties for the composition of this intermediate range are brought out when it is solution treated at 1650° F. for 1 hour followed by primary aging at 1325° F. and final aging at 1150° F. The beneficial effect of this aging treatment is apparent from the 264-hour life and good ductility of Test No. 11. Good properties are also provided by solution treating as low as about 1625° F. as is apparent from Test No. 14. However, a sharp drop in stress rupture life is apparent when solution treatment is carried out at as low as 1600° F. as in the case of Test No. 15, clearly indicating that that temperature is below the effective solvus temperature of the gamma prime/gamma double prime phases and therefore too low.

The adverse effects of solution treating at 1800° F. are not rectified by the so-called stabilization treatments of the prior art. The seeming improvement in stress rupture ductility brought on by using a stabilization treatment at 1650° F. for 8 hours is seen to be at the expense of stress rupture life when the 71-hour life of Test No. 19 is compared to the 264-hour life of Test No. 11 which was subjected to the same primary and final aging treatment as Test No. 19. It should be noted that the solution and stabilization treatment of Test No. 19 also resulted in a sharp drop in the 0.2% yield strength of the composition as measured at room temperature and 1200° F.—a further indication that the material was thereby overaged. By overaging it is here meant that a cellular structure of eta phase is formed which extends into the grains and weakens the over-all structure.

A further important feature of the present invention resides in the fact that it makes possible the provision of controlled expansion-type alloys characterized by high strength and ductility for use at high temperatures. Thus, a further intermediate range to which the process of the present invention is applicable consists essentially in weight percent of about

|                 | Broad     | Preferred   |
|-----------------|-----------|-------------|
| Carbon.....     | 1.0-1     | 0.01-0.05   |
| Manganese.....  | 1.0-5.0   | 1.0-2.0     |
| Silicon.....    | 1.0-5.0   | 1.0-2.0     |
| Phosphorus..... | 1.0-0.020 | 1.0-0.020   |
| Sulfur.....     | 1.0-0.020 | 1.0-0.020   |
| Chromium.....   | 1.0-5     | 1.0-5       |
| Molybdenum..... | 1.0-5     | 1.0-5       |
| Nickel.....     | 35-40     | 36-39       |
| Cobalt.....     | 13-17     | 14.5-16.5   |
| Columbium.....  | 2.5-6     | 2.75-3.2    |
| Titanium.....   | 1-3       | 1.65-1.85   |
| Aluminum.....   | 0.1-2     | 0.85-1.15   |
| Boron.....      | 1.0-0.030 | 0.005-0.020 |

† Maximum

The balance of the composition is iron and incidental impurities which are preferably kept low which is facilitated by using a multiple vacuum melting practice such as that previously described hereinabove. While the broad range for columbium is indicated as about 2.5% to 6%, the better practice is to limit columbium to no more than about 3.5%. In the case of aluminum, the larger amounts tend to provide better properties, and thus an intermediate broad range of 0.5% to 1.5% is preferred. While the absence of boron can be tolerated, when elevated temperature stress rupture ductility is not desired, a small but definite amount of at least about 0.003% boron is required to obtain the outstanding stress rupture properties of the present invention. For best results 0.005% to 0.015% is used.

To provide a mean coefficient of linear expansion

(alpha I<sub>1</sub>) of about 3×10<sup>-6</sup>/° F. to 6×10<sup>-6</sup>/° F. from room temperature up to a Curie temperature or inflection temperature (T<sub>c</sub>) ranging from about 600° F. to 950° F., the composition is balanced within the foregoing intermediate range so as to satisfy the following two equations in which percents are also by weight:

$$T_c = 33.28(\%Ni + \%Co) - 77.85(\%Al) - 129.23(\%/Ti) - 24.34(\%Cb) - 590.10$$

$$\text{Alpha}_{11} = .3074(\%Ni + \%Co) - .5935(\%Al) - 1.159(\%Ti) - .0967(\%Cb) - 9.561$$

Preferably, the composition is balanced within the preferred range so as to provide a value of alpha<sub>11</sub> of 4.0×10<sup>-6</sup> to 4.5×10<sup>-6</sup>/° F. and a Curie temperature range of 760° F. to 860° F.

