United States Patent Office 3,026,198
Patented Mar. 20, 1962



3,026,198

# NICKEL BASE CASTING ALLOY

Rudolf H. Thielemann, Palo Alto, Calif., assignor to Sierra Metals Corporation, a corporation of Delaware

No Drawing. Filed Apr. 11, 1960, Ser. No. 21,123
11 Claims. (Cl. 75—171)

This invention relates to nickel base alloys. More particularly, it relates to nickel base casting alloys particularly adapted for use at elevated temperatures such as are encountered in the operation of gas turbines, and the like.

In recent years, gas turbine engines have been adapted to operate at higher temperatures because of improved performance at the higher temperature levels. When operating at higher temperatures, the gas turbine engine provides increased thrust and decreased consumption of fuel per pound of thrust.

One of the serious problems which has hampered the development of jet aircraft engines of improved performance has been the materials available for constructing the turbine blades and turbine nozzle vanes. These materials must be cast to close tolerances and must possess high orders of strength and oxidation resistance at the combustion gas temperatures and at the same time be resistant to thermal shock, i.e., withstand rapid heating and cooling without cracking.

Because of the severity of the nozzle vane application, for example, a wide variety of construction materials have been tried, including cermets, ceramics and coated metal alloys. Fabrication difficulties and property deficiencies have, insofar as I am aware, prevented these materials from attaining general commercial acceptance. In present day jet engines, the jet engine nozzle vanes are generally made of precision cast cobalt alloys which alloys perform satisfactorily as long as the operating temperatures remain below about 1800° F. or do not exceed about 1800° F. for any substantial time period. At these higher temperatures of about 1800° F., with these prior art cobalt alloys plastic deformation and oxidation is so serious as to substantially reduce the expected life of the vane.

Normal operating temperatures of jet engines designed for flight speeds up to about Mach 1.5, at the first stage nozzle vanes is about 1800° F., and this appears to be about the maximum for the cobalt base alloys in current use such as those identified by the trade names Vitallium and WI–52, although at this high temperature these alloys have a relatively short life. A check of operating temperatures for these jet engines during starting and acceleration, has indicated nozzle vane temperatures in excess of 2000° F. for short periods of time. Areas of incipient melting detected on used vanes, indicate local temperatures approaching 2350° F., which is the approximate melting point of these cast cobalt base alloys.

Advanced jet engine design is requiring higher operating temperatures. In jet engines for flight speeds up to Mach 4, alloys capable of operating for substantial periods of time at average nozzle vane temperatures of 2000° F. with intermittent temperatures of 2200° F. or higher, are required. It has now been discovered in accordance with the invention that an alloy which is a modified nickel-tungsten alloy meets the requirements of advanced jet engine design.

Nickel-tungsten binary alloys of between 25% and 45% tungsten content have melting points slightly in excess of about 2730° F. These alloys were studied by Sykes and Ellinger and the results reported in the Trans. ASM, 1940, pages 619–643. Additional work with these nickel-tungsten binary alloys is reported by Kornilov and Budberg in Doklady Akad, Nauk 100, pages 73–75, 1955.



While these nickel-tungsten binary alloys have a high melting point, they have not been useful because of their low strength at elevated temperatures and their low resistance to oxidation.

The new and useful alloys of the invention are nickel-tungsten base alloys having melting points approaching the melting point of pure nickel. These alloys have high strength and good oxidation resistance for practical periods of time at temperature in the range of 1850° F. to 2000° F., and even higher. Such alloys also exhibit characteristics which render them useful as a base upon which coatings may be deposited to provide surfaces of, for example, heightened oxidation resistance. Such coatings may be metals or alloys which have the required oxidation resistance and melt appreciably above, for example, 2000° F., but may be commercially unacceptable for use as turbine nozzle vanes because of poor strength, such as diffused chromium, chromium-nickel, chromium-aluminum, platinum, platinum-rhodium alloys, and the like.

The nickel-tungsten base alloys of the invention, having the improved high temperature strength and oxidation resistance properties, can be produced by incorporating in the composition controlled amounts of the essential elements; tungsten, tantalum, chromium, aluminum, titanium, zirconium, boron and carbon. Optionally the alloys may include other elements such as cobalt, columbium, iron, etc., in amounts up to the hereinafter discussed maximums which can be tolerated without deleteriously affecting the properties.

The alloy of the present invention comprises by weight 20% to 35% tungsten, 2% to 10% chromium, 0.5% to 8% tantalum, 1% to 6% aluminum, 0.1% to 3% titanium, .01% to 0.5% carbon, 0.001% to 1.0 of zirconium, and the balance nickel.

In addition to the above elements, the alloy may include up to 0.25% boron, up to 5% molybdenum, up to 5% iron, up to 15% cobalt, up to 1% manganese, up to 1% silicon and, of course, other metals or impurities which do not substantially alter the basic characteristics and properties of the alloy.

Of the essential alloying elements listed, tungsten in the amounts stated is important to develop the desired high temperature strength and metallurgical stability. Chromium in the amounts stated is essential for the development of the necessary oxidation stability in the alloy of the invention. When the alloy contains chromium in amounts of less than 2%, it does not possess the desired oxidation stability. When the alloy contains chromium in amounts in excess of about 10% the high temperature strength characteristics of the alloy are adversely affected. Preferably, the amount of chromium present is maintained between about 3% and about 6%.

Tantalum serves the double purpose of improving the oxidation resistance and the strength of the alloy at elevated temperatures. One theoretical explanation for the role of tantalum is that the high melting point of tantalum oxide ($Ta_2O_5$) has the effect of increasing the stability and melting point of tungstic oxide ($WO_3$) as it forms on the alloy surface. The net result is to greatly improve the oxidation resistance of the alloy at temperatures over 1800° F. Although a tantalum content of approximately 1/10 of the tungsten content is preferable from the point of view of oxidation resistance, it has been found necessary to vary the tantalum content of the alloy within the range stated in accordance with solubility restrictions which develop as other alloying elements are added or the proportions of the various elements are changed. Preferably the amount of tantalum present in the alloy is maintained between about 2.75% and about 5%.

Molybdenum is not the equivalent of tungsten in the alloys of this invention. Tungsten can be replaced by molybdenum only in small amounts without deleteriously lowering the oxidation resistance of the alloy. Molybdenum may be tolerated up to a maximum of 5% by weight of the alloy but is preferably maintained as low as possible.

In some types of alloys, tantalum and columbium have been recognized as equivalents. These elements are not equivalents in the alloys of this invention. If columbium is present, it cannot be used to replace more than 50% of the amount of tantalum present without exhibiting an adverse effect upon oxidation stability. While columbium can be used in amounts up to 3%, preferably the columbium content of the alloys is limited to amounts not exceeding about 1.5% by weight.

Within the limits specified, aluminum and titanium are very effective in hardening and strengthening the alloy. One explanation of the effects produced by aluminum and titanium is that the hardening and strengthening results from the precipitation of a face centered cubic gamma prime phase [$Ni_3(Al, Ti)$], from the solid solution nickel base alloy upon cooling. This gamma prime phase may appear both as agglomerates in the dendritic grain boundaries or as a dispersed phase within the grains themselves. Preferably the aluminum content of the alloy is maintained between about 3% and 5%. The zirconium content is preferably limited to between about 0.1% and 0.6%.

The ratio of aluminum to titanium content is not critical as far as development of high temperature strength is concerned. However, other important properties, such as grain size, elongation at fracture, adherence of oxide scale to the surface, oxidation resistance and resistance to thermal shock can be varied appreciably by varying the ratio of the aluminum to the titanium present. In particular, about 1½% of titanium, with about 3% of aluminum present, is extremely beneficial in improving oxidation resistance by making the oxide scale adherent. If more than about 2½% of titanium is present along with 3% of aluminum, the alloy may exhibit severe surface cracking in creep rupture and thermal shock tests. In addition, if the titanium content exceeds the aluminum content, the alloy may exhibit a hot short condition.

The minor essential alloying elements in the nickel base alloy of the invention are carbon, zirconium and boron. It has been found that up to about 0.5% of carbon is beneficial in controlling the grain size of the alloy, apparently as a result of the formation of high melting point carbides. Larger amounts of carbon tend to make the alloy brittle. Preferably the carbon content of the instant alloy is limited to between 0.1% and 0.2% by weight.

Boron and zirconium when present in amounts up to about 0.25% and 1.0%, respectively, are effective as grain boundary strengtheners. Best results are obtained when the weight ratio of zirconium to boron is 4 to 1, which is the stoichiometric ratio for the formation of the stable $ZrB_2$. Zirconium apparently has the additional effect of increasing the adherence and refractoriness of the protective oxide scale which is formed on the alloy at elevated temperatures. Boron, it has been noted, has the adverse effect of reducing oxidation resistance of the alloy and it is important, therefore, if boron is present in the alloy of the invention, the amount of boron present should not appreciably exceed one fourth the weight of zirconium present in the alloy if oxidation and thermal shock resistance are of importance.

