PROCESS FOR MAKING NICKEL BASE PRECIPITATION HARDENABLE ALLOYS

Filed July 26, 1968

FIG. 1

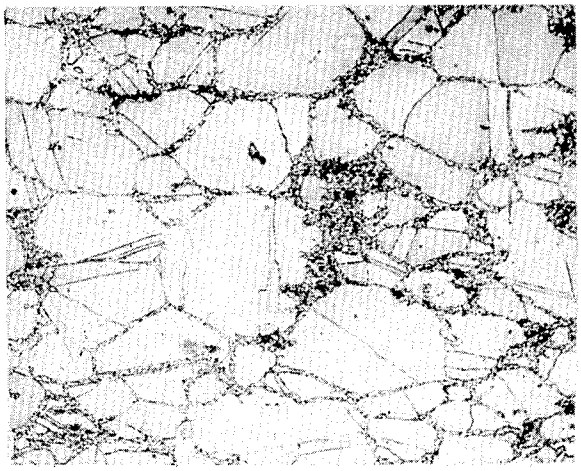


FIG. 2

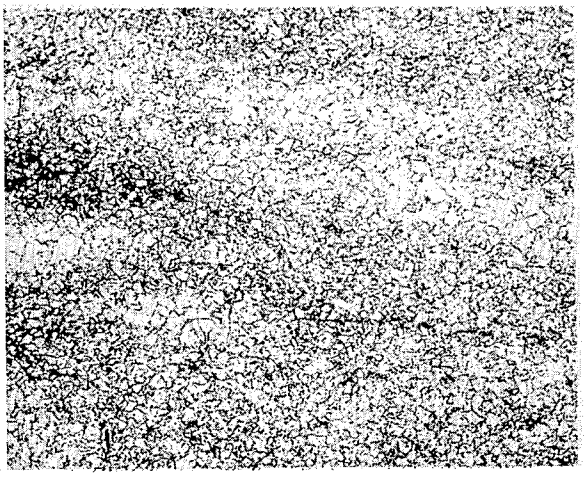
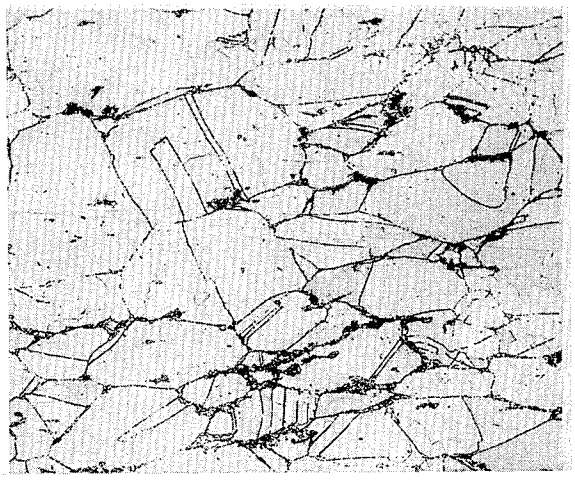


FIG. 3



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PROCESS FOR MAKING NICKEL BASE PRECIPITATION HARDENABLE ALLOYS

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ABSTRACT OF THE DISCLOSURE

A process for making nickel base precipitation hardenable alloys, and alloys made thereby, which includes treating the metal while in a molten state under vacuum or an inert gas at low pressure with a reactive element selected from the group consisting of magnesium, calcium, neodymium, and the rare earth elements having a melting point greater than neodymium.

This invention relates to precipitation hardenable nickel base alloys and, more particularly, to such an alloy and a method for making the same which facilitates fabrication of relatively thick parts with consistently good properties.

An alloy that hitherto has been made and sold under the designation 718 alloy for use where an outstanding combination of strength and ductility was required from below room temperature up to about 1400° F. has the following composition in percent by weight in keeping with good commercial metallurgical practice except for incidental impurities:

	Percent
Carbon	0.10 maximum.
Manganese	0.35 maximum.
Silicon	0.35 maximum.
Phosphorus	0.015 maximum.
Sulfur	0.015 maximum.
Chromium	17.00–21.00.
Nickel (+cobalt) [1]	50.00–55.00.
Molybdenum	2.80–3.30.
Columbium (+tantalum) [2]	4.75–5.50.
Titanium	0.65–1.15.
Aluminum	0.35–0.85.
Boron	0.001–0.010.
Copper	0.15 maximum.
Iron	[3].

[1] Cobalt is present only as an incidental impurity with nickel and usually in an amount not exceeding 1%.
[2] Some tantalum is normally present with commercially acceptable columbium alloys, approximately 10% of the amount stated usually being tantalum.
[3] Balance except for incidental impurities.

Because of the high yield strength and good ductility at room temperature and the high stress rupture strength and notch ductility at an elevated temperature of about 1200° F. to 1400° F. that it can provide, the 718 type alloy has been in demand for and has been successfully used to provide forgings for jet engine and high-speed airframe parts.

That alloy can be readily hot worked from ingots of the usually small size made in laboratories for test purposes. However, in the carrying out of commercial forging operations in the field, the results left much to be desired. An excessively high proportion of the larger, more intricately shaped parts had to be scrapped because of inadequate stress rupture ductility and a concomitant tendency to being notch sensitive.

We have determined that there is a definite correlation between the stress rupture ductility of such forgings and their tendency to being notch sensitive on the one hand and their grain size. When the grain size of the forgings as heretofore made are in the range of about ASTM 6–8, no difficulties are encountered in realizing fully the high notch rupture life and stress rupture ductility characteristic of the alloy. When the grain size becomes finer than ASTM 8, there is an accompanying decrease in stress rupture life, but useful properties are still attainable with grain sizes ranging as fine as about ASTM 9. With grain sizes finer than about ASTM 9.5, the forgings usually have an unacceptably low stress rupture life. We have also found that the stress rupture properties of the forging were also adversely affected as the grain size became coarser than ASTM 6. With grain size ranging finer than ASTM 4, but coarser than ASTM 6, the results attained were increasingly erratic as the size became more closely that of ASTM 4 until with a grain size of ASTM 4 or coarser, the stress rupture properties were entirely unacceptable. That is, the minimum required elongation under a stress of 100,000 p.s.i. at 1200° F. could not be attained, or combination notch-smooth test specimens failed at the notch, thereby indicating they were notch sensitive.

In commercial practice, the inability to achieve the required properties with the coarser grain sizes has proven to be particularly troublesome. Because of equipment limitations coupled with the large size and the intricacy of the shape being forged, the grain size necessarily was limited to sizes coarser than ASTM 6, and often fell to a grain size of ASTM 3–4 and even coarser in the thicker sections of the forgings.

We have found that the drawbacks hitherto associated with the presence of the relatively coarse grain size in nickel base alloy forgings can be minimized, if not eliminated, by means of a carefully controlled use of the reactive elements magnesium, calcium, and neodymium. From our experiments, we conclude that, when one or more reactive elements such as magnesium, calcium, and the rare earth elements neodymium and those of higher melting point, is utilized in accordance with our invention, the elevated temperature stress rupture ductility or notch rupture properties of large and even intricate forgings formed of a nickel base alloy such as the 718 alloy are not adversely affected as heretofore by the presence of grain sizes coarser than ASTM 6. Indeed, in many instances, the properties attainable with the coarser grained forgings, e.g., coarser than ASTM 6, if not equal to those attainable with the optimum fine grain size, are not significantly lower. The improvement achieved by the present invention substantially eliminates the erratic results hitherto caused, as we have found, when the grain size present in a forging was not substantially uniform and within the grain size range of ASTM 6–8, but also included in its cross section areas of coarser grain size below ASTM 6 to as coarse as ASTM 4. Furthermore, in accordance with the present invention, the required properties can be attained in forgings having a grain size of ASTM 4 or coarser. Thus, the present invention makes possible the manufacture and heat treatment of forgings of relatively large cross-sectional thickness and/or intricate shape by commercial producers without the need for special, expensive equipment.

Further advantages as well as objects of the present invention will be apparent from the following detailed description thereof and the accompanying drawing in which

FIG. 1 is a view showing a photomicrograph of the grain structure enlarged 100 times of a test specimen of Heat A which was treated in accordance with the present invention in which the grain size is about ASTM 3;

FIG. 2 is a similar view of a test specimen of Heat B having a composition which differs in no material way

from the composition of Heat A from which the specimen of FIG. 1 was prepared; the specimen shown in this figure has a grain size of about ASTM 7–8, and was not treated in accordance with the present invention; and

FIG. 3 is a similar view of a test specimen prepared from Heat B as was the specimen of FIG. 2 but treated so as to have a grain size of about ASTM 3, and which also was not treated in accordance with the present invention.

The foregoing problems are solved, and the objects of the present invention are attained by treating the molten metal, after it has been deoxidized, with from about 0.01 to 0.2%, preferably with no more than about 0.1%, of a reactive element selected from the group consisting of magnesium, calcium, neodymium and the rare earth elements having a melting point higher than that of neodymium. The reactive element can be added and the treatment carried out in the crucible or ladle, but if that is done, then care must be exercised in introducing the reactive element to carry it well below the surface of the melt so as to ensure a thorough treatment. If desired, the reactive element can be placed at the bottom of the ladle before the heat is tapped into the ladle or the reactive element can be encapsulated in a metal which melts when the molten heat is added to the ladle.

To consistently achieve the overall properties required in high temperature nickel base alloys such as type 718 alloy, it is preferred to utilize at least a double melting technique in making the alloy. That is to say, a first heat is melted and then cast into one or more intermediate ingots which are then remelted. When such a multiple melting practice is utilized in making the alloy, the treatment with the reactive element in accordance with the present invention is carried out during the melting of the initial heat in a given series and preferably just before completion of melting of the initial heat. Any remelting technique suitable for the alloy and its intended use may be utilized, e.g. flux submerged or electroslag remelting under atmospheric pressure, and consumable electrode melting under vacuum.

While the treatment of the present invention can be effective in improving a wide variety of nickel base alloys, uniquely outstanding results have been attained in the treatment of nickel base alloys having the following analysis in weight percent within the tolerances of good commercial practice:

	Broad ranges		Narrow range
Carbon	Up to 0.1	Up to 0.1	0.04 to 0.08.
Manganese	Up to 1.0	Up to 1.0	Up to 0.35.
Silicon	Up to 0.5	Up to 0.5	Do.
Phosphorus	Up to 0.015	Up to 0.015	Up to 0.015.
Sulfur	do	do	Do.
Phosphorus	Up to 0.015	Up to 0.015	Up to 0.015.
Sulfur	do	do	Do.
Chromium	15.0 to 23.0	15.0 to 23.0	17.0 to 21.0.
Nickel	30 to 60	45 to 60	50.0 to 55.0.
Cobalt	Up to 30	[1]	[1].
Molybdenum	2.0 to 4.0	2.0 to 4.0	2.80 to 3.30.
Columbium (+Ta) [2]	4.0 to 8.0	4.0 to 6.0	4.75 to 5.50.
Titanium	0.2 to 2.0	0.65 to 1.15	0.65 to 1.15.
Aluminum	do	0.35 to 0.85	0.35 to 0.85.
Ti+Al	Up to 2.0		
Boron	Up to 0.15	0.002 to 0.015	0.004 to 0.008.
Reactive element [3] added.	0.01 to 0.2	0.01 to 0.1	0.03 to 0.1
Reactive element [3] retained.	Up to 0.01	Up to 0.01	Up to 0.005.
Iron	Balance [4]	Balance [4]	Balance.[4]

[1] Cobalt is present only as an incidental impurity with nickel and usually in an amount not exceeding 1%.

[2] Some tantalum is normally present with commercially acceptable columbium alloys, approximately 10% of the amount stated usually being tantalum.

[3] By reactive element is meant an element selected from the group consisting of magnesium, calcium, and the rare earth elements neodymium and those having a melting point higher than neodymium.

[4] The balance is iron except for incidental impurities or other additions which do not materially detract from the effectiveness of the treatment of the present invention.

In the foregoing table and throughout this application, the expression "up to" is used to mean from zero to no more than the amount stated.

In carrying out the present invention, if the properties of the alloy required for its intended use can be provided when the alloy is prepared by a single melting procedure, remelting of the alloy may be dispensed with as was pointed out hereinabove. In that event, care is to be exercised in refining the melt under subatmospheric pressure after the reactive element has been added to ensure that the treatment is continued long enough for the reactive element to have its desired effect. To avoid poor surface appearance that occurs when larger amounts of the reactive element are retained in the composition, the treatment under low pressure should be long enough so that the amount of the reactive element retained in the composition is no more than about 0.01%. Preferably, the amount of the reactive element retained in the composition is no more than about 0.005%.

In the case of alloys melted in the conventional basic electric furnace, just before or just after the addition of the reactive element, the melt is transferred to a vacuum treating vessel where refinement of the melt is completed while it is subjected to subatmospheric pressure less than 100 mm. Hg, preferably about 100 microns Hg or less.

When, as is preferred in the preparation of high temperature alloys, multiple melting techniques are utilized, the initial heat can be melted using any commercially acceptable melting technique. Final melting is preferably carried out by utilizing an intermediate ingot as a consumable electrode which is remelted under vacuum by means of an electric arc.

As an example of a preferred embodiment of the present invention, Heat A of type 718 alloy was prepared having the following composition in weight percent:

Carbon	0.052
Manganese	0.08
Silicon	0.11
Phosphorus	0.002
Sulfur	0.006
Chromium	18.13
Nickel	53.67
Molybdenum	3.05
Titanium	1.05
Boron	0.0035
Aluminum	0.46
Columbium	5.26
Magnesium	0.003

The balance was iron except for incidental impurities which in this instance included 0.02% copper, 0.08% cobalt and 14 parts per million oxygen.

Heat A was prepared using a conventional double melting practice except for the treatment with magnesium. A charge of about 9,300 pounds made up of type 718 revert scrap plus virgin alloying elements was placed in a vacuum induction furnace which was then pumped down, whereupon the charge was melted and refined. After about two hours, the pressure in the furnace was raised to about 150 mm. Hg by the introduction of argon although other inert gases such as helium could also be used. With the pressure in the furnace at about 150 mm. Hg, magnesium in the form of a nickel-magnesium alloy containing 15% magnesium was added in an amount to provide a magnesium addition equal to about 0.05% by weight of the melt. The furnace was then again pumped down, this time to about 20 mm. Hg, and the heat was refined further, about 10 minutes, for the purpose of reducing the amount of magnesium retained in the ingots poured from the heat. After a sample was withdrawn for analysis, the finished heat was teemed under vacuum into molds shaped to provide 3 ingots for use as consumable electrodes having a diameter of about 10 inches and each weighing about 3,000 pounds. After removal of scale and trimming of ends, the ingots were ready for remelting as consumable electrodes. At this stage, the magnesium content was determined and found to be 0.014%.

Heat A was then remelted at the rate of about 295 pounds per hour using the ingots produced by the vacuum induction furnace as consumable electrodes under a vacuum of about 4 microns Hg by means of an electric arc to provide the final ingots having the analysis noted above.

A pilot bar, sometimes called a capability bar, was formed by hotworking a length of one 14-inch round ingot to an 8-inch rough forged round from which a 2-inch section was cut which was in turn cut to provide a 2-inch square, 8-inch long bar, and this bar was forged from a furnace temperature of 2000° F. first to a 1.75-inch square cross section, reheated and then forged to form the pilot bar having a 1.5-inch by 1.5-inch cross section. Smooth bar room temperature tensile test specimens were formed from the pilot bar, each having a gage diameter of 0.252 inch and a gage length 4 times its diameter. For testing at 1200° F., smooth bar test specimens were formed, each having a gage diameter of 0.357 inch and a gage length 4 times the diameter. Combination smooth-notch stress rupture specimens were also made, each having a smooth section 0.178 inch in diameter with a gage length 4 times the diameter; and a notched section having a major gage diameter of 0.252 inch, a notch diameter of 0.178 inch, and a notch root radius of 0.005 inch to provide a stress concentration factor of 3.8.

All specimens were heat treated by heating at 1750° F. for one hour, cooling in air to room temperature, then heating at 1325° F. for eight hours, then cooling at the rate of 100° F. per hour to 1150° F. at which temperature they were held for eight hours followed by cooling in air.

At room temperature the .2% yield strength (.2% YS) was 184,000 p.s.i. The ultimate tensile strength (UTS) was 202,000 p.s.i. with an elongation (percent El.) of 14.2% and a 29.3% reduction in area (percent RA). At 1200° F. the .2% YS was 152,000 p.s.i., and the UTS was 163,000 p.s.i. with 12.2% El. and 20.6% RA. The stress rupture tests were carried out at 1200° F. under a load of 100,000 p.s.i. One specimen failed in the smooth section after 305.4 hours under load with 9.0% El. and 14.0% RA. A second specimen also failed in its smooth section, this time after 262.2 hours under load, with 8.8% El and 16.0% RA.

Shown in FIG. 1 is a photomicrograph having a magnification of 100× prepared from the threaded section of one of the broken tensile specimens formed from Heat A. The microstructure shown is believed to be representative of the test specimens formed from Heat A, and has a grain size of about ASTM 3 accompanied by an insignificant amount of smaller grains having a size about ASTM 8.

To facilitate comparison, the foregoing test data of Heat A is included hereinbelow in Table I in which is also listed data from the same tests carried out on two different groups of specimens formed from Heat B. Heat B was prepared in essentially the same way as Heat A except that the charge weighed about 12,000 pounds, and it was not treated with magnesium or any other reactive element in accordance with the present invention. In the case of Heat B, the remelting was at a rate of about 345 pounds per hour under a vacuum of about 5 microns Hg, which rate and pressure were considered to be the same as that for Heat A fo rall practical purposes. Two pilot bars were prepared from which were made two different groups of test specimens. One pilot bar was formed from a billet as was described in connection with Heat A except that after having been hot worked to a cross section of 3 inches by 2 inches, it was forged to 1⅜ inches square at 2000° F., air cooled, then heated at 1800° F. for one hour, and then flattened to 1¼ inches by 1⅜ inches. From this pilot bar the same type of test specimens were formed as was described in connection with Heat A, and the results of the corresponding tests are set out in Table I after the designation Heat B_1. The grain size of the Heat B_1 specimens was measured and found to be primarily ASTM 7–8. Shown in FIG. 2 is a photomicrograph prepared in the same way and corresponding to that shown in FIG. 1 with a magnification of 100× showing the grain structure of the thread section from one of the broken tensile specimens of Heat B_1. The microstructure shown in FIG. 2 is believed to be representative of the specimens formed from the pilot bar and making up the group designated as Heat B_1.

The second pilot bar made from Heat B was prepared in the same way as was described in connection with the pilot bar made from Heat A. Similarly, test specimens corresponding in every way to those formed and tested in the case of Heat A were prepared from the second pilot bar and tested in the same way. The results of these tests are also set out in Table I and are designated Heat B_2.

As in the case of Heat A and the Heat B_1 specimens, a photomicrograph, magnification 100×, was prepared from the thread section of one of the broken tensile specimens formed from the second pilot bar, Heat B_2, and is reproduced in FIG. 3. The microstructure shown in FIG. 3 is believed to be representative of the microstructure of the specimens forming the group Heat B_2 and was found to be primarily ASTM 3 with an insignificant amount of grain of a smaller size ranging about ASTM 8.

The composition of Heat B, in weight percent, was as follows:

Carbon	0.052
Manganese	0.08
Silicon	0.10
Phosphorus	0.003
Sulfur	0.009
Chromium	18.27
Nickel	52.77
Molybdenum	3.04
Titanium	1.01
Boron	0.004
Aluminum	0.50
Columbium	5.22
Magnesium	0.001

The balance was iron except for incidental impurities which included 0.01% copper, 0.08% cobalt, and 33 parts per million oxygen. It is to be noted that the 0.001% magnesium did not result from any intended addition of magnesium.

TABLE I

	Heat A	Heat B_1	Heat B_2	Cur. spec. reqs.
Room temperature:				
.2% YS*	184	181	183	150
UTS*	202	209	203	185
Percent El	14.2	18.0	15.0	12
Percent RA	29.3	32.7	29.3	15
1200° F.:				
.2% YS*	152	157	156	125
UST*	163	174	166	145
Percent El	12.2	14.2	10.5	12
Percent RA	20.6	36.0	31.3	18
Stress rupture, 1200° F./100,000 p.s.i.:				
Hours to fail	305.4	-------	204.1	-------
	262.2	360.3	299.8	25.0
Percent El	9.0	-------	3.9	-------
	8.8	14.0	1.4	5.0
Percent RA	14.0	-------	10.8	-------
	16.0	-------	6.9	-------
ASTM grain size	3	7-8	3	-------

*1,000 p.s.i.

Included in the right hand column of Table I under the heading "Cur. Spec. Regs." are the latest specification requirements of which we are aware published by General Electric Company, Cincinnati, Ohio, Flight Propulsion Division under No. C50TF6–S3 dated Mar. 31, 1967, to which type 718 alloy is currently being manufactured and sold. Except for a little more lenient stress rupture ductility of 4% elongation, AMS 5662B published by the Society of Automotive Engineers, Inc., Sept. 1, 1965 (revised Nov. 1, 1967) calls for the same or equivalent tensile and stress rupture properties.

The test data and specification requirements shown in Table I demonstrate the problem that has hitherto troubled parts fabricators working with 718 alloy. In practice, erratic results were attained, particularly in the area of stress rupture ductility and a susceptibility to notch failure. Up to now, the fabricator discovered the shortcoming of his product and its inability to meet the minimum required elongation of 5% under a load of 100,000 p.s.i. at 1200° F. only after an expensive investment of time and labor. Though the B_1 and B_2 specimens were prepared from the same melt of steel and thus had, for all practical purposes, identical compositions, their stress rupture ductility is significantly different.

It was our discovery that the significant difference between satisfactory and unsatisfactory parts under stress at 1200° F. was their grain size which led us to make our present invention. The test results clearly demonstrate that without the treatment with the reactive element magnesium, the B_1 specimens having the finer grain size of ASTM 7–8 are entirely satisfactory, but that the B_2 specimens having the coarser grain size of ASTM 3 are unsatisfactory and fail to meet the specification requirements for rupture ductility of 5% or even 4% elongation at 1200° F. under 100,000 p.s.i. On the other hand, when essentially the same composition is treated with magnesium in accordance with the present invention, as demonstrated by the Heat A specimens, the specification requirements are satisfied even though the test specimens had the coarse grain size of ASTM 3. The importance of our discovery may be better appreciated when it is understood, as was pointed out hereinabove, that the equipment used by many fabricators does not lend itself to maintaining the fine grain structure throughout relatively thick cross sections that is required if their products are to be capable of successfully meeting all of the specification requirements without the benefit of our invention.

In addition to magnesium, there are other reactive elements that can be used in accordance with our invention to make fabricated parts capable of demonstrating the required stress rupture ductility independent of whether its grain size is fine or coarse within the range of sizes stated hereinabove. Such other reactive elements include neodymium and those rare earth elements having a melting point higher than neodymium. Lower melting point rare earth elements including the mixture commonly designated as misch metal will not provide the benefit of our invention.

While Heats A and B were commercial scale production heats, Heats C and D were 17 pound experimental heats prepared for the purpose of demonstrating the use of neodymium in carrying out the present invention and had the following composition in weight percent:

	Heat C	Heat D
Carbon	0.043	0.046
Manganese	0.11	0.11
Silicon	0.12	0.15
Phophorus	0.005	0.005
Sulfur	0.005	0.003
Chromium	18.35	18.57
Nickel	52.64	53.04
Molybdenum	3.11	3.19
Columbium	5.35	5.16
Boron	0.0032	0.0032
Titanium	0.96	0.97
Aluminum	0.54	0.46
Neodymium		(*)

*None could be detected spectrographically.

The balance of Heats C and D was iron and the usual incidental impurities which included 19 and 16 parts per million oxygen respectively for Heats C and D. Heats C and D were each prepared using the same techniques in a vacuum induction furnace except that in the case of Heat D 0.05% neodymium was added when the heat would otherwise have been ready for tapping. After the addition of the neodymium, the heat was held under vacuum for 5 minutes before it was cast as an ingot. As was described in connection with Heat A, test specimens

were prepared from Heats C and D and were subjected to the same tests with the results indicated in Table II. In the same manner as was done in connection with the Heat A, B_1 and B_2 specimens, the grain size was measured and found to be ASTM 3–4 with an insignificant amount of about ASTM 7.5 in the case of both Heat C and Heat D.

TABLE II

	Heat C	Heat D
Room temperature:		
.2% YS*	186	184
UTS*	205	206
Percent El	16.9	14.6
Percent RA	38.3	34.6
1200° F.:		
.2% YS*	159	153
UTS*	171	168
Percent El	13.9	14.0
Percent RA	35.8	32.8
Stress rupture, 1200° F./100,000 p.s.i.:		
Hours to fail	197.4	146.3
	24.43	188.4
Percent El	11.2	27.6
	10.5	23.5
Percent RA	16.0	57.4
	15.2	49.8
ASTM grain size	3–4	3–4

*1,000 p.s.i.

The marked improvement in stress rupture ductility under a load of 100,000 p.s.i. at 1200° F. is demonstrated by the results of the tests in which Heat C, which was not treated with neodymium, had only an 11.2 and 10.5% elongation as compared to the 27.6 and 23.5% elongation demonstrated by Heat D which was treated with neodymium in accordance with the present invention.

It is to be noted, as is well known, the tensile and stress rupture test results obtained from the small, 17-pound, Heats C and D cannot be compared directly with the much larger, commercial scale heats, Heats A and B. It has long been recognized in the art that when a small ingot such as one weighing 17 pounds is hot worked, the effect is much more homogeneously distributed throughout the metal than when an ingot of the same composition but having a much thicked cross section is hot worked. This effect can be seen by comparing the mechanical properties of Heat C with the Heat B_2 specimens having essentially the same composition and a comparable grain size. The deterioration in stress rupture ductility with the larger sized nickel base ingot is demonstrated by the values of 3.9 and 1.4% elonga-elongation for the small Heat C. However, it is evident from the improved rupture ductility of Heat D compared to that of Heat C, that large heats treated with ductility characteristic of our invention over heats of corresponding size and composition not treated in accordance with this invention.

Calcium also was found to be effective as a reactive element in accordance with the present invention. As was described in connection with Heat D, a 17-pound experimental heat was prepared which had the following composition in weight percent:

	Heat E
Carbon	0.052
Manganese	0.05
Silicon	0.16
Phosphorus	0.001
Sulfur	0.002
Chromium	18.38
Nickel	52.93
Molybdenum	3.09
Columbium	5.28
Boron	0.0042
Titanium	1.00
Aluminum	0.41
Calcium	<0.001

The balance of Heat E was iron and the usual incidental impurities. Heat E was prepared in a vacuum induction furnace in the same way as was Heat D except that

0.05% calcium was added when the heat would otherwise have been ready for tapping. After the addition of the calcium, the heat was held under vacuum for 5 minutes before it was cast as an ingot. As was described in connection with Heat A, test specimens were prepared from Heat E and were subjected to the same tests. At room temperature, the .2% yield strength was 178,000 p.s.i., the ultimate tensile strength was 205,000 p.s.i. with an elongation of 16.9% and a reduction in area of 39.6%. At 1200° F. the .2% YS was 154,000 p.s.i., and the UTS was 169,000 p.s.i. with 18.7% El. and 54.9% RA. Stress rupture tests were also carried out at 1200° F. under a load of 100,000 p.s.i. One specimen failed in the smooth section after 208 hours with 21.1% El. and 56.2% RA. The second specimen also failed in the smooth section, this time after 262.5 hours with 21.9% El. and 57.3% RA. In the same manner as was done in connection with the other heath, the grain size of Heat E was measured and it was found to have a mixed grain size made up of about 50% ASTM 4 and about 50% ASTM 8.

Because of its small size, Heat E cannot be compared directly with Heat A for the reasons pointed out hereinabove in connection with Heat C and D, but the results from the tests carried out on Heat E can be compared with the test results from Heat C. The improvement in stress rupture ductility is apparent from the 21.1% and 21.9% elongation obtained under a load of 100,000 p.s.i. at 1200° F. as compared to the 11.2% and 10.5% elongation under the same conditions obtained with the test specimens of Heat C.

The alloys produced in accordance with the present invention differ significantly from those hitherto available. However, careful chemical analysis as well as examination of the microstructure of our alloy by means of X-ray diffraction and electron microprobe techniques have failed to provide any quantitative basis for distinguishing our alloy from the prior alloy. The alloy of our invention demonstrates its improved properties independent of the amount of the reactive element with which it is treated and is retained in the composition so long as the amount retained does not exceed the maximum of about 0.01%. The amount retained may be less than can be detected spectrographically. No significant differences could be found in the amount of oxygen, sulfur or nitrogen present, or in the form in which those elements were present, which could be correlated with whether or not the alloy had been prepared in accordance with the present invention except that in the case of the heats treated with magnesium, the electron microphobe results suggest that the mechanism involved may be the formation of magnesium sulfide (MgS) at the expense of titanium sulfide (TiS) since MgS was found throughout the matrix, but no TiS could be detected. However, this is offered only as a tentative explanation. At the present time, the analytic techniques available do not permit quantitative measurement of the amounts of the specific sulfides present in the alloy with meaningful precision.

We have definitely established that the effect of the reactive element is not that of a deoxidizing agent. For example, with more or less oxygen present than the amounts in Heats A, B, C, and D, the improved stress rupture ductility of our alloy is not obtained unless it is treated with a reactive element in accordance with the present invention and, when so treated, variations in the amount of oxygen over a range of about 50 parts per million do not appear to affect the stress rupture ductility of the alloy. Furthermore, though zirconium is a well-known deoxidizing agent for a wide variety of compositions including an alloy such as type 718, it does not provide the effect of a reactive element of the present invention.

As was described in connection with Heat A, the better practice in accordance with our invention when a double melting practice is used, is to re-evacuate the furnace after the addition is made to the first melt and then hold the heat for about 5 to 20 minutes or longer, depending upon the size of the heat, at a low pressure, below about 100 mm. Hg and preferably below about 100 microns Hg. While such a practice is not essential to obtaining the improved rupture ductility characteristic of our invention, it does result in a better surface appearance on the ingots obtained from remelting the initial ingots using vacuum consumable electrode techniques. However, it is an essential feature of our invention that the metal be subjected to a low pressure while in the molten state after the addition of the reactive element for a time long enough for it to take effect. When, as was described hereinabove, the alloy is remelted as a consumable electrode under vacuum, no additional treatment under vacuum is required. In that event, the initial heat to which the reactive element is added can be teemed immediately after the addition of the reactive element is made. However, when only a single melting practice is used, or a multiple melting practice such as flux submerged consumable electrode remelting which is not carried out at low pressure, then after the addition of the reactive element it is essential that the heat, if not already in a vacuum vessel, be transferred to a vacuum vessel where it is subjected to a pressure below about 100 mm. Hg and preferably below about 100 microns Hg.

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 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 a process for making a precipitation hardened part from a nickel base alloy which in its hardened condition is characterized by good stress rupture ductility under load at a temperature of about 1200° F. while having a grain size a major portion of which is coarser than ASTM 6, the steps of forming a melt of a nickel base alloy under subatmospheric pressure, at least partially refining the melt, then while said melt is under subatmospheric pressure adding a reactive element selected from the group consisting of magnesium, calcium, neodymium and the rare earth elements having a melting point higher than that of neodymium in an amount ranging from about 0.01 to 0.2% of the weight of said melt, thereafter subjecting the alloy while in a molten state to subamospheric pressure below about 100 mm. Hg for at least 5 minutes, followed by casting said melt, and then forming said alloy to provide a part having a grain size a major portion of which is coarser than ASTM 6 and which contains up to about 0.01% by weight of said reactive element.

2. The process of claim 1 in which said melt consists in weight percent essentially of up to about 0.1% carbon, up to about 1% manganese, up to about 0.5% silicon, up to about 0.015% phosphorus, up to about 0.015% sulfur, about 15 to 23% chromium, about 30 to 60% nickel, up to about 30% cobalt, about 2 to 4% molybdenum, about 4 to 8% columbium, about 0.2 to 2% titanium, about 0.2 to 2% aluminum, the sum of the titanium and aluminum being no more than about 2%, up to 0.15% boron, and the balance consisting essentially of iron, and said part formed therefrom having in its hardened condition a stress rupture ductility of at least 5% elongation under a load of 100,000 p.s.i. at a temperature of 1200° F. when tested in accordance with AMS 5662B.

3. The process of claim 2 in which the reactive element is magnesium.

4. The process of claim 2 in which the reactive element is calcium.

5. The process of claim 2 in which the reactive element is neodymium.

6. A process for making a precipitation hardened part from a nickel base alloy which in its hardened condition is characterized by a stress rupture ductility of at least 5% elongation under a load of 100,000 p.s.i. at a temperature of 1200° F. when tested in accordance with AMS 5662B while having a grain size the majority of which is coarser than ASTM 6; comprising forming under subatmospheric pressure a melt of a nickel base alloy consisting in weight percent essentially of up to about 0.1% carbon, up to about 1% manganese, up to about 0.5% silicon, up to about 0.015% phosphorus, up to about 0.015% sulfur, 15 to 23% chromium, 45 to 60% nickel, 2 to 4% molybdenum, 4 to 6% columbium, 0.65 to 1.15% titanium, 0.35 to 0.85% aluminum, 0.002 to 0.015% boron, and the balance essentially iron; at least partially refining the melt; then while said melt is under subatmospheric pressure adding a reactive element selected from the group consisting of magnesium, calcium, neodymium and the rare earth elements having a melting point higher than that of neodymium in an amount ranging from about 0.01 to 0.2% of the weight of said melt; thereafter subjecting the alloy while in a molten state to subatmospheric pressure below about 100 mm. Hg for at least 5 minutes, followed by casting said melt, and then forming said alloy to provide a part having a grain size a major portion of which is coarser than ASTM 6 and which contains up to about 0.01% by weight of said reactive element.

7. The process of claim **6** in which said reactive element is magnesium.

8. The process of claim **6** in which said reactive element is calcium.

9. The process of claim **6** in which said reactive element is neodymium.

10. A process for making a precipitation hardened part from a nickel base alloy which in its hardened condition is characterized by a stress rupture ductility of at least 5% elongation under a load of 100,000 p.s.i. at a temperature of 1200° F. when tested in accordance with AMS 5662B while having a grain size the majority of which is coarser than ASTM 6; comprising forming under subatmospheric pressure a melt of a nickel base alloy consisting in weight percent essentially of about 0.04 to 0.08% carbon, up to about 0.35% manganese, up to about 0.35% silicon, up to about 0.015% phosphorus, up

to about 0.015% sulfur, about 17 to 21% chromium, about 50 to 55% nickel, about 2.8 to 3.3% molybdenum, about 4.75 to 5.50% columbium, about 0.65 to 1.15% titanium, about 0.3 to 0.87 aluminum, about 0.004 to 0.008% boron, and the balance essentially iron; at least partially refining the melt; then while said melt is under subatmospheric pressure adding a reactive element selected from the group consisting of magnesium, calcium, neodymium and the rare earth elements having a melting point higher than that of neodymium in an amount ranging from about 0.03 to 0.1% of the weight of said melt; thereafter subjecting the alloy while in a molten state to subatmospheric pressure below about 100 mm. Hg for at least 5 minutes, followed by casting said melt, and then forming said alloy to provide a part having a grain size a major portion of which is coarser than ASTM 6 and which contains up to about 0.01% by weight of said reactive element.

11. The process of claim **10** in which the melt after the addition of said reactive element and while in a molten state is subjected to subatmospheric pressure below about 100 microns Hg for at least 5 minutes, and said part contains no more than about 0.005% by weight of said reactive element.

12. The process of claim **11** in which said reactive element is magnesium.

13. The process of claim **11** in which said reactive element is calcium.

14. The process of claim **11** in which said reactive element is neodymium.

References Cited

UNITED STATES PATENTS

2,570,193	10/1951	Bieber et al.	75—171
2,621,122	12/1952	Gresham et al.	75—171
3,046,108	7/1962	Eiselstein	75—171
3,322,534	5/1967	Shaw et al.	75—171
3,343,950	9/1967	Richards et al.	75—171

RICHARD O. DEAN, Primary Examiner

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75—82, 170, 171; 148—12.7, 32.5, 162

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,575,734 Dated April 20, 1971

Inventor(s) Donald R. Muzyka and Clyde Raymond Whitney

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, lines 53 and 54, Delete these two lines as they are duplicates of lines 51 and 52 referring to phosphorus and sulfur contents.

Column 5, line 63, "fo rall" should be -- for all --.

Column 6, line 56, "UST*" should be -- UTS* --.
line 66, "Regs." should be -- Reqs. --.

Column 8, Table II, "Hours to fail" under "Heat C", "24.43" should be -- 244.3 --.
line 41, "thicked" should be -- thicker --.
line 47, after "elonga" insert -- tion for Heat B_2 a compared to 11.2 and 10.5% --.
line 50, after "with" insert -- neodymium will demonstrate the improved rupture --.

Column 9, line 18, "heath," should be -- heats, --.
line 49, "microphobe" should be -- microprobe --.

Column 10, line 48, "subamospheric" should be -- subatmospheri

Column 12, line 4, "0.3" should be -- 0.35 --.
"0.87" should be -- 0.85% --.

Signed and Sealed this

thirteenth Day of January 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks