

1

3,183,084

HIGH TEMPERATURE AUSTENITIC ALLOY

Gerald B. Heydt, Reading, and Clyde Raymond Whitney, Wyomissing, Pa., assignors to The Carpenter Steel Company, Reading, Pa., a corporation of New Jersey
No Drawing. Filed Mar. 18, 1963, Ser. No. 266,009
8 Claims. (Cl. 75-171)

This invention relates to an austenitic nickel base alloy which is age hardenable and more particularly to such an alloy having high strength at elevated temperatures.

Hitherto, for use where high strength at elevated temperature had been required austenitic nickel base alloys were provided having a composition balanced so as to respond to an aging or precipitation hardening treatment. More particularly such alloys were balanced so that upon aging they underwent a precipitation hardening and strengthening mechanism such that a precipitate was formed having a lattice structure the same as that of the alloy matrix in which it is formed and also having a lattice parameter which is close to but yet constitutes a misfit with the lattice parameter of the matrix.

The present invention is particularly concerned with improving those nickel base austenitic precipitation hardening alloys which harden during aging by a mechanism involving the formation of a face centered cubic precipitate known as "gamma prime." The usefulness of such alloys has been limited by the fact that the gamma prime precipitate transformed during use at elevated temperature after a relatively short time so that the composition lost its strength. This transformation results from the fact that the gamma prime, face centered cubic structure formed in the original aging treatment underwent a further transformation to a hexagonal close packed structure, known as "eta phase." The extent of the transformation depends upon the duration of the exposure to temperatures between about 1100° F. to 1700° F. and the degree of stress to which the part formed of the alloy is subjected, the transformation proceeding more rapidly as the temperature or the stress is increased.

It is therefore a principal object of the present invention to provide an age hardening austenitic nickel base alloy characterized by high strength, high stress rupture ductility and longer useful life under stress at elevated temperatures up to about 1400° to 1600° F. by means of the formation of a gamma prime precipitate with an optimum lattice parameter relative to the matrix and which has enhanced stability against transformation to the undesired eta phase.

The alloy of the present invention is particularly well suited for use in forming such parts as wheels and rings for use in jet engines. Thus, the alloy of the present invention is not only characterized by high strength and stress rupture ductility at elevated temperatures but also is characterized by good resistance to oxidation and corrosion at such temperatures.

A more specific object of the present invention is to provide such an alloy which may be readily melted and cast into ingots that may be economically hot worked and formed into parts.

We have discovered that the foregoing objects can be achieved with an austenitic alloy having the following analysis in percent by weight within the tolerances of good commercial melting practices:

Carbon	Up to .10% maximum.
Manganese	Up to 2%.
Silicon	Up to 1% maximum.
Chromium	12% to 20%.
Nickel	35% to 55%.
Molybdenum	3% to 7%.
Cobalt	1.5% to 7%.

2

Vanadium	Up to 1.0%.
Titanium	2.75% to 3.75%.
Aluminum	.75% to 2.0%.
Boron	.003% to .025%.

the balance consisting essentially of iron except for incidental impurities such as phosphorus, sulfur, nitrogen, oxygen and the like.

The proper balance of the alloying elements of this composition is highly critical and must be carefully maintained if sound steel having the required properties at temperatures as high as 1600° F. is to be obtained suitable for such use as in the fabrication of jet engine parts.

In this alloy, the maximum carbon content must not exceed about .10% and is preferably maintained at a much lower level below about .07% maximum. Vanadium may be included in this composition in amounts ranging up to about 1% when desired to tie up the carbon and reduce the formation of a titanium carbide. Manganese may be present in amounts up to about 2% but is preferably limited to no more than .25%.

When large commercial ingots are melted, silicon, when present in more than very small amounts, results in the formation of a nickel-titanium-silicide segregate, believed to be $Ni_{13}Ti_8Si_6$ identified as G phase in forged billets. For many purposes such segregate areas in the billets are considered unsound and, to avoid their formation, silicon is limited to no more than about .25%.

Small additions of boron work to improve the rupture strength of our alloy at elevated temperatures. For this purpose, from about .003% to .025% boron provides good results. When present in amounts above .025%, boron tends to form borides, particularly with nickel, and this has a detrimental effect upon the forgeability and mechanical properties of the alloy. Preferably, lower amounts below .013% boron are utilized to provide optimum results.

Chromium from about 12% to 20% provides the required degree of oxidation and corrosion resistance. Because chromium does not enhance the high temperature strength of our alloy and because it tends to form an embrittling carbide, we preferably use the smaller amounts of chromium, from about 12.5% to 15%.