In order to keep the melting point of the alloy as high as possible and the oxidation resistance thereof at elevated temperature at a maximum, the balance of the alloy should be essentially nickel. When it is stated that nickel constitutes the balance of the alloy, it is to be understood that the balance will be substantially all nickel but can contain small amounts of other elements or impurities as hereinabove indicated. Nickel, for example, can be replaced in part with cobalt but cobalt must not exceed 25% by weight of the total amount of nickel plus cobalt present in the alloy. Although cobalt does not critically affect any of the mechanical properties of the high tungsten nickel base alloy, it does have mild effects which are both beneficial and detrimental depending upon conditions. It has been observed that with more than about 5% of cobalt in the alloy, the elongation after fracture in a high temperature pressure test is somewhat higher and this property may be important in a specific application. If more than 15% by weight of the alloy is cobalt, the effect is detrimental in that both the high temperature rupture strength and the oxidation resistance are adversely effected, even though the ductility of fracture in a sustained load test at elevated temperatures is greatly increased.

As noted hereinbefore, molybdenum in amounts up to about 5% may be present in the alloy. Preferably molybdenum does not constitute more than 2% by weight of the alloy. Silicon and manganese contents also should be as low as possible, since each of these elements has the effect of lowering both the melting point and high temperature strength of the alloy. Iron, although exhibiting no beneficial effects in the alloy, does not appear to be detrimental if present in amounts of less than 5%. When iron is present in amounts above 5%, the high temperature strength of the alloy is reduced and the alloy is subject to failure by intergranular cracking.

It has also been discovered that the amounts of the alloying elements tungsten, chromium, tantalum, columbium, titanium and aluminum required to produce strength in alloys of the instant type, can be varied on an equivalent solubility basis, provided each element is maintained within the broad limits specified, to maintain the type of alloy in which the individual alloying elements may be adjusted to obtain optimum properties. While the above group of elements includes columbium, it must be borne in mind that this discussion relates to high temperature strength and does not alter the fact that the adverse effect of columbium upon oxidation resistance limits the amount of columbium which can be tolerated in an alloy having the desired strength and oxidation resistance properties at temperatures of the order of 1850° F. to 2000° F. or even higher. Attention is directed to the role of columbium for the reason that the problem of developing strength without incurring brittleness was less difficult than the problem of discovering a combination of alloying elements which would concurrently impart oxidation resistance at temperatures up to about 2000° F.

If the equivalent solubility factor as calculated by the equation

$$(1\times\text{percent Cr}+1.1\times\text{percent W}+1.2\times\text{percent Ta}+3.4\times\text{percent Cb}+4.3\times\text{percent Ti}+6\times\text{percent Al})$$

is between 60 and 71, the type of metallurgical structure developed has good high temperature strength and stability without being brittle. It must be understood that the equivalent solubility factor by itself does not guarantee a minimum rupture strength since other metallurgical factors are also pertinent. However, the equivalent solubility factor is helpful in delineating the alloy limitations that have been observed when balancing changes in amounts of the various essential elements. Optimum properties in the alloys of this invention are obtained when the equivalent solubility factor is on the high side of the range, i.e., within the range 65 to 68. When the equivalent solubility factor is below about 60, the equation implies that the alloy will not have been sufficiently strengthened to have the required high temperature properties. When the equivalent solubililty factor is about 71 or above, the equation implies that the practical limit to the total amount of alloying has been reached.

In preparing the alloys, conventional vacuum melting

and casting techniques are employed. In general, it is preferable that the more active metals such as aluminum, boron, zirconium be the last to be introduced into the melt. After an alloy is melted and the correct temperature attained for casting, a casting is poured and the casting allowed to cool to room temperature before removing the investment.

The invention is further illustrated by the following examples which are given by way of illustration and without any intention that the invention be limited to the particular compositions shown.

*Example I*

An 1800 gram alloy melt of a nickel base alloy composition containing 25% of tungsten, 5% of chromium, 5% of tantalum, 3.25% of aluminum, 2.25% of titanium, 0.15% carbon, 0.10% zirconium, 0.025% boron and the balance essentially nickel, was prepared by melting the nickel in a magnesia crucible, following which the high melting point constituents, tungsten and tantalum were added. After completely melting this mixture, more active metals, chromium, alumium, titanium, boron, zirconium, and carbon were added. After the melt was completely outgassed and the casting temperature attained, the alloy was poured into molds.

A cluster of six test bars was cast using a zirconium silicate-alumina "shell" type investment mold. The test bars were each 3 inches long and ¼ inch in diameter.

Test bars were tested to determine ultimate strength and elongation at room temperature, rupture life at 1800° F., at 1900° F. and at 2000° F. and the oxidation resistance. Results of tests are listed in the table following the examples.

*Example II*

An 1800 gram alloy melt of a nickel base alloy composition containing 28% of tungsten, 5% of chromium, 3% of tantalum, 3.25% of aluminum, 2% titanium, .15% carbon, .12% zirconium, .03% boron and the balance essentially nickel, was prepared by melting the nickel in a magnesia crucible, following which the high melting point constituents, tungsten and tantalum were added. After completely melting this mixture, the more active metals, chromium, aluminum, titanium, boron, zirconium, and carbon were added. After the melt was completely outgassed and the casting temperature attained, the alloy was poured into molds.

A cluster of six test bars was cast using a zirconium silicate-alumina "shell" type investment mold.

The test bars were each 3 inches long and ¼ inch in diameter.

Test bars were tested to determine ultimate strength and elongation at room temperature, rupture life at 1800° F., at 1900° F. and at 2000° F. and the oxidation resistance. Results of tests are listed in the table following the examples.

*Example III*

An 1800 gram alloy melt of a nickel base alloy composition containing 28% of tungsten, 5% chromium, 3% tantalum, 3.50% aluminum, 1.5% titanium, .15% carbon, .12% zirconium, .03% boron and the balance essentially nickel, was prepared by melting the nickel in a magnesia crucible, following which the high melting point constituents, tungsten and tantalum were added. After completely melting this mixture, the more active metals, chromium, aluminum, titanium, boron, zirconium, and carbon were added. After the melt was completely outgassed and the casting temperature attained, the alloy was poured into molds.

A cluster of six test bars was cast using a zirconium silicate-alumina "shell" type investment mold.

The test bars were each 3 inches long and ¼ inch in diameter.

Test bars were tested to determine ultimate strength and elongation at room temperature, rupture life at 1800° F., at 1900° F. and at 2000° F. and the oxidation resistance. Results of tests are listed in the table following the examples.

*Example IV*

An 1800 gram alloy melt of a nickel base alloy composition containing 28% of tungsten, 5% chromium, 3.25% tantalum, 3.50% aluminum, 1.50% titanium, .15% carbon, .12% zirconium, .03% boron and the balance essentially nickel was prepared as described in Example I.

A cluster of six test bars was cast using a zirconium silicate-alumina "shell" type investment mold.

The test bars were each 3 inches long and ¼ inch in diameter.

Test bars were tested to determine ultimate strength and elongation at room temperature, rupture life at 1800° F., at 1900° F. and at 2000° F. and the oxidation resistance. Results of tests are listed in the able.

Test results were as follows:

| Test | Alloy of Ex. I | Alloy of Ex. II | Alloy of Ex. III | Alloy of Ex. IV |
|---|---|---|---|---|
| Eq. Solubility Factor | 67.2 | 67.5 | 66.9 | 67.2 |
| Room Temp. Properties: | | | | |
| Ultimate Str., p.s.i | 162,800 | 150,500 | 139,900 | 152,000 |
| Percent Elong | 2.3 | 3. | 1.5 | .76 |
| Rupture Str.—1,800° F.: | | | | |
| at 25,000 p.s.i.—hours | 266.5 | 108.3 | 179.5 | 153.4 |
| Percent Elong | 3. | 2.3 | 1.5 | 1.5 |
| Rupture Str.—1,900° F.: | | | | |
| at 20,000 p.s.i.—hours | 77.4 | 72.3 | 131.1 | 87.7 |
| Percent Elong | 3.8 | 2.3 | 2.3 | 1.5 |
| at 17,500 p.s.i.—hours | 167.1 | 167.9 | 251.6 | 150.4 |
| Percent Elong | 4.6 | 2.3 | 2.3 | .8 |
| Rupture Str.—2,000° F.: | | | | |
| at 15,000 p.s.i.—hours | 29.9 | 24. | 50.2 | 28.2 |
| Percent Elong | 3. | 1.5 | 4.6 | 1.5 |
| at 12,500 p.s.i.—hours | 85. | 82.3 | 109.4 | 75.6 |
| Percent Elong | 3.2 | 3.8 | 1.5 | 1.5 |
| Relative Oxidation Resistance | Good | Good | Good | Good |

In the claims, the expression "consisting essentially of" is intended to recite an alloy containing the named elements as the essential alloying elements of the claimed alloy. This expression is to be construed in the light of the preceding portion of this specification.

I claim:

1. A nickel base alloy consisting essentially of 20% to 35% tungsten, 2% to 10% chromium, 0.5% to 8% tantalum, 1% to 6% aluminum, 0.1% to 3% titanium, 0.1% to 0.5% carbon, 0.001% to 1.01% zirconium, and the balance essentially nickel.

2. A nickel base alloy consisting essentially of 20% to 35% tungsten, 2% to 10% chromium, 0.5% to 8% tantalum, 1% to 6% aluminum, 0.1% to 3% titanium, 0.1% to 0.5% carbon, 0.001% to 1.0% zirconium, up to 0.25% boron, up to about 1% manganese, up to about 1% silicon, up to about 5% molybdenum, up to about 5% iron, up to about 15% cobalt with the cobalt content being no more than 25% of the total amount of nickel plus cobalt present, up to about 3% columbium with the columbium content being no more than 50% of the amount of tantalum in the alloy, and the balance nickel.

3. The alloy of high strength at elevated temperatures according to claim 2 in which the equivalent solubility factor calculated according to the equation

$$(1\times\text{percent Cr}+1.1\times\text{percent W}+1.2\times\text{percent Ta}+3.4\times\text{percent Cb}+4.3\times\text{percent Ti}+6\times\text{percent Al})$$

is between 60 and 71.

4. The alloy of high strength at elevated temperature according to claim 2 in which the equivalent solubility factor calculated according to the equation

$$(1\times\text{percent Cr}+1.1\times\text{percent W}+1.2\times\text{percent Ta}+3.4\times\text{percent Cb}+4.3\times\text{percent Ti}+6\times\text{percent Al})$$

is between 65 and 68.

5. A nickel base alloy consisting essentially of 20% to 35% tungsten, 3% to 6% chromium, 2.75% to 5% tantalum, 3% to 5% aluminum, 0.1% to 3% titanium,

0.1% to 0.2% carbon, 0.1% to 0.6% zirconium and the balance essentially nickel.

6. A nickel base alloy consisting essentially of 25% of tungsten, 5% of chromium, 5% of tantalum, 3.25% of aluminum, 2.25% of titanium, 0.15% carbon, 0.10% zirconium, 0.025% boron and the balance essentially nickel.

7. A nickel base alloy consisting essentially of 28% of tungsten, 5% chromium, 3% tantalum, 3.50% aluminum, 1.5% titanium, .15% carbon, .12% zirconium, .03% boron and the balance essentially nickel.

8. A nickel base alloy consisting essentially of 28% of tungsten, 5% chromium, 3.25% tantalum, 3.50% aluminum, 1.50% titanium, .15% carbon, .12% zirconium, .03% boron and the balance essentially nickel.

9. A cast air foil section for use in the combustion section of a gas turbine engine formed of an alloy consisting essentially of 20% to 35% tungsten, 2% to 10% chromium, 0.5% to 8% tantalum, 1% to 6% aluminum, 0.1% to 3% titanium, 0.1% to 0.5% carbon, 0.001% to 1.0% zirconium, and the balance essentially nickel.

10. A cast air foil section for use in the combustion section of a gas turbine engine formed of an alloy consisting essentially of 20% to 35% tungsten, 2% to 10% chromium, 0.5% to 8% tantalum, 1% to 6% aluminum, 0.1% to 3% titanium, 0.1% to 0.5% carbon, 0.001% to 1.0% zirconium, up to 0.25% boron, up to about 1% manganese, up to about 1% silicon, up to about 5% molybdenum, up to about 5% iron, up to about 15% cobalt with the cobalt content being no more than 25% of the total amount of nickel plus cobalt present, up to about 3% columbium, with the columbium content being no more than 50% of the amount of tantalum in the alloy, and the balance nickel.



11. A cast air foil section for use in the combustion section of a gas turbine engine formed of an alloy consisting essentially of 28% of tungsten, 5% chromium, 3% tantalum, 3.50% aluminum, 1.5% titanium, .15% carbon, .12% zirconium, .03% boron and the balance essentially nickel.

**References Cited** in the file of this patent

UNITED STATES PATENTS

2,951,757 Brown ---------- Sept. 6, 1960