TREATING NICKEL BASE ALLOYS

Inventor: Ronald E. Bailey, New York Mills, N.Y.
Assignee: Special Metals Corporation, New Hartford, N.Y.
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References Cited
UNITED STATES PATENTS
3,329,535 7/1967 Langer et al. 148/11.5 F

ABSTRACT

A method of treating a nickel base alloy so as to produce an alloy having a structure characterized by dispersed discrete fine spherical carbides. The method comprises the steps of casting an ingot of nickel base alloy, homogenizing the ingot at a temperature of from 2,200°F to 2,400°F so as to dissolve primary carbides present in the alloy and increase the chemical homogeneity thereof; cooling the ingot at least to a temperature of from 1,750°F to 2,185°F at a rate which substantially precludes the precipitation of coarse and film-like carbides; and hot working the ingot with the primary carbides in solution with sufficient intensity to cause dispersed discrete fine spherical carbides to precipitate.

20 Claims, 2 Drawing Figures
TREATING NICKEL BASE ALLOYS

The outstanding high temperature properties of nickel base superalloys have made their use in turbines and other high temperature applications quite extensive. However, as in all areas of technology, metallurgists and other scientists and engineers are constantly striving to develop improved alloys. This work has primarily centered around new alloys with dissimilar chemistries, but has also embraced new heat treatments for those already developed, and it is this latter type of work which led to the present invention.

It has commonly been observed that fracture in nickel base super-alloys (particularly in the direction normal to metal flow) occurs by crack propagation along carbide stringers, and this is especially true when the stringers are associated with remnant dendritic segregation. The stringers which include large elongated carbide particles and aligned discrete carbide particles or a combination of both, provide paths which facilitate fracture.

The present invention provides a sophisticated heat treatment which decreases dendritic segregation and minimizes the formation of carbide stringers. Instead of coarse and/or film-like carbides, it produces a structure characterized by dispersed discrete fine spherical carbides and an alloy with a high degree of chemical homogeneity. As a result the alloy has improved tensile strength and/or tensile ductility and/or stress rupture properties, and particularly in the direction transverse to metal solidification and/or metal flow. More specifically, the invention involves a high homogenization temperature and critically controlled cooling and hot working, as well as casting. Moreover, it is in part based upon processing which was previously considered detrimental. Previous technical reports have indicated that so called "high" homogenization temperatures cause a subsequent formation of carbide films and thereby decrease ductility.

It is accordingly an object of this invention to provide a method of treating nickel base superalloys, so as to improve their properties.

The foregoing and other objects of the invention will be best understood from the following description, reference being had to the accompanying photomicrographs wherein:

FIG. 1 is a photomicrograph at 50X of a billet processed in accordance with the present invention; and FIG. 2 is a photomicrograph at 50X of a billet processed in accordance with prior art techniques.

Nickel base alloys, having a structure characterized by dispersed discrete fine spherical carbides, are produced, in accordance with the present invention, by a method which comprises the steps of: casting an ingot of nickel base alloy; homogenizing the ingot at a temperature of from 2,200° to 2,400° F and preferably at a temperature of from 2,250° to 2,400° F, thereby dissolving primary carbides present in the alloy and increasing the chemical homogeneity thereof; cooling the ingot at least to a temperature of from 1,750° to 2,185° F at a rate which substantially precludes the precipitation of coarse and film-like carbides; and hot working the ingot with the primary carbides in solution with sufficient intensity to cause dispersed discrete fine spherical carbides to precipitate. The primary carbides are generally MC or M₄C carbides. MC carbides are comprised of titanium with optional amounts of molybdenum, nickel, chromium and zirconium, and M₄C carbides are comprised of molybdenum with optional amounts of tungsten, chromium, iron and cobalt. It is essential to dissolve the primary carbides in order for the desired dispersed discrete fine spherical carbides to form during hot working, and in order to do so homogenization must be at a temperature of at least 2,200° F. A maximum homogenization temperature of 2,400° F is, however, imposed as carbides melt at higher temperatures. Prior to the present invention, it was generally accepted that carbide films would subsequently form following homogenization at temperatures as high as 2,200° F, and that these films would detrimentally affect the alloys' ductility. For homogenization, a sufficient period of time is preferably allowed for the primary carbides to dissolve and to permit carbon and other elements to diffuse over a distance at least approaching one half the dendrite-arm spacing. As a general rule the required period for homogenization is in excess of 4 hours, although the specific homogenization time can be set as it is dependent upon the homogenization temperature and the thickness of the ingot. To obtain the desired carbide structure the ingot must hot worked with the primary carbides in solution and with an intensity which results in an overall reduction in area to the cross section of the ingot of at least 20 percent, and preferably at least 30 percent. Moreover, the hot working must occur at a temperature lower than that at which the primary carbides dissolve and within a range of from 1,750° to 2,185° F, and preferably within a range of from 1,800° to 2,150° F. The ingot tends to excessively crack at lower hot working temperatures and cannot be uniformly deformed without cracking at higher temperatures. Prior to hot working, the ingot must be cooled to at least its hot working temperature at a rate which substantially precludes the precipitation of coarse and film-like carbides. This cooling rate is in excess of 25° F per hour, and is preferably in excess of 70° F per hour, and moreover, can be to a temperature as low as room temperature. Of course, ingots cooled to room temperature must be reheated for hot working. By hot working, the present invention includes forging, swaging, extrusion, rolling, drawing, pressing and all other processes known to the art. Furthermore hot working temperatures and all other temperatures referred to herein as well as rates involving temperatures are based upon furnace temperatures rather than metal temperatures, as it is more practical to talk about furnace temperatures when discussing production size ingots and billets. Furnace temperatures are lower than metal temperatures during cooling, and cooling as discussed above is a critical part of the present invention. Metal temperatures do, however, reach furnace temperatures during homogenization due to the prolonged exposure at temperature. The nickel base alloy being treated is most often a gamma prime strengthened alloy and generally, but not necessarily, consists essentially of, in weight percent: up to 0.2 percent carbon, up to 2.0 percent manganese, up to 2 percent silicon, from 5 to 25 percent chromium, up to 20 percent cobalt, up to 10 percent molybdenum, up to 10.0 percent titanium, up to 5 percent aluminum, up to 0.05 percent boron, up to 0.5 percent nickel, up to 40.0 percent iron, up to 1.0 percent of metal from the group consisting of columbium, tantalum and hafnium, up to 2.0 percent vanadium, up to 10 percent
tungsten, up to 0.5 percent rhenium, up to 0.02 percent of metal from Group II A of the periodic table, up to 0.5 percent of rare earth metal, balance essentially nickel, said percentage of nickel being at least 40 percent. Within this broad range an alloy which has proven to be particularly well suited for the treatment of the present invention consists essentially of, in weight percent, up to 0.15 percent carbon, up to 1.0 percent manganese, up to 1.0 percent silicon, from 15 to 23 percent chromium, from 10 to 18 percent cobalt, from 3 to 6 percent molybdenum, from 2 to 3.5 percent titanium, from 1.0 to 2.0 percent aluminum, from 0.0025 to 0.0125 percent boron, from 0.02 to 0.2 percent zirconium, up to 2 percent iron, up to 4.0 percent of metal from the group consisting of columbium, tantalum and hafnium, up to 0.5 percent vanadium, up to 0.02 percent of metal from Group II A of the periodic table, up to 0.5 percent of rare earth metal, balance essentially nickel. Another alloy within the broad range for which there is reason to believe that it is particularly well suited for the treatment of the present invention, consists essentially of, in weight percent, up to 0.15 percent carbon, up to 2.0 percent manganese, up to 1.0 percent silicon, from 5.0 to 15.0 percent chromium, up to 10.0 percent cobalt, from 2 to 7 percent molybdenum, from 1.0 to 3.75 percent titanium, up to 2 percent aluminum, up to 0.05 percent boron, from 25 to 40 percent iron, balance essentially nickel. For purposes of definition gamma prime is defined and believed to have the general composition Mo(sAl and/or Ti and possibly one or more additional metals from the group comprised of tantalum, columbium, molybdenum and/or chromium). As used herein, the "M" portion of the gamma prime is regarded as consisting mainly of nickel with possible one or more metals from the group comprised of chromium, cobalt, molybdenum and iron.

The following examples are illustrative of the invention.

A nickel base alloy ingot was cast and homogenized for 48 hours at 2,300°F. From the homogenization temperature the ingot was cooled to room temperature at a rate which substantially precluded the precipitation of coarse and film-like carbides and kept the primary carbides in solution. After cooling the ingot was reheated at a temperature of 2,125°F and worked from a 20 inch ingot to a 14%-inch octagon billet, which was subsequently ground to a 13%-inch octagon billet. Dispersed discrete fine spherical carbides precipitated during hot working. This desirable carbide morphology and distribution is seen in FIG. I which is a photomicrograph of the hot worked billet. The composition of the ingot was, in weight percent, 0.05 percent carbon, less than 0.10 percent manganese, less than 0.10 percent silicon, 19.1 percent chromium, 13.7 percent cobalt, 4.20 percent molybdenum, 3.10 percent titanium, 1.34 percent aluminum, 0.005 percent boron, 0.06 percent zirconium, 0.72 percent iron, balance essentially nickel.

A number of ingots having a composition, in weight percent, of from 0.05 to 0.07 percent carbon, less than 0.10 percent manganese, less than 0.10 percent silicon, 18.7 percent to 19.7 percent chromium, 13.0 to 14.5 percent cobalt, 3.75 to 4.5 percent molybdenum, 2.9 to 3.2 percent titanium, 1.30 to 1.38 percent aluminum, 0.0040 to 0.0055 percent boron, 0.055 to 0.075 percent zirconium, less than 1.50 percent iron, balance essentially nickel, were processed in accordance with prior art techniques. The ingots were homogenized at a maximum temperature of 2,175°F, subjected to haphazard furnace cooling to a temperature of from 1,500°F to 1,700°F, air cooled to room temperatures therefrom and hot worked from 2,125°F into 14%-inch octagon billets which were subsequently ground to 13%-inch octagon billets. FIG. 2 is a photomicrograph at 50X of one of these billets. Note that the carbides therein are concentrated in bands.

Pancake property data for both the alloy treated in accordance with the present invention and for the average of the prior art billets is set forth below in Table I. The data which is more indicative of transverse properties than longitudinal properties clearly shows the value of the heat treatment of the present invention.

| TABLE I |
|-----------------|-----------------|-----------------|-----------------|
| Stress Rupture Properties 1350°F/80 ksi Notch | 1000°F Tensile Properties | Room Temperature Tensile Properties |
|                  |                  |                  |
|                  | U.T.S.          | Y.S.            | Elongation (%)  |
|                  | (ksi)           | (ksi)           |                  |
| PRESENT          | 201.0           | 148.0           |                  |
| INVENTION ART    | 190.4           | 137.5           |                  |

It will be apparent to those skilled in the art that the novel principles of the invention disclosed herein in connection with specific examples thereof will suggest various other modifications and applications of the same. It is accordingly desired that in construing the breadth of the appended claims they shall not be limited to the specific examples of the invention described herein. I claim:

1. A method of treating a nickel base alloy so as to produce an alloy having a structure characterized by dispersed discrete fine spherical carbides, which comprises the step of: casting an ingot of nickel base alloy; homogenizing said ingot at a temperature of from 2,200°F to 2,400°F, thereby dissolving primary carbides present in said alloy and increasing the chemical homogeneity thereof; cooling said ingot at least to a temperature of from 1,750°F to 2,185°F at a rate which substantially precludes the precipitation of coarse and film-like carbides, said cooling rate being in excess of 25°F per hour; and hot working said ingot with said primary carbides in solution with sufficient intensity to cause dispersed discrete fine spherical carbides to precipitate, said hot working occurring at a temperature lower than...
that at which said primary carbides dissolve and within a temperature range of from 1,750° to 2,185° F, said hot working resulting in an overall reduction in area to the cross section of the ingot of at least 20 percent.

2. A method according to claim 1 wherein said nickel base alloy consists essentially of, in weight percent, up to 0.2 percent carbon, up to 2.0 percent manganese, up to 2.0 percent silicon, from 5.0 to 25.0 percent chromium, up to 23 percent cobalt, up to 10 percent molybdenum, up to 10.0 percent titanium, up to 5 percent aluminum, up to 0.05 percent boron, up to 0.5 percent zirconium, up to 40.0 percent iron, up to 8.0 percent of metal from the group consisting of columbium, tantalum and hafnium, up to 2.0 percent vanadium, up to 10 percent tungsten, up to 0.5 percent rhenium, up to 0.02 percent of metal from Group II A of the periodic table, up to 0.5 percent of rare earth metal, balance essentially nickel, said percentage of nickel being at least 40 percent.

3. A method according to claim 1 wherein said nickel base alloy consists essentially of, in weight percent, up to 0.15 percent carbon, up to 1.0 percent manganese, up to 1.0 percent silicon, from 15–23 percent chromium, from 10 to 18 percent cobalt, from 3 to 6 percent molybdenum, from 2 to 3.5 percent titanium, from 1.0 to 2.0 percent aluminum, from 0.0025 to 0.0125 percent boron, from 0.02 to 0.2 percent zirconium, up to 2 percent iron, up to 4 percent of metal from the group consisting of columbium, tantalum and hafnium, up to 0.5 percent vanadium, up to 0.02 percent of metal from Group II A of the periodic table, up to 0.5 percent of rare earth metal, balance essentially nickel.

4. A method according to claim 1 wherein said nickel base alloy consists essentially of, in weight percent, up to 0.15 percent carbon, up to 2.0 percent manganese, up to 1.0 percent silicon, from 5.0 to 15.0 percent chromium, up to 10.0 percent cobalt, from 2 to 7 percent molybdenum, from 1.0 to 3.75 percent titanium, up to 2 percent aluminum, up to 0.05 percent boron, from 25 to 40 percent iron, balance essentially nickel.

5. A method according to claim 1 wherein said nickel base alloy is a gamma prime strengthened alloy.

6. A method according to claim 1 wherein said homogenized ingot is cooled to room temperature with said primary carbides in solution and reheated to said hot working temperature.

7. A method according to claim 1 wherein said homogenized ingot is cooled directly to said hot working temperature with said primary carbides in solution.

8. A method according to claim 1 wherein said hot working occurs within a temperature range of from 1,800° – 2,150° F.

9. A method according to claim 1 wherein said overall reduction in area to the cross section of said ingot is at least 30 percent.

10. A method according to claim 1 wherein said ingot is homogenized for a period of time in excess of 4 hours.

11. A method according to claim 1 wherein said ingot is homogenized at a temperature of at least 2,250° F.

12. A method according to claim 11 wherein said nickel base alloy consists essentially of, in weight percent, up to 0.2 percent carbon, up to 2.0 percent manganese, up to 2.0 percent silicon, from 5.0 to 25.0 percent chromium, up to 23 percent cobalt, up to 10 percent molybdenum, up to 10.0 percent titanium, up to 5 percent aluminum, up to 0.05 percent boron, up to 0.5 percent zirconium, up to 40.0 percent iron, up to 8.0 percent of metal from the group consisting of columbium, tantalum and hafnium, up to 2.0 percent vanadium, up to 10 percent tungsten, up to 0.5 percent rhenium, up to 0.02 percent of metal from Group II A of the periodic table, up to 0.5 percent of rare earth metal, balance essentially nickel, said percentage of nickel being at least 40 percent.

13. A method according to claim 11 wherein said nickel base alloy consists essentially of, in weight percent, up to 0.15 percent carbon, up to 1.0 percent manganese, up to 1.0 percent silicon, from 15–23 percent chromium, from 10 to 18 percent cobalt, from 3 to 6 percent molybdenum, from 2 to 3.5 percent titanium, from 1.0 to 2.0 percent aluminum, from 0.0025 to 0.0125 percent boron, from 0.02 to 0.2 percent zirconium, up to 2 percent iron, up to 4 percent of metal from the group consisting of columbium, tantalum and hafnium, up to 0.5 percent vanadium, up to 0.02 percent of metal from Group II A of the periodic table, up to 0.5 percent of rare earth metal, balance essentially nickel.

14. A method according to claim 11 wherein said nickel base alloy consists essentially of, in weight percent, up to 0.15 percent carbon, up to 2.0 percent manganese, up to 1.0 percent silicon, from 5.0 to 15.9 percent chromium, up to 10.0 percent cobalt, from 2 to 7 percent molybdenum, from 1.0 to 3.75 percent titanium, up to 2 percent aluminum, up to 0.05 boron, from 25 to 40 percent iron, balance essentially nickel.

15. A method according to claim 11 wherein said nickel base alloy is a gamma prime strengthened alloy.

16. A method according to claim 1 wherein said cooling rate is in excess of 70° F per hour.

17. A method according to claim 16 wherein said nickel base alloy consists essentially of, in weight percent, up to 0.2 percent carbon, up to 2.0 percent manganese, up to 2.0 percent silicon, from 5.0 to 25.0 percent chromium, from 23 percent cobalt, up to 10 percent molybdenum, up to 10.0 percent titanium, up to 5 percent aluminum, up to 0.05 percent boron, up to 0.5 percent zirconium, up to 40.0 percent iron, up to 8.0 percent of metal from the group consisting of columbium, tantalum and hafnium, up to 2.0 percent vanadium, up to 10 percent tungsten, up to 0.5 percent rhenium, up to 0.02 percent of metal from Group II A of the periodic table, up to 0.5 percent of rare earth metal, balance essentially nickel, said percentage of nickel being at least 40 percent.

18. A method according to claim 16 wherein said nickel base alloy consists essentially of, in weight percent, up to 0.15 percent carbon, up to 1.0 percent manganese, up to 1.0 percent silicon, from 15–23 percent chromium, from 10 to 18 percent cobalt, from 3 to 6 percent molybdenum, from 2 to 3.5 percent titanium, from 1.0 to 2.0 percent aluminum, from 0.0025 to 0.0125 percent boron, from 0.02 to 0.2 percent zirconium, up to 2 percent iron, up to 4.0 percent of metal from the group consisting of columbium, tantalum and hafnium, up to 0.5 percent vanadium, up to 0.02 percent of metal from Group II A of the periodic table, up
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7

to 0.5 percent of rare earth metal, balance essentially nickel.

19. A method according to claim 16 wherein said nickel base alloy consists essentially of, in weight percent, up to 0.15 percent carbon, up to 2.0 percent manganese, up to 1.0 percent silicon, from 5.0 percent to 15.0 percent chromium, up to 10.0 percent cobalt,

8

from 2 to 7 percent molybdenum, from 1.0 to 3.75 percent titanium, up to 2 percent aluminum, up to 0.05 percent boron, from 25 to 40 percent iron, balance essentially nickel.

20. A method according to claim 16 wherein said nickel base alloy is a gamma prime strengthened alloy.