#### EXAMPLE 2

As an example of the preferred controlled expansion alloy of the present invention, an experimental vacuum induction heat having the following composition in weight percent was prepared:

|                |        |
|----------------|--------|
| Carbon.....    | 0.032  |
| Manganese..... | 0.01   |
| Silicon.....   | 0.01   |
| Nickel.....    | 38.35  |
| Cobalt.....    | 16.02  |
| Columbium..... | 2.77   |
| Titanium.....  | 1.76   |
| Aluminum.....  | 1.05   |
| Boron.....     | 0.0049 |

The balance was iron and incidental impurities which included no more than 0.001% phosphorus, no more than 0.001% sulfur, less than 0.1% chromium, and less than 0.1% molybdenum. The ingot was forged to bar stock which was then used for making test blanks which were heat treated, machined and tested. In addition to stress rupture test specimens, 1200° F. tensile specimens having a 0.252-in. diameter and a 1.0-in. long gage section were also prepared. Solution treatment of all of the specimens was for 1 hour at the temperature indicated followed by aging at 1325° F. for 8 hours, then cooling at the rate of 100° F. per hour to 1150° F., holding that temperature for 8 hours and then cooling in air. The effect of solution-treating temperatures from 1550° F. to 1700° F. on the stress rupture properties of the alloy of Example 2 measured at 1150° F. under a load of 110,000 p.s.i. are set forth in the following table.

TABLE II

| Soln. Temp. (° F.): | Rupt. life (hrs.) |      | Percent |
|---------------------|-------------------|------|---------|
|                     | El.               | R.A. |         |
| 1,550.....          | 22.6              | 15.5 | 54.0    |
| 1,575.....          | 158.3             | 11.7 | 44.4    |
| 1,600.....          | 237.3             | 14.3 | 37.3    |
| 1,625.....          | 305.3             | 12.3 | 30.8    |
| 1,650.....          | 4.3               | 1.4  | 2.0     |
| 1,675.....          | 2.9               | 1.4  | .....   |
| 1,700.....          | 172.6             | 1.4  | 3.2     |

The foregoing data demonstrates that the effective solvus temperature of the eta and delta phases in this composition occurs between about 1625° F. and 1650° F. for such solution treatments. While useful properties can still be obtained by solution treating for 1 hour at 1575° F., 1550° F. is too low probably because it is below the effective solvus temperature of the gamma prime and gamma double prime phases.

The results of tensile tests carried out at 1200° F. on specimens subjected to the same heat treatments as those

to which the stress rupture specimens just described were subjected are set forth in the following table.

TABLE III

| Soln. Temp. (° F.): | .2% Y.S.<br>(K.s.i.) | U.T.S.<br>(K.s.i.) | Percent |      |
|---------------------|----------------------|--------------------|---------|------|
|                     |                      |                    | El.     | R.A. |
| 1,550.....          | 140.1                | 152.3              | 26.3    | 63.6 |
| 1,575.....          | 147.2                | 161.3              | 20.2    | 60.0 |
| 1,600.....          | 146.5                | 158.1              | 22.6    | 56.8 |
| 1,625.....          | 148.1                | 164.3              | 22.1    | 54.5 |
| 1,650.....          | 137.3                | 161.5              | 15.0    | 22.3 |
| 1,675.....          | 132.9                | 158.2              | 11.6    | 18.9 |
| 1,700.....          | 130.9                | 155.0              | 10.0    | 19.7 |

For this composition, optimum elevated temperature properties are provided by a solution-treating temperature of about 1575° F. to 1625° F., the effect being mainly on the .2% yield strength (.2% Y.S.) rather than on the ultimate tensile strength (U.T.S.).

For comparison purposes, a heat was prepared as described in connection with Example 2 having an equivalent analysis except that the boron content was 0.0022% and containing 0.031% carbon, 37.73% nickel, 16.19% cobalt, 3.02% columbium, 1.74% titanium, 1.00% aluminum, and the balance iron except for inconsequential impurities. Two stress rupture specimens were prepared which were solution treated at 1625° F. for 1 hour followed by primary aging at 1325° F. and final aging at 1150° F. as was described in connection with Example 2. When subjected to a stress of 110 k.s.i. at 1150° F., both specimens failed at the notch one after only 1.2 hours and the other after only 2.1 hours.

EXAMPLE 3

As a further example of a controlled expansion alloy and its heat treatment in accordance with the present invention, a vacuum induction heat was prepared as described in connection with Example 2 having the following composition in weight percent:

|                 |        |
|-----------------|--------|
| Carbon .....    | 0.031  |
| Manganese ..... | 0.01   |
| Silicon .....   | <0.01  |
| Nickel .....    | 37.44  |
| Cobalt .....    | 13.99  |
| Columbium ..... | 3.10   |
| Titanium .....  | 1.53   |
| Aluminum .....  | 0.58   |
| Boron .....     | 0.0047 |

The balance was iron and incidental impurities which included less than 0.1% each of chromium and molybdenum, and no more than 0.001% each of phosphorus and sulfur. Combination smooth/notch stress rupture specimens prepared from the composition of Example 3 as was described in connection with Example 2, were subjected to a stress of 110,000 p.s.i. at a temperature of 1150° F., and the results are set forth in Table IV.

TABLE IV

| Soln. temp. (° F.): | Rupt. life<br>(hrs.) | Percent |      |
|---------------------|----------------------|---------|------|
|                     |                      | El.     | R.A. |
| 1,550.....          | 103.3                | 13.8    | 48.2 |
| 1,575.....          | 119.4                | 14.3    | 45.9 |
| 1,600.....          | 113.0                | 14.7    | 48.3 |
| 1,625.....          | 13.6                 | (1)     | (1)  |
| 1,650.....          | 2.6                  | (1)     | (1)  |
| 1,675.....          | 1.5                  | (1)     | (1)  |
| 1,700.....          | 0.6                  | (1)     | (1)  |

<sup>1</sup> Notch breaks.

Except for the critical amount of boron present therein, the alloy of Example 3 corresponds to that of said Pat. No. 3,157,495. The unique stress rupture ductility provided by the present invention is clearly brought out by the data in Table IV. It may be noted that the difference in the aluminum content of about 0.5% between the compositions of Example 2 and Example 3 is believed to account for the difference in optimum solution-treating

temperatures between the two alloys, that of Example 2 being higher because of the greater amount of aluminum.

For comparison with Example 3, a composition of said Pat. No. 3,157,495 was prepared as described in connection with Example 3 and having the following analysis in weight percent:

|                 |        |
|-----------------|--------|
| Carbon .....    | 0.032  |
| Manganese ..... | 0.02   |
| Silicon .....   | 0.01   |
| Nickel .....    | 36.77  |
| Cobalt .....    | 14.08  |
| Columbium ..... | 2.94   |
| Titanium .....  | 1.51   |
| Aluminum .....  | 0.55   |
| Boron .....     | 0.0005 |

The balance was iron and incidental impurities which included 0.004% phosphorus, 0.001% sulfur, 0.04% chromium, and less than 0.01% molybdenum. Combination smooth/notch stress rupture specimens were prepared as was described in connection with Example 3 and after being solution treated at 1575° F. for 1 hour and subjected to the same aging treatment as the specimens of Example 3, the specimens were subjected to a load of 110,000 p.s.i. at 1150° F. One specimen failed after only 0.9 hour with 10.3% elongation and 18.0% reduction in area, and a second such test specimen failed after only 0.6 hour with 18% elongation and 30.9% reduction in area, indicating a stress rupture life which is too short to be acceptable. When specimens of this composition were solution treated at 1625° F. but otherwise treated and tested in the same way as was just described, all specimens suffered notch breaks indicating that they did not have stress rupture ductility, as was expected.

Throughout this specification and the appended claims, when the element columbium is referred to, it is to be understood as including a certain amount of tantalum ranging from about 1% to 20% of the amount of columbium. That amount of tantalum usually is present in commercial supplies of columbium customarily used for alloying purposes. Further, additional amounts of columbium can be replaced if desired by tantalum. Thus "columbium" is to be read as including tantalum or as the combined columbium plus tantalum content of the composition.

The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed.

What is claimed is:

1. In the method of heat treating a nickel-iron base alloy which consists essentially by weight of about

|                  |               |
|------------------|---------------|
| Carbon .....     | Up to 0.1%.   |
| Manganese .....  | Up to 1%.     |
| Silicon .....    | Up to 0.5%.   |
| Chromium .....   | Up to 20%.    |
| Molybdenum ..... | Up to 3%.     |
| Tungsten .....   | do            |
| Nickel .....     | 30% to 50%    |
| Cobalt .....     | Up to 20%.    |
| Columbium .....  | 2.5% to 6%.   |
| Titanium .....   | 1% to 3%.     |
| Aluminum .....   | 0.1% to 2%.   |
| Vanadium .....   | Up to 1%.     |
| Zirconium .....  | Up to 0.1%.   |
| Hafnium .....    | Up to 2%.     |
| Boron .....      | Up to 0.030%. |

and the balance iron, the iron being at least about 30% and which is strengthened by precipitation hardening to bring out gamma prime and gamma double prime phases, the steps of solution treating said alloy at a temperature which is above the effective solvus temperature of the

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gamma prime and double prime phases and below the effective solvus temperature of eta and delta phases so as to form a precipitate in the grain boundaries of said alloy made up of said eta and delta phases, and then aging said alloy at a temperature below the effective solvus temperature of said gamma prime and gamma double prime phases to form a fine dispersion thereof of said gamma prime and gamma double prime phases within the grains of said alloy.

2. In the method of heat treating a nickel-iron base alloy which consists essentially by weight of about

|                  |                  |
|------------------|------------------|
| Carbon .....     | 0.01% to 0.05%.  |
| Manganese .....  | Up to 0.35%.     |
| Silicon .....    | do               |
| Chromium .....   | 14.5% to 17.5%.  |
| Molybdenum ..... | Up to 1%.        |
| Nickel .....     | 39% to 44%.      |
| Cobalt .....     | Up to 1%.        |
| Columbium .....  | 2.5% to 3.3%.    |
| Titanium .....   | 1% to 2%.        |
| Aluminum .....   | 0.15% to 0.40%.  |
| Boron .....      | 0.001% to 0.01%. |

and the balance iron, said alloy being strengthened by precipitation hardening to bring out gamma prime and gamma double prime phases and which includes the steps of solution treating said alloy at a temperature which is above the effective solvus temperature of the gamma prime and double prime phases and below the effective solvus temperature of eta and delta phases so as to form a precipitate in the grain boundaries of said alloy made up of said eta and delta phases, and then aging said alloy at a temperature below the effective solvus temperature of said gamma prime and gamma double prime phases to form a fine dispersion of said gamma prime and gamma double prime phases within the grains of said alloy.

3. In the method of heat treating a nickel-iron base alloy which consists essentially by weight of about

|                  |               |
|------------------|---------------|
| Carbon .....     | Up to 0.1%.   |
| Manganese .....  | Up to 0.50%.  |
| Silicon .....    | Up to 0.50%.  |
| Chromium .....   | Up to 0.5%.   |
| Molybdenum ..... | do            |
| Nickel .....     | 35% to 40%.   |
| Cobalt .....     | 13% to 17%.   |
| Columbium .....  | 2.5% to 6%.   |
| Titanium .....   | 1% to 3%.     |
| Aluminum .....   | 0.1% to 2%.   |
| Boron .....      | Up to 0.030%. |

and the balance iron, said alloy being strengthened by precipitation hardening to bring out gamma prime and gamma double prime phases and which includes the steps of solution treating said alloy at a temperature which is about the effective solvus temperature of the gamma prime and double prime phases and below the effective solvus temperature of eta and delta phases so as to form a precipitate in the grain boundaries of said alloy made up of said eta and delta phases, and then aging said alloy at a temperature below the effective solvus temperature of said gamma prime and gamma double prime phases to form a fine dispersion of said gamma prime and gamma double prime phases within the grains of said alloy.

4. The method of claim 3 in which said alloy consists essentially of about 0.01% to 0.05% carbon, about 0.20% max. manganese, about 0.20% max. silicon, about 0.5% max. chromium, about 0.5% max. molybdenum, about 36% to 39% nickel, about 14.5% to 16.5% cobalt, about 2.75% to 3.2% columbium, about 1.65% to 1.85% titanium, about 0.85% to 1.15% aluminum, about 0.005% to 0.020% boron, and the balance iron, and includes forging said alloy before said solution treatment, said forging at least in part being carried out within about 100° F. of the effective solvus temperature of the eta and delta phases of said alloy so as to establish a grain size which is substantially no coarser than about A.S.T.M. 8.

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