Nickel also provides oxidation and corrosion resistance, but more importantly nickel takes part in the aging mechanism by which our alloy is strengthened. A minimum of about 35% nickel is required for this purpose. When nickel is present in amounts above about 55%, insufficient advantage is derived therefrom to justify the additional cost. Best results are achieved when nickel is present in amounts ranging from about 40% to 45%.

Molybdenum is included because it improves the high temperature strength of the alloy. For this purpose, molybdenum is included in an amount ranging from about 3% to 7%.

Titanium largely contributes to the rupture strength and the tensile strength of the alloy and for this purpose about 2.75% to 3.75% titanium is utilized. When titanium is present in an amount less than about 2.75%, both the high room temperature tensile strength and the high rupture strength at elevated temperatures characteristic of our alloy are not attainable. Best results are achieved with a minimum of about 3% titanium. Larger amounts of titanium than about 3.75% tend to impair the hot workability of the composition. Titanium, in the absence of at least about .75% aluminum reacts with nickel during aging to provide a meta stable face centered cubic phase which in turn transforms to the undesired hexagonal close packed eta phase at the elevated temperature at which parts formed from the alloy are intended to be used.

When aluminum is present in our alloy in amounts

varying from about .75% to 2.0%, the more stable gamma prime phase is formed on aging identified as $\text{Ni}_3(\text{Ti}, \text{Al})$, most consistent results being attained when aluminum is present in an amount varying from about 1% to 1.5%. Larger amounts of aluminum not only detract from the high temperature strength of our alloy but also work with the titanium to make hot working of the alloy increasingly difficult.

With the elements balanced as already described hereinabove and with critically controlled additions of cobalt as now to be described, our alloy has outstanding strength at high temperature. In fact, though our preferred alloy contains as much as about 25% to 35% iron, nevertheless its strength at elevated temperatures up to 1600° F. is essentially equivalent to the high temperature strength at corresponding temperatures of much more expensive precipitation hardenable nickel base alloys containing as little as 0.5% iron.

Our experiments have shown that the unique high temperature strength of our alloy results from a definite but small degree of misfit between the lattice parameter of the matrix and the lattice parameter of the gamma prime phase formed by aging, that is, the face centered cubic $\text{Ni}_3(\text{Al}, \text{Ti})$. By maintaining the cobalt content between about 1.5% and 7%, the lattice parameters are kept so close to each other that the percent misfit characteristic of our alloy is uniquely small. When smaller or larger amounts of cobalt than the amount specified is present, then the required low percent misfit between the lattice parameters and the high temperature strength characteristic of our alloy are not attained. Best results are achieved when the cobalt content ranges from about 3% to 5%.

Thus, the alloy which we have produced with preferred results has the following composition in percent by weight within the tolerances of good commercial melting practice:

Carbon	Up to .07% maximum.
Manganese	Up to .25% maximum.
Silicon	Up to .25% maximum.
Chromium	12.5% to 15%.
Nickel	40% to 45%.
Molybdenum	4% to 6%.
Cobalt	3% to 5%.
Titanium	3% to 3.5%.
Aluminum	1% to 1.5%.
Boron	.003% to .013%.
Vanadium	Up to 1%.

the balance consisting essentially of iron except for incidental impurities.

Our alloy is readily prepared and worked in accordance with good standard commercial practice. Our alloy may be prepared with a high degree of purity in commercial quantities using conventional vacuum-induction or consumable-electrode melting techniques. No special heat treatment is required. Solution treatment is about 180° F. to 2050° F. followed by a single or double aging or precipitation hardening treatment in the range of about 1200° F. to 1600° F. provides good results.

As a specific example of our alloy, an ingot was melted and cast containing, in percent by weight:

	Percent
Carbon	0.04
Manganese	0.10
Silicon	0.15
Phosphorus	0.014
Sulfur	0.004
Chromium	12.9
Nickel	42.9
Molybdenum	5.75
Titanium	3
Aluminum	1.10
Cobalt	3.75
Boron	0.009

and the balance all iron except for incidental impurities. The ingot was hot worked into ¾ inch bars, then solution treated and aged. In this instance, the solution treatment was carried out at 2000° F. for two hours followed by water quenching. Aging was carried out by holding the solution treated alloy for two hours at 1525° F., air cooling and then holding for twenty-four hours at 1400° F. and air cooling.

The aged bars were machined to form standard combination smooth-notch stress rupture specimens having a smooth section 0.178 inch in diameter and a gauge length of 0.712 inch merging with a thicker section 0.250 inch in diameter in which a circular notch was formed having a 0.178 inch diameter at the root of the notch, a root radius of 0.005 inch and a notch angle of 60°, thereby providing a stress concentration factor of 3.8. At 1400° F., a stress load of 39,000 p.s.i. was sustained for 573 hours before rupture with a 10.5% elongation and 23.3% reduction in area. The failure occurred in the smooth portion of the test specimens and not at the notch, indicating that the alloy has good stress rupture ductility.

