

[54] TREATING NICKEL BASE ALLOYS

[75] Inventor: **Ronald E. Bailey**, New York Mills, N.Y.

[73] Assignee: **Special Metals Corporation**, New Hartford, N.Y.

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[51] Int. Cl. **C22f 1/10**

[58] Field of Search **148/2, 11.5 R, 11.5 F**

[56] **References Cited**

UNITED STATES PATENTS

3,329,535 7/1967 Langer et al. **148/11.5 F**

Primary Examiner—Richard O. Dean

Attorney—Vincent G. Gioia et al.

[57] **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° to 2,400° F so as to dissolve primary carbides present in the alloy and increase the chemical homogeneity thereof, cooling the alloy at a rate which substantially precludes the precipitation of coarse and film-like carbides at temperatures above 1,900° F and at a second rate in which dispersed fine spherical carbides precipitate at temperatures below 1,900° F; and hot working the alloy at a temperature lower than that at which the primary carbides dissolve.

17 Claims, 4 Drawing Figures

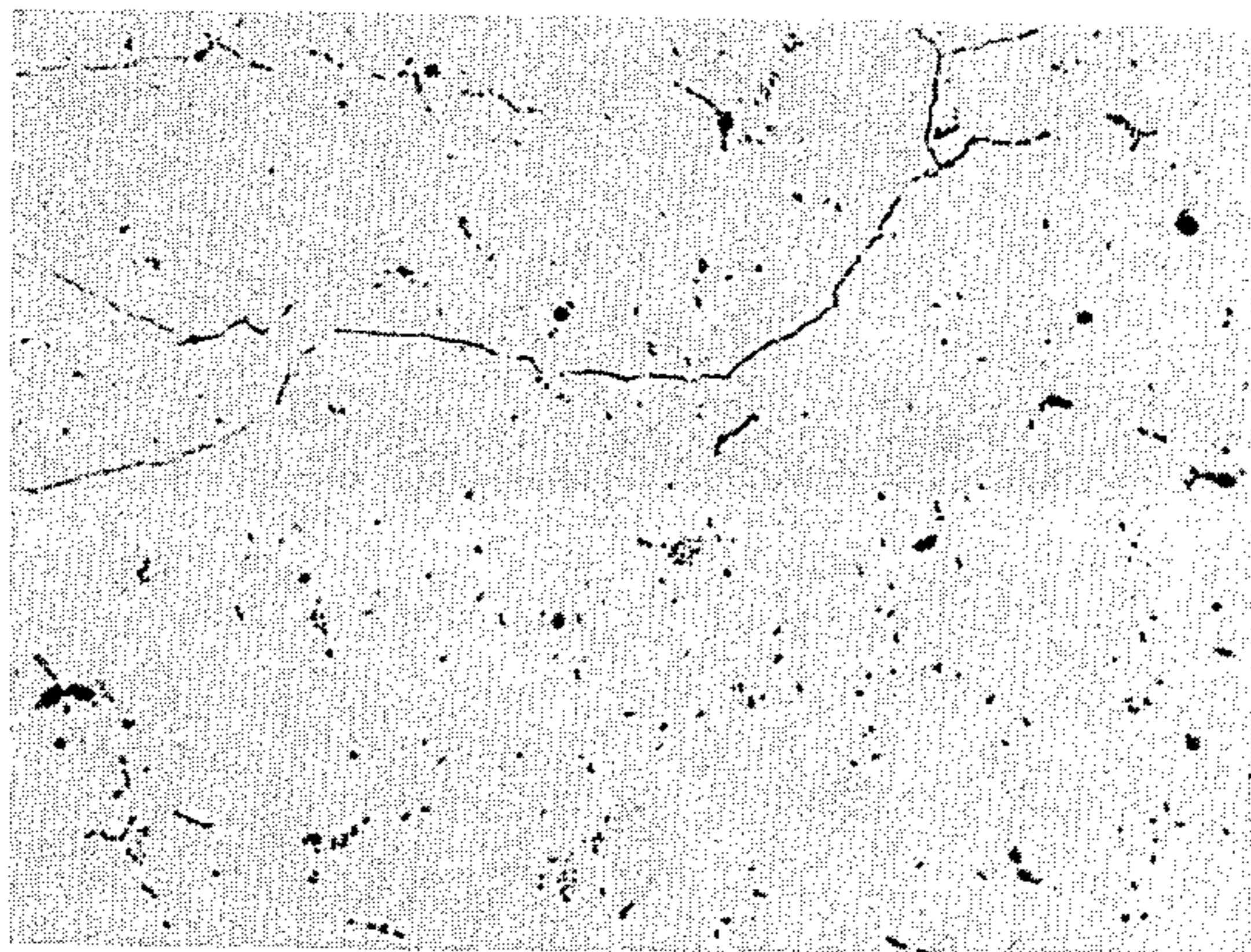


FIG. 2

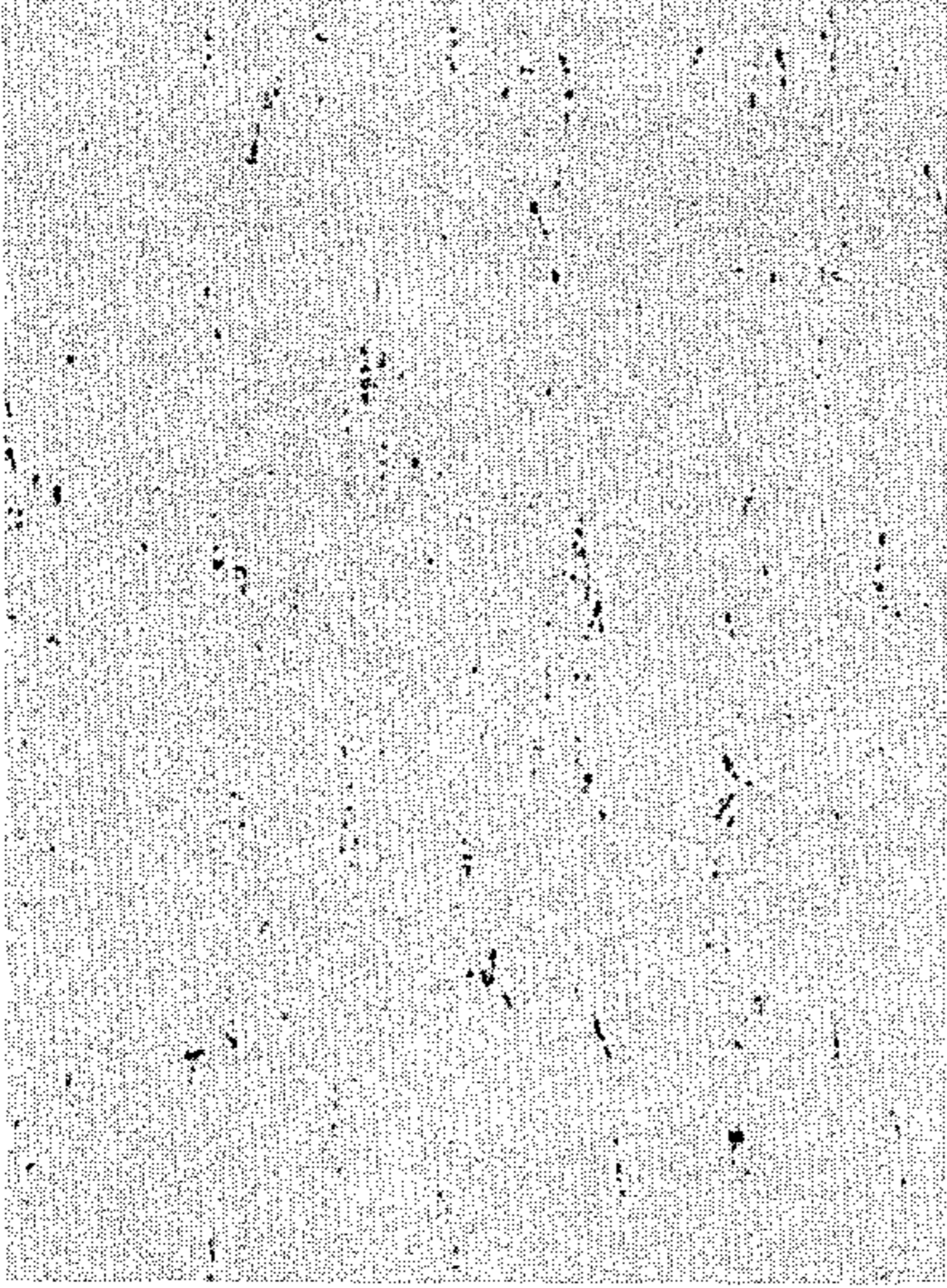


FIG. 4

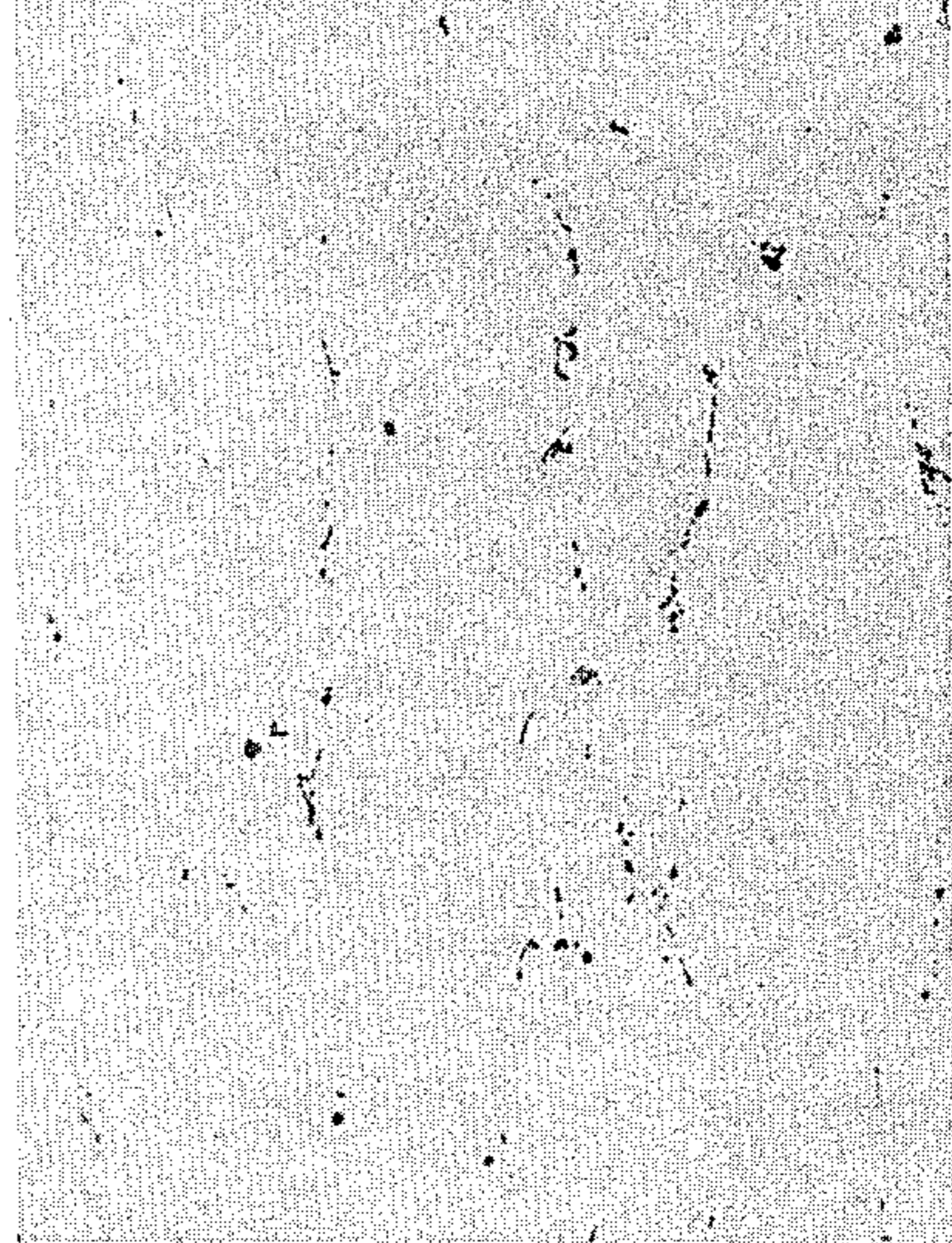


FIG. 1

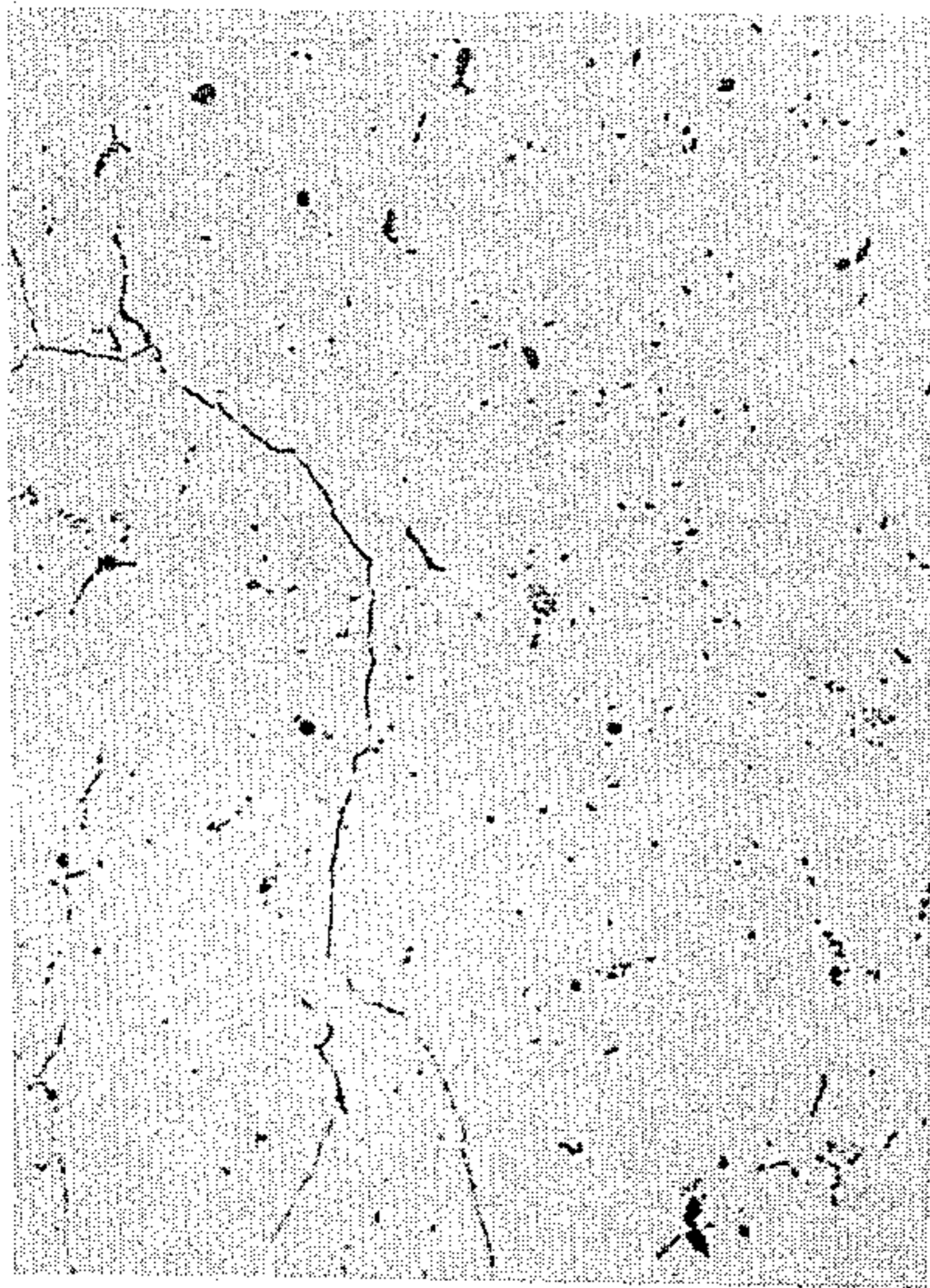
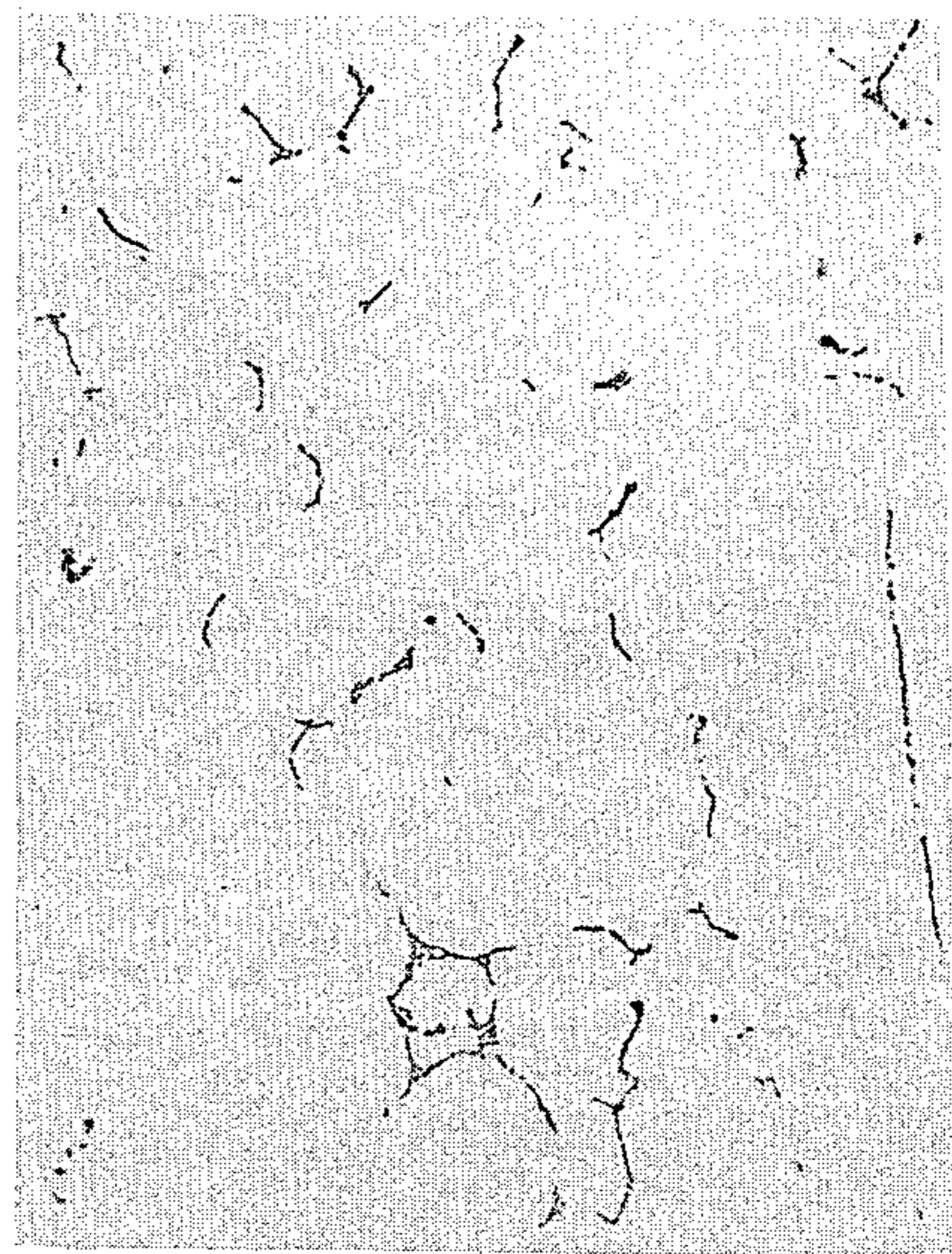


FIG. 3



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 superalloys (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 rates, as well as casting and hot working. 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 50 \times of an ingot processed in accordance with the present invention.

FIG. 2 is a photomicrograph at 50 \times of a billet processed in accordance with the present invention;

FIG. 3 is a photomicrograph at 50 \times of an ingot processed in accordance with prior art techniques; and

FIG. 4 is a photomicrograph at 50 \times 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 alloy at a rate which substantially precludes the precipitation of coarse and film-like carbides at temperatures above 1,900° F and at a rate in which dispersed fine spherical carbides precipitate at temperatures below 1,900° F; and hot working the alloy at a temperature

lower than that at which the primary carbides dissolve. The primary carbides which form during the solidification of the ingot and/or during the cooling thereof are generally MC or M₆C carbides. MC carbides are comprised of titanium with optional amounts of molybdenum, nickel, chromium and zirconium, and M₆C 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 cooling, 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 alloy's 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 local dendrite-arm spacing. As a general rule the required period for homogenization is in excess of 4 hours, although no specific time period can be set as it is dependent upon the homogenization temperature and the thickness of the ingot. To obtain the desired carbide structure cooling from the homogenization temperature to 1,900° F must be conducted at a rate fast enough to preclude the precipitation of coarse and film-like carbides. The cooling rate to 1,900° F must be in excess of 25° F per hour, and is preferably in excess of 70° F per hour. The cooling rate at temperatures below 1,900° F and during the period at which precipitation occurs is, on the other hand, one which is intentionally kept down. More specifically, it is maintained below 125° F per hour and preferably below 60° F per hour. Of course, the cooling rate to 1,900° F is in excess of that employed during the period of precipitation at temperatures below 1,900° F. No specific numerical range can, however, be placed upon the period of time at which precipitation occurs, as the period is dependent upon both the cooling rate and the thickness of the ingot. Moreover, the cooling rate during the period at which precipitation occurs often encompasses holding periods, as the desired carbide structure can be obtained by holding the alloy at a particular temperature for a period of time. For example, if the alloy is held at 1,200° F for 1 hour the 1 hour is included in calculating its cooling rate from 1,900° to 1,200° F. With regard to this, a preferred holding temperature is from 950° to 1,350° F. After cooling the alloy is hot worked; e.g., forged, swaged, extruded, rolled, drawn or pressed, within a temperature range of from 1,750° to 2,185° F and preferably within a temperature range of from 1,800° to 2,150° F. At lower temperatures alloys tend to excessively crack and at higher temperatures they cannot uniformly deform without cracking. The 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 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. 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 15-23 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 M_3 (Al 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

of 87.5° F per hour. Cooling was performed at a rate sufficiently fast to substantially preclude the precipitation of coarse and film-like carbides. From 1,900° F the ingot was cooled at a slower rate of 33.3° F per hour, to 900° F. Dispersed discrete fine spherical carbides precipitated during the cooling from 1,900° F. This desirable carbide morphology and distribution is seen in FIG. 1 which is a photomicrograph of the cooled ingot at 50X. The composition of the ingot was, in weight percent, 0.06 percent carbon, less than 0.10 percent manganese, less than 0.10 percent silicon, 19.1 percent chromium, 13.4 percent cobalt, 4.15 percent molybdenum, 3.15 percent titanium, 1.34 percent aluminum, 0.005 percent boron, 0.06 percent zirconium, 0.9 percent iron, balance essentially nickel.

The ingot was subsequently hot worked from 2,125° F and then ground. More specifically, the ingot was worked from a 20 inch ingot to a 14½ inch octagon billet and then ground to a 13¼-inch octagon billet. FIG. 2 is a photomicrograph of the hot worked and ground billet at 50X. Note that the billet is still characterized by dispersed discrete fine spherical carbides.

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 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 - 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° to 1,700° F, air cooled to room temperature therefrom and hot worked from 2,125° F into 14½-inch octagon billets which were subsequently ground to 13¼-inch octagon billets. FIGS. 3 and 4 respectively show photomicrographs at 50X of one of these typical prior art ingots and billets. Note that the carbides in FIG. 3 are large and angular, and that the carbides in FIG. 4 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

	ROOM TEMPERATURE TENSILE PROPERTIES				1000°F TENSILE PROPERTIES				STRESS RUPTURE PROPERTIES 1350°F/80ksi NOTCH	
	U.T.S. (ksi)	Y.S. (ksi)	Elongation (%)	Reduction Of Area (%)	U.T.S. (ksi)	Y.S. (ksi)	Elongation (%)	Reduction Of Area (%)	Life (hrs)	Elongation (%)
Present invention	201.0	148.0	24.3	29.7	183.0	138.0	21.2	25.9	47.3	28.4
Prior art	190.4	137.5	18.3	22.0	170.8	125.0	16.4	19.9	43.0	25.0

with 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 2,250° F. From the homogenization temperature the ingot was cooled to 1,900° F at a rate

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 steps of: casting an ingot of nickel base alloy; homogenizing said ingot at a temperature of from 2,200° to 2,400° F, thereby dissolving primary carbides present in said alloy and increasing the chemical homogeneity thereof; cooling said alloy at a rate which substantially precludes the precipitation of coarse and film-like carbides at temperatures above 1,900° F and at a rate at which discrete fine spherical carbides precipitate at temperatures below 1,900° F, said cooling from said homogenizing temperature to 1,900° F being at a first cooling rate, said cooling at temperatures below 1,900° F and during the period at which precipitation occurs being at a second cooling rate, said first cooling rate being in excess of said second cooling rate, said first cooling rate being in excess of 25° F per hour, said second cooling rate being less than 125° F per hour; and hot working said alloy at a temperature lower than that at which said primary carbides dissolve, said hot working occurring within a temperature range of from 1,750° to 2,185° F.

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 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 4.0 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.

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 first cooling rate is in excess of 70° F per hour and said second cooling rate is less than 60° F per hour.

7. A method according to claim 6 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.

8. A method according to claim 6, 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 to 0.5 percent of rare earth metal, balance essentially nickel.

9. A method according to claim 6 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.

10. A method according to claim 6 wherein said nickel base alloy is a gamma prime strengthened alloy.

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

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

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

14. A method according to claim 13 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.

15. A method according to claim 13 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

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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.

16. A method according to claim 13 wherein said nickel base alloy consists essentially of, in weight percent, up to 0.15 percent carbon, up to 2.0 percent man-

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ganese, 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.

17. A method according to claim 13 wherein said nickel base alloy is a gamma prime strengthened alloy.

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