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3,562,024

COBALT-NICKEL BASE ALLOYS CONTAINING CHROMIUM AND MOLYBDENUM

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10 Claims

ABSTRACT OF THE DISCLOSURE

Corrosion-resistant alloys which can be work-strengthened to have a combination of very high ultimate tensile strength, yield strength and ductility, the alloys containing as essential elements, by weight, 33 to 37% nickel, 7 to 10.5% molybdenum, 19 to 21% chromium, carbon in a maximum amount of 0.025%, the balance being cobalt in the proportion of at least 33%, the sum of cobalt and nickel being from 66 to 74% and said sum divided by the percent chromium being from 3.1 to 3.9.

CROSS REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of my copending application Ser. No. 637,613, filed Apr. 10, 1967, now Pat. No. 3,356,542, as a continuation-in-part of my then copending application Ser. No. 584,029, filed Aug. 18, 1966, now abandoned, and also as a continuation-in-part of my then copending application Ser. No. 565,088, filed July 14, 1966, now abandoned, both of said prior applications being filed as continuations-in-part of my then copending application Ser. No. 452,054, filed Apr. 30, 1965, now abandoned.

BACKGROUND OF THE INVENTION

This invention is in the field of nickel-base and cobalt-base alloys, particularly such alloys containing chromium and molybdenum and a critically small amount of carbon.

Manufacturing and processing conditions and procedures in chemical, mechanical, and metallurgical operations have advanced in recent years to the point where the currently-used materials for the construction of equipment have inadequate strength and resistance to oxidation and corrosion.

Prior to the invention of my above-identified application Ser. No. 637,613, now Pat. No. 3,356,542, cobalt- and nickel-base alloys had not had the combination of ductility and high yield strength or ultimate tensile strength desired for the above-noted and other high service requirements. Cold-work strengthening has generally been accompanied by excessive loss of ductility; conversely, recrystallization or annealing to improve ductility has been accompanied by loss of strength derived from working. In many prior art alloys the lack of ductility is so great as to amount to brittleness, but it had not been evident how such brittleness could be avoided while retaining very high or enhanced strengths.

There had also been a need for ductile, strong alloys of the type just described which, additionally, had a high degree of resistance to corrosion under stress, especially in sea water. Stress-corrosion may lead to sudden, premature failure in such marine hardware as wire and cable. Obviously, failure without warning is incompatible with marine safety.

According to the invention of my prior application Ser. No. 637,613, now Pat. No. 3,356,542, the above-discussed

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problems of the prior art were solved by the therein-described novel alloys which in their broadest aspects were strong and adequately ductile, and were highly resistant to stress-corrosion in sea water. These alloys consist essentially of, by weight, 5 to 45% nickel, 7 to 16% molybdenum, 13 to 25% chromium, up to 0.05% carbon, up to 2% aluminum, up to 2% zirconium, the sum of aluminum, titanium and zirconium being no greater than 4%, up to 0.5% silicon, up to 6% copper, up to 6% iron, and incidental elements and not exceeding 0.1%, the balance being cobalt in the proportion of at least 25%, the sum of the cobalt and nickel being in the range of 62 to 80% and the sum of the percents of cobalt and nickel divided by the percent chromium being at least 2.6. Preferably the nickel is 5 to 40%, the sum of nickel and cobalt is 65 to 75%, the molybdenum is 8 to 14%, and the chromium is 15 to 22%.

SUMMARY

Now according to the present invention it has been found that within the scope of alloy compositions described in my prior application Ser. No. 637,613 now Pat. No. 3,356,542, there is a limited combination of elements which give novel alloy compositions capable of being work-strengthened to products having an unexpectedly optimum combination of high tensile strength, high yield strength, and ductility. The novel compositions are corrosion resistant. They consist essentially of, by weight, 33 to 37% nickel, 7 to 10.5% molybdenum, 19 to 21% chromium, carbon in a maximum amount of 0.025%, the balance being cobalt in the proportion of at least 33%, the sum of cobalt and nickel being from 66 to 74% and said sum divided by the percent chromium being from 3.1 to 3.9.

In a preferred aspect, alloys of the above-stated composition are work-strengthened to give alloy products which retain their resistance to stress-corrosion in sea water and which consist essentially of a matrix phase having dispersed therein at least 5 volume percent of a platelet phase, said matrix phase being a solid solution of the alloy composition having a face-centered-cubic crystal structure and said platelet phase being a solid solution of the alloy composition having a hexagonal-close-packed crystal structure, the platelets being about from 20 to 1000 A. thick and being distributed substantially on the [111] planes of the matrix phase crystals, said work-strengthened alloy being characterized by having, in a tensile test at 68° F., an ultimate tensile strength of greater than 260,000 p.s.i., a 0.2% yield strength of greater than 240,000 p.s.i., and a ductility, as measured by reduction in area, of greater than 40%.

By working a body of the alloy composition, at a temperature between its melting temperature and the upper temperature of its transformation zone but at least about 1200° F., until its cross-sectional area has been reduced by at least 5%, an intermediate material is obtained which is capable of being work-strengthened. Another intermediate material, similarly work-strengthened but having maximum ductility, is prepared by heat-treating a body of the alloy at a temperature above 1950° F. until it is substantially homogenized, whereby the body has sufficient ductility that its cross-sectional area can be reduced at least 40% at about 68° F. Rather than prepare the intermediate alloy and work-strengthen it, one may work-strengthen a body of the alloy composition directly by working it at a temperature below the upper temperature of its transformation zone until its cross-sectional area has been reduced at least 5%, preferably 10 to 80%.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Novel alloy compositions of the invention can be made by melting the component element metals together at a

suitable temperature, as in the range of 2300 to 3300° F., casting the molten mass and cooling to form a solid-state body. Alternatively, the molten mass can be atomized and a solid-state, consolidated body can be formed by shaping, pressing and sintering the powder so obtained. The body formed by either of these methods can be work-strengthened, by working, at a temperature below the upper temperature of the transformation zone, to at least 5% reduction of cross-sectional area.

The novel products obtained by the work-strengthening processes are alloys consisting essentially of two phases: a matrix phase and at least 5 volume percent and as high as 70 volume percent or higher, preferably 5-50 volume percent, of a second phase of fine platelets, the matrix phase being a solid solution of the alloy components having a face-centered-cubic (fcc) crystal structure, and the platelets being a solid solution of the alloy components having a hexagonal-close-packed (hcp) crystal structure, the platelets being distributed on the [111] planes of the crystals of the matrix phase. The platelets are from three atom layers (approximately 4.15 angstrom units) to 2500 angstrom units thick, preferably 20-1000 angstrom units thick, their width and length being at least 5 times, and as high as 10,000 times, their thickness; and the platelets are separated from one another by a distance of about 100-10,000 angstrom units, but preferably no greater than about 5,000 angstrom units, i.e., one-half micron. Many of the platelets display twinning within their hexagonal-close-packed structure, the principal slip planes of the twins being approximately at right angles to the planes of the untwinned regions.

It is believed that the strain-induced formation of the platelets, induced during the working step, within the face-centered-cubic structure of the metastable matrix phase is responsible for the important improvements in the properties of the products of this invention. Specifically, it has been discovered that within and below a limiting temperature "transformation zone," the face-centered-cubic structure (which exists at temperatures above the zone) can, by the defined working step, be caused to transform into the strength-producing hexagonal-close-packed crystal form.

The products of this invention resulting from this described working step, have unusually high strength properties at room temperature. Specifically, their ultimate tensile strength is at least 260,000 p.s.i. and ranges to about 350,000 p.s.i. Their 0.2% yield strength is greater than 240,000 p.s.i. Their ductility, as defined by reduction in area, is at least 40% and may be as high as 75% or even higher. It should be noted that the strength properties of the products of this invention are from 3 to 4 or more times the strength properties of the alloy material as cast. Furthermore, these products will retain these strength properties to a substantial extent after being subjected to temperatures as high as 1200° F. for 100 hours. Some products within the scope of the claims will substantially retain such properties after 100 hours exposure to temperatures as high as 1400° F.

Products of the invention are extremely useful as fasteners, wire, and cable, and as dies for extruding such metals as aluminum and brass. Specifically, their hot strength and their hot strength retention will permit the extrusion in quantity of red brass, heretofore impossible with conventional hot-worked tool steel dies. Furthermore, these products are sufficiently tough to serve as port or bridge dies for aluminum extrusion where sharp corners and inadequately supported tongues require low notch sensitivity and the ability to deflect without fracturing. The products of this invention, being resistant to thermal stress, oxidation, and certain corrosive media, such as caustic, saline, and acid solutions, are suitable for use as such structural components as holders, backers, extrusion press liners and rams in extrusion; hot forging and coining dies; hot metal shears; hot metal swaging dies; and similar hardware. The intermediate alloy products

hereindescribed, even before work-strengthening, have unique resistance to stress-corrosion, especially in sea water, and are suitable for use in marine hardware.

In the preparation of these products, it is especially convenient to use commercially pure elements. Since only minor changes in the relative proportions of the essential elements will occur during the processing, it is possible to start with amounts of the components that are desired in the final product. Thus, these amounts are melted in a furnace designed for melting alloys in a temperature range of 2300-3300° F. and the resulting molten composition is cast in molds or crucibles of graphite, cast iron, copper or ceramics. The composition may be melt cast in air, vacuum or in an inert atmosphere. Conventional shell and investment molds may be used for casting the shaped objects.

In a specific process, the elemental composition is melted in an open-air induction furnace lined with magnesium oxide or silicon dioxide and is cast into cast iron molds. Initially, the desired amounts of cobalt and nickel are melted, after which the molybdenum and chromium are added. If vacuum melting is used, carbon is preferably employed to deoxidize the molten metal; any silicon which is to act as a deoxidant is added just prior to pouring the alloy composition. The conventional hot-topping compounds may be used to minimize porosity and pipe in the articles cast.

The amounts of chromium, molybdenum and cobalt, are critical in obtaining the desired final product. Thus, if the percentages of cobalt, chromium and/or molybdenum are above the maxima stated, the material will be too brittle to work at temperatures within and below the transformation zone. If the percentages of molybdenum and/or chromium are below the stated minima, the alloy will not respond adequately to the work-strengthening step. In short, to respond to the work-strengthening step and produce the novel end products the alloy must contain the named components in the proportions specified.

It is critically important that the alloy composition contain, even as impurities, no more than 0.05% of boron, oxygen, nitrogen or beryllium, and that the carbon content be below 0.025%, the total of these components being no more than 0.1%. Amounts greater than this, particularly amounts of carbon greater than that specified, will