Thus, highly beneficial results are attained when our alloy is prepared having the following composition in percent by weight within the tolerances of good commercial melting practice:

Carbon	Up to .06% maximum.
Manganese	Up to .25% maximum.
Silicon	Up to .25% maximum.
Chromium	12.5% to 13.5%.
Nickel	42.5% to 43.5%.
Molybdenum	5.0% to 6.0%.
Cobalt	3.5% to 4.5%.
Titanium	2.8% to 3.3%.
Aluminum	1.0% to 1.4%.
Boron	.008% to .01%.

the balance consisting essentially of iron except for incidental impurities.

On the other hand, tests carried out with similarly prepared specimens having essentially the same analysis but not containing cobalt were characterized by significantly poorer stress rupture strength. For example, an alloy containing, in percent by weight:

	Percent
Carbon	0.048
Manganese	0.15
Silicon	0.16
Phosphorus	0.003
Sulfur	0.005
Chromium	12.47
Nickel	42.99
Molybdenum	5.75
Titanium	2.93
Aluminum	1.04
Boron	0.009

no cobalt, and the balance iron except for incidental impurities, was prepared as was described in connection with the alloy of the present invention and formed into a standard smooth stress rupture test specimen having a 0.178 inch gauge diameter and a 0.712 inch gauge length. When subjected to a stress load of 39,000 p.s.i. at 1400° F., rupture occurred in 436 hours with 16.9% elongation and 26.1% reduction in area.

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.

We claim:

1. An age hardening austenitic nickel base alloy which in its hardened condition has good strength and ductility at temperatures up to about 1600° F. and which within

the tolerances of good melting practices consists essentially of:

	Percent
Carbon -----	Up to .10
Manganese -----	Up to 2
Silicon -----	Up to 1
Chromium -----	12 to 20
Nickel -----	35 to 55
Molybdenum -----	3 to 7
Cobalt -----	1.5 to 7
Vanadium -----	Up to 1
Titanium -----	2.75 to 3.75
Aluminum -----	.75 to 2
Boron -----	.003 to .025

the balance consisting essentially of iron and in which the aluminum serves to stabilize the gamma prime phase formed by age hardening against transformation to an eta phase at elevated temperature and under stress, and in which the amount of cobalt provides substantially minimum misfit between the lattice parameters of the matrix of the alloy and of the gamma prime phase when the aged alloy is exposed to stress at high temperature over a long time.

2. An age hardening austenitic nickel base alloy which in its hardened condition has good strength and ductility at temperatures up to about 1600° F. and which within the tolerances of good melting practices consists essentially of:

	Percent
Carbon -----	Up to .07
Manganese -----	Up to .25
Silicon -----	Up to .25
Chromium -----	12.5 to 15
Nickel -----	40 to 45
Molybdenum -----	4 to 6
Cobalt -----	3 to 5
Titanium -----	3 to 3.5
Aluminum -----	1 to 1.5
Boron -----	.003 to .013
Vanadium -----	Up to 1

the balance consisting essentially of iron and in which the aluminum serves to stabilize the gamma prime phase formed by age hardening against transformation to an eta phase at elevated temperature and under stress, and in which the amount of cobalt provides substantially minimum misfit between the lattice parameters of the matrix of the alloy and of the gamma prime phase when the aged alloy is exposed to stress at high temperature over a long time.

3. An age hardening austenitic nickel base alloy which in its hardened condition has good strength and ductility at temperatures up to about 1600° F. and which within the tolerances of good melting practices consists essentially of:

Carbon -----	Up to .06% maximum.
Manganese -----	Up to .25% maximum.
Silicon -----	Up to .25% maximum.
Chromium -----	12.5% to 13.5%.
Nickel -----	42.5% to 43.5%.
Molybdenum -----	5.0% to 6.0%.
Cobalt -----	3.5% to 4.5%.
Titanium -----	2.8% to 3.3%.
Aluminum -----	1.0% to 1.4%.
Boron -----	.008% to .01%.

the balance consisting essentially of iron and in which the aluminum serves to stabilize the gamma prime phase formed by age hardening against transformation to an eta phase at elevated temperature and under stress, and in which the amount of cobalt provides substantially minimum misfit between the lattice parameters of the matrix of the alloy and of the gamma prime phase when the aged alloy is exposed to stress at high temperature over a long time.

4. An article subjected in use to severe stress at elevated temperatures up to about 1600° F. and formed of an age hardened austenitic nickel base alloy which within the tolerances of good melting practices consists essentially of:

	Percent
Carbon -----	Up to .10
Manganese -----	Up to 2
Silicon -----	Up to 1
Chromium -----	12 to 20
Nickel -----	35 to 55
Molybdenum -----	3 to 7
Cobalt -----	1.5 to 7
Vanadium -----	Up to 1
Titanium -----	2.75 to 3.75
Aluminum -----	.75 to 2
Boron -----	.003 to .025

the balance consisting essentially of iron and in which the aluminum serves to stabilize the gamma prime phase formed by age hardening against transformation to an eta phase at elevated temperature and under stress, and in which the amount of cobalt provides substantially minimum misfit between the lattice parameters of the matrix of the alloy and of the gamma prime phase when the aged alloy is exposed to stress at high temperature over a long time.

5. An article subjected in use to severe stress at elevated temperatures up to about 1600° F. and formed of an age hardened austenitic nickel base alloy which within the tolerances of good melting practices consists essentially of:

	Percent
Carbon -----	Up to .07
Manganese -----	Up to .25
Silicon -----	Up to .25
Chromium -----	12.5 to 15
Nickel -----	40 to 45
Molybdenum -----	4 to 6
Cobalt -----	3 to 5
Titanium -----	3 to 3.5
Aluminum -----	1 to 1.5
Boron -----	.003 to .013
Vanadium -----	Up to 1

the balance consisting essentially of iron and in which the aluminum serves to stabilize the gamma prime phase formed by age hardening against transformation to an eta phase at elevated temperature and under stress, and in which the amount of cobalt provides substantially minimum misfit between the lattice parameters of the matrix of the alloy and of the gamma prime phase when the aged alloy is exposed to stress at high temperature over a long time.

6. An article subjected in use to severe stress at elevated temperatures up to about 1600° F. and formed of an age hardened austenitic nickel base alloy which within the tolerances of good melting practices consists essentially of:

Carbon -----	Up to .06% maximum.
Manganese -----	Up to .25% maximum.
Silicon -----	Up to .25% maximum.
Chromium -----	12.5% to 13.5%.
Nickel -----	42.5% to 43.5%.
Molybdenum -----	5.0% to 6.0%.
Cobalt -----	3.5% to 4.5%.
Titanium -----	2.8% to 3.3%.
Aluminum -----	1.0% to 1.4%.
Boron -----	.008% to .01%.

the balance consisting essentially of iron and in which the aluminum serves to stabilize the gamma prime phase formed by age hardening against transformation to an eta phase at elevated temperature and under stress, and in which the amount of cobalt provides substantially minimum misfit between the lattice parameters of the matrix

7

of the alloy and of the gamma prime phase when the aged alloy is exposed to stress at high temperature over a long time.

7. An age hardening austenitic nickel base alloy which in its hardened condition has good strength and ductility at temperatures up to about 1600° F. and which within the tolerance of good melting practice consists essentially of:

	Percent	
Carbon -----	Up to .07	5
Manganese -----	Up to .25	
Silicon -----	Up to .25	10
Chromium -----	12 to 15	
Nickel -----	40 to 45	
Molybdenum -----	4 to 7	15
Cobalt -----	About 4.5	
Titanium -----	2.8 to 3.5	
Aluminum -----	1 to 1.5	
Boron -----	.003 to .01	
Vanadium -----	Up to 1	20

the balance consisting essentially of iron.

8. An article subjected in use to severe stress at elevated temperatures up to about 1600° F. and formed of

8

an age hardened austenitic nickel base alloy which within tolerances of good melting practices consists essentially of:

	Percent
Carbon -----	Up to .07
Manganese -----	Up to .25
Silicon -----	Up to .25
Chromium -----	12 to 15
Nickel -----	40 to 45
Molybdenum -----	4 to 7
Cobalt -----	About 4.5
Titanium -----	2.8 to 3.5
Aluminum -----	1 to 1.5
Boron -----	.003 to .01
Vanadium -----	Up to 1

the balance consisting essentially of iron.

References Cited by the Examiner

UNITED STATES PATENTS

3,065,067 11/62 Aggen ----- 75—124

DAVID L. RECK, *Primary Examiner.*

WINSTON A. DOUGLAS, *Examiner.*

**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

Patent No. 3,183,084

May 11, 1965

Gerald B. Heydt et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected, below.

Column 3, lines 57 and 58, for "is about 180° F to 2050° F." read -- at about 1800° F. to 2050° F. --; column 5, line 65, for ".008/ to .01%" read -- .008% to .01% --.

Signed and sealed this 21st day of September 1965.

(SEAL)

Attest.

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents