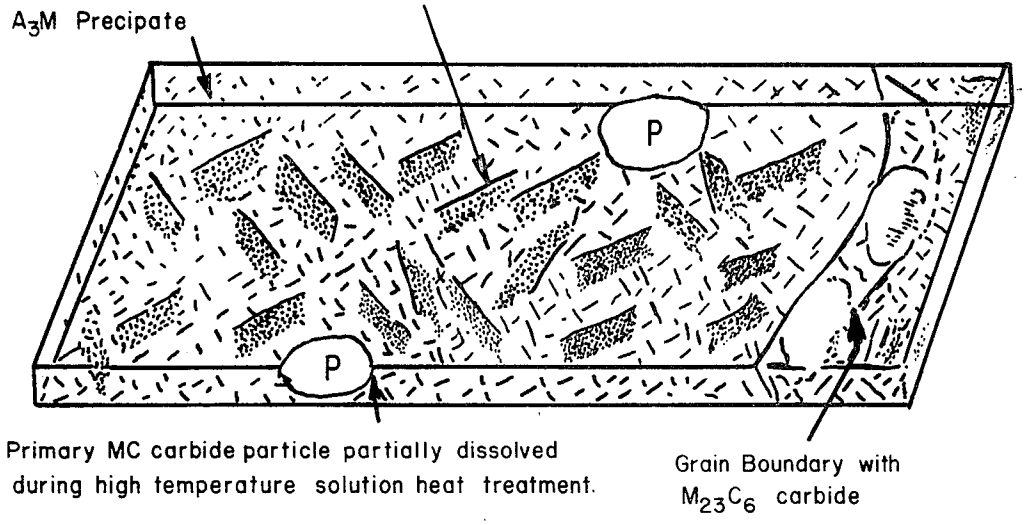
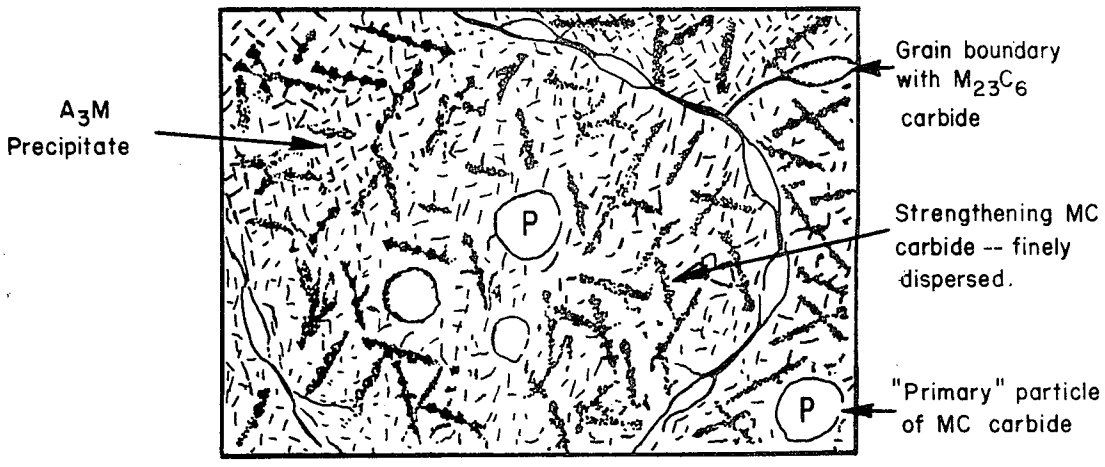
March 14, 1972 P. S. KOTVAL 3,649,379
CO-PRECIPITATION-STRENGTHENED NICKEL BASE ALLOYS
AND METHOD FOR PRODUCING SAME
Filed June 20, 1969 2 Sheets-Sheet 1

Fine Particles of MC carbide distributed (in association with planar lattice defects) throughout the alloy matrix.



(approx. 10,000 X)

Fig. 1.



(approx. 8,000 X)

Fig. 2.

INVENTOR
Peshotan Sohrab Kotval
BY
ATTORNEY

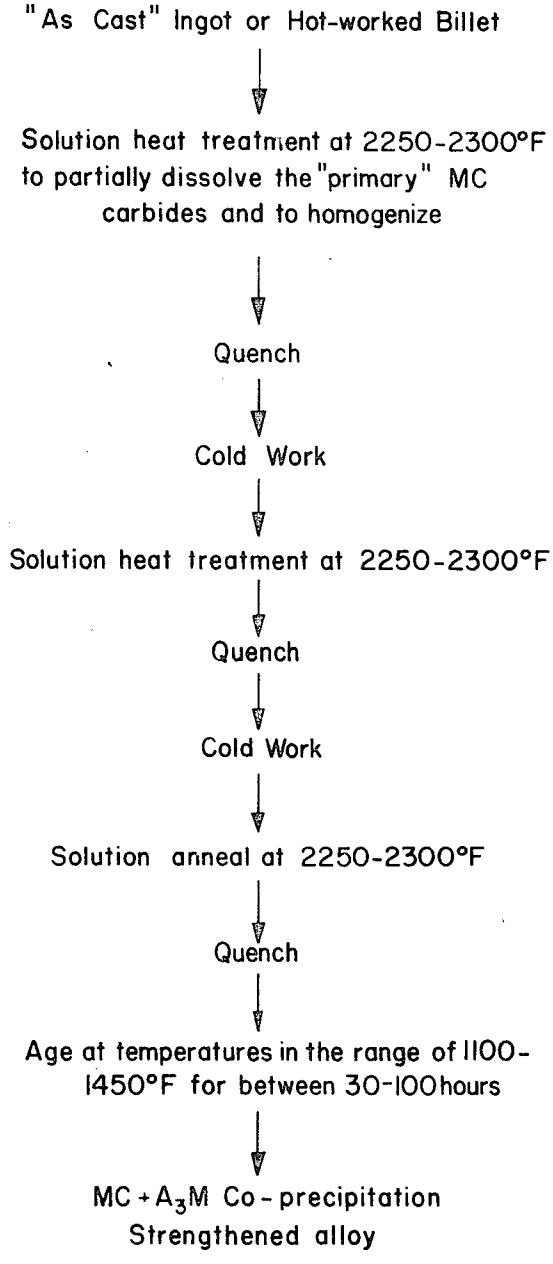


Fig. 3.

INVENTOR
Peshotan Sohrab Kotval
BY
ATTORNEY

United States Patent Office 3,649,379
Patented Mar. 14, 1972

3,649,379

CO-PRECIPITATION-STRENGTHENED NICKEL BASE ALLOYS AND METHOD FOR PRODUCING SAME

Peshotan Sohrab Kotval, Indianapolis, Inc., assignor to Cabot Corporation, Boston, Mass.

Filed June 20, 1969, Ser. No. 834,942
Int. Cl. C22c 19/00; C21d 7/00
U.S. Cl. 148—12.7 10 Claims

ABSTRACT OF THE DISCLOSURE

Nickel base alloys of 15–22% Cr, 3–12% Mo; at least one of the group consisting of 6–10% Ta, 6–9% Cb and 6–9% V, and 0.03–0.15% C, balance nickel and residual impurities are strengthened by co-precipitating dispersed monocarbides having particle sizes of less than 250 angstroms and an intermetallic phase by sequentially: (1) solution heat treating the alloy at a temperature of 2250–2300° F. (2) quenching and (3) cold-working in repetitive cycles. The material is thereafter finally annealed, quenched and aged to produce the co-precipitation-strengthened structure.

This invention relates to precipitation strengthened nickel base alloys and more particularly to alloys of this type which are strengthend by the co-precipitation of monocarbides and an intermetallic phase. The invention also relates to a method for producing co-precipitation strengthened nickel base alloys.

Precipitation strengthened nickel base alloys have heretofore been based upon the formation of the well known aluminum-titanium rich phase known as gamma prime. This strengthening mechanism requires the presence of aluminium and titanium in an amount of as much as 8% by weight.

It is the main object of this invention to provide a nickel base alloy which is strengthened by the co-precipitation of two new phases.

Another object is to provide a precipitation strengthened nickel base alloy which does not require the presence of aluminum and titanium therein.

A further object is to provide a nickel base alloy which has been strengthened by the co-precipitation of an A_3M phase and an MC monocarbide phase wherein A consists essentially of nickel and M consists essentially of one or more elements selected from the group consisting of Ta, Cb and V, wherein C is carbon.

Yet another object is to provide a method for producing a co-precipitation strengthened nickel base alloy having an A_3M phase and a MC monocarbide phase as defined above.

Other objects and advantages will be apparent to those skilled in the art after consideration is given to the following specification, drawings and appended claims.

In the drawings:

FIGS. 1 and 2 are schematic representations of the microstructure of the alloys of the present invention; and FIG. 3 is a diagrammatic process flow chart outlining the steps required for making the alloys of the invention.

The present invention is based upon two discoveries which are utilized in combination to produce new nickel base alloys as well as a method for producing same.

The first discovery resides in the fact that it is possible to precipitate an intermetalic strengthening phase of the A_3M type as defined above from a nickel base matrix. It should be understood that this precipitation phase is distinct from the above mentioned gramma prime phase achieved through the use of aluminum and titanium in combination. It is known that the gamma prime phase has

a crystal structure of the ordered face centered cubic (FCC) type. In marked contrast to this, the A_3M phase produced within the alloys of the present invention is non-cubic in crystal structure. Although the precise crystal structure of the precipitation-strengthening phase in the alloys of the invention has not been conclusively established, the best crystallographic evidence suggests that it is a tetragonal structure wherein the axes of the unit cell of the crystal structure are of unequal length thus the crystal structure is clearly not of the cubic type. It has also been found that this phase may be precipitated without the presence of aluminum and titanium in the alloy composition.

The second discovery resides in the fact that it is possible to precipitate a well dispersed distriubtion of monocarbides having particle sizes of less than 250 angstroms in the alloy. Most prior art wrought nicket base alloys contain sufficient carbon so as to form monocarbides of a simple face centered cubic structure whenever monocarbide forming elements such as V, Ta and Cb are present. It is important to note that these monocarbides are usually in the form of undissolved "primary" particles present in the alloy matrix but which do not effectively strengthen the same. Typically, primary monocarbide particles have particle diameters of between 10 and 20 microns in nickel base alloys. By partially dissolving the abovementioned "primary" monocarbides, as will be explained further hereinafter, it is possible to precipitate a dispersion of monocarbides having a particle size of less than 250 angstroms.

This invention contemplates the co-precipitation of the abovementioned intermetallic and the monocarbide phases concurrently.

According to the invention, nickel-base alloy compositions are provided having a new microstructure. This microstructure is comprised of intermetallic-cum-monocarbide co-precipitated phases. The intermetallic phase may be defined as A_3M wherein A consists essentially of Nickel and M consists essentially of one or more elements selected from the group consisting of Ta, Cb and V. The monocarbide phase may be defined as MC wherein M consists essentially of one or more elements selected from the group consisting of Ta, Cb and V, and C is carbon, the MC monocarbides being in the form of fine particles of less than 250 angstroms size. The structure would also contain primary monocarbides of 5 microns or less in size.

The chemical composition of the abovementioned alloys of the invention consists essentially of (by weight): 15–22% Cr, 3–12% Mo, at least one of the group consisting of 7–10% Ta, 6–9% Cb and 6–9% V, the total Ta+Cb+V content not exceeding 10%. The alloy must also contain 0.03–0.15% carbon with the balance being nickel and residual impurities. The impurities should have not more than 7% Fe and not more than 8% Co.

The ability to produce the abovementioned nickel base alloy results from the discovery that by controlling the level of certain impurities in the nickel base alloy, (i.e. Fe) it is possible to solution heat treat the alloy at temperatures of about 2280° F. without causing liquation and melting. Although, ideally, higher temperatures would normally be required to dissolve monocaribdes, it is possible to achieve partial dissolution thereof by progressively subjecting the material to an alternating sequence of high temperature solution heat treatments at about 2280° F. and quenching together with controlled cold working steps.

Chromium is required in the alloy within the range disclosed above to provide strengthening and corrosion resistance. Less than 15% Cr yields an alloy with minimal corrosion resistance; over 22% Cr yields an alloy with reduced ductility. Molybdenum is present in the alloy

within the ranges shown above to provide further solution strengthening and corrosion resistance as required. Molybdenum is preferred in the alloy, although tungsten may replace molybdenum in whole or in part. Tungsten may be present in greater quantities than molybdenum, i.e., up to a maximum of 16 percent, but preferably about 12 percent nominally. Carbon must be present in the alloy within the range about 0.03 to 0.15% by weight to promote the formation of carbides in the alloy. Less than 0.03% carbon is insufficient to produce the carbides while over 0.15% carbon tends to yield a more brittle alloy. Alloys containing over 0.15% carbon are also more difficult to work. The alloy system of this invention must also contain at least one of the group including tantalum, columbium, and vanadium. At least one of these elements must be present in the alloy together with carbon to provide the metal monocarbides that are precipitated in the nickel-chromium (molybdenum) matrix. The presence of these precipitated carbides in addition to the aforementioned A_3M intermetallic phase together with the critical proccessing steps that promote the controlled precipitation are the heart of the present invention. Each element in this group must be present within the ranges stated above when that element is the principal carbide and intermetallic former. The total content of tantalum+columbium+vanadium in the alloy system must not exceed 10% by weight. Iron may be present up to a maximum of 7%. This requirement results from the fact that the higher iron content tends to lower the melting point of the alloy thereby prohibiting the higher solution heat treatment temperature required to cause the dissolution of the "primary" monocarbides so that subsequent reprecipitation can be achieved as will be hereinafter described. Cobalt may be present up to a maximum of 8%. Higher cobalt contents tend to lower the matrix stacking fault energy and thereby cause impediments in the nucleation of the dislocation reaction which is a necessary precondition for the desired morphology of monocarbide precipitation.

As aforementioned, the use of aluminum and titanium in the alloy compositions of the invention is not required. It is desirable that the aluminum plus titanium content should be as low as possible, and preferably less than 1.4%. If the aluminum plus titanium level is low, it will be possible to produce a good quality alloy with an air melting practice.

Boron, silicon, manganese, magnesium, and copper up to a total of about 2.5% may be present in the alloy within the ranges known in the art to be effective to enhance certain characteristics associated with these elements; i.e. the deoxidation step, casting fluidity, ductility and the like.

The balance of the alloy is nickel and adventitions impurities generally known to be present in this class of alloys.

Referring now to the drawings, FIG. 1 is a three-dimensional representation of the microstructure as would be observed in a thin foil sample using transmission electron microscopy. FIG. 2, on the other hand, is a representation of microstructure as would be observed by a replica of the surface of the specimen. It should be understood that this type of structure cannot be observed and resolved by normal optical metallographic techniques. In FIGS. 1 and 2, the microstructure of the alloys of the invention as shown, consists of the usual grain structure with some precipitation of the chromium rich $M_{23}C_6$ carbide phase at the grain boundaries. Unique to this microstructure however is the highly refined particles of the "primary" MC monocarbides P. The actual size of the primary MC monocarbides P shown is about 1–2 microns. The unique structure further has dispersed within it, fine precipitates of MC monocarbides K which are associated with sheets of planar lattice defects. The precipitates K are of about 250 angstroms or less in size and being coherent with the matrix strengthen it. The unique structure still further has, uniformly dispersed within the matrix, an A_3M intermetallic phase which is coherent therewith and which in combination with the precipitated MC monocarbide phase greatly strengthens the entire alloy system.

Referring now to FIG. 3, the alloys of the invention can be made by providing an alloy material with 15–22% Cr, 3–12% Mo, at least one member selected from the group consisting of 7–10% Ta, 6–9% Cb and 6–9% V, the total of Ta+Cb+V not exceeding 10%, and 0.03–0.15% C, the balance being nickel and residual impurities said impurities consisting of not more than 7% Fe and not more than 8% Co, said alloy being in a form capable of being cold-worked.

The material is solution heat-treated at a temperature within the range 2250°–2300° F. for a period of about 24 hours to homogenize the matrix and to at least partially dissolve the "primary" monocarbide particles and thereby cause the monocarbide-forming element and the carbon to be put into solid solution in the alloy matrix. Following this solution-heat-treatment the material is water-quenched and cold worked. Until the final desired dimensions of the product are achieved, the abovementioned sequence of solution-heat-treatment followed by quenching and cold-working is repeated. Thereafter, the cold-worked material is annealed for a period not exceeding one hour within the solution heat-treatment temperature range of 2250–2300° F. After annealing, the material is water-quenched to about ambient temperature and is thereafter aged at a temperature within the range of 1100–1450° F. for a period of 24 to 100 hours. As a result of this aging step, both the A_3M intermetallic phase and the fine (less than 250 angstroms) monocarbide phase are precipitated uniformly throughout the matrix. The occurrence of these two coherent phases in combination is the desired strengthening-mechanism of this invention. The invention will now be illustrated by the following examples:

EXAMPLE I

A 5 lb. heat of material consisting of (by wt.): 20.34% Cr, 8.90% Mo, 0.11% C, 8.58% Ta, 4.8% Fe, 0.08% Cb, 0.23% Al, 0.01% Ti, the balance being nickel was electron-beam melted and cast into a 1.5" round bar. This bar was solution heat treated at a temperature of 2282° F. for a period of 24 hours and water-quenched. Thereafter, the material was sequentially cold-worked, solution-heat-treated at 2282° F. and quenched. After the process was repeated five times, the resultant 0.004" sheet produced was solution heat treated (annealed) for a period of 1 hour at 2282° F. and quenched. Thereafter, the material was cut into various specimens, each of which was aged at a different temperature and time. The range of aging temperatures was 1100–1450° F. and the range of aging times was 0.5 hours to 1500 hours. In all cases, thin foil transmission electron microscopy and diffraction revealed that the requisite structure, as depicted in FIGS. 1 and 2, and consisting of a uniform intragranular distribution of the two co-precipitated coherent phases i.e. an A_3M intermetallic phase and a MC monocarbide phase was obtained. The examination further showed a complete absence of a face centered cubic gamma prime phase.

EXAMPLE II

A 50 lb. heat of material consisting of (by weight): 20.47% Cr, 5.41% Mo, 0.089% C, 9.82% Ta, 5.59% Fe and 5.02% Co, the balance being nickel was vacuum induction melted and cast. After homogenization at a temperature of about 2282° F. over a period of 24 hours the ingot was forged to one inch square bar. This as-forged material was thereafter solution heat treated (homogenized) at 2282° F. for a period of 24 hours and water-quenched. Thereafter, the material was sequentially cold-worked, solution heat-treated at 2282° F. and quenched until a form of 0.004" sheet was attained. The material was thereafter further processed as in Example I. Electron microscopy and diffraction analysis revealed

that the structure shown in FIGS. 1 and 2 and described in Example I was attained. As in Example I, there was a complete absence of any gamma prime formation present in the alloy produced.

While the invention has been described in connection with specific alloy compositions and heat treatment steps, it should be understood that minor variations may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. A nickel-base alloy consisting essentially by weight of 15 to 22% Cr, 3 to 12% Mo, 0.03 to 0.15% C and at least one of the group consisting of 7 to 10% Ta, 6 to 9% Cb and 6 to 9% V, the total of said group not exceeding about 10%, and with the balance being nickel and residual impurities, provided that the alloy is essentially free of aluminum and titanium and contains not more than 7% Fe and not more than 8% Co, said alloy having both a coherent, non-cubic intermetallic phase represented by general formula A_3M and a coherent face-centered cubic monocarbide phase represented by the general formula MC wherein A consists essentially of Ni, M is a metal from the group consisting of Ta, Cb and V and C is carbon, said monocarbide phase being present both as primary particles of up to about 5 microns in size and as fine particles of less than 250 angstroms in size which are co-precipitated with the said intermetallic A_3M phase.

2. A nickel-base alloy as claimed in claim 1 wherein W is substituted for at least part of the Mo content.

3. A nickel-base alloy as claimed in claim 1 which is essentially free of conventional precipitated gamma prime phase.

4. A nickel-base alloy as claimed in claim 1 wherein the Cr content is about 20%, the Ta content is about 10%, the C content is about 0.09%, and the Mo content is about 5 to 8%, and the balance consists essentially of nickel and residual impurities.

5. A nickel-base alloy as claimed in claim 1 wherein M is principally Ta with some Cb associated therewith.

6. A method for producing a nickel-base alloy strengthened by co-precipitation of two coherent phases, namely a non-cubic intermetallic phase A_3M and a FCC monocarbide phase MC, wherein A consists essentially of Ni, C is carbon, and M is a metal from the group consisting of Ta, Cb and V, said MC monocarbide phase being dispersed as fine particles of less than 250 angstroms in size in addition to primary particles of up to about 5 microns in size, comprising the steps of:

(a) providing in a form capable of being cold-worked an alloy material consisting by weight of 15 to 22% Cr, 3 to 12% Mo, 0.03 to 0.15% C and at least one member of the group consisting of 7 to 10% Ta, 6 to 9% Cb and 6 to 9% V provided that the total of said group does not exceed about 10%, the balance being Ni and residual impurities, provided that the alloy is essentially free of aluminum and titanium and contains not more than 7% Fe and not more than 8% Co;

(b) solution heat-treating said material at a temperature between 2250 and 2300° F. to dissolve at least partially primary monocarbide particles of the MC type; thereafter

(c) quenching the material; thereafter

(d) cold-working the material until the desired form is attained; thereafter

(e) annealing the material at a temperature in the range of 2250 to 2300° F. for a period not exceeding 1 hour; thereafter

(f) quenching the material to substantially ambient temperature; and thereafter

(g) aging the material within a temperature range of 1100 to 1450° F. until said two co-precipitated coherent phases, A_3M and MC, are both achieved in effective strengthening amounts.

7. A method as claimed in claim 6 wherein steps (d), (e) and (f) are repeated as necessary in order to attain the desired form before aging step (g) is carried out.

8. A method as claimed in claim 6 wherein the material is aged in step (g) for a period of about 30 to 100 hours.

9. A method as claimed in claim 6 wherein W is substituted for at least part of the Mo content specified in step (a).

10. A method as claimed in claim 6 wherein M is principally Ta with some Cb associated therewith.

References Cited

UNITED STATES PATENTS

3,046,108	7/1962	Eiselstein	75—171
3,069,258	12/1962	Haynes	75—171
3.085,005	4/1963	Michael et al.	75—171
3,151,981	10/1964	Smith et al.	75—171
3,372,068	3/1968	White	148—32.5 X
3,466,171	9/1969	Fletcher et al.	75—171
3,497,349	2/1970	Eppich	75—171
3,411,899	11/1968	Richard et al.	75—171

CHARLES N. LOVELL, Primary Examiner

U.S. Cl. X.R.

75—171; 148—32.5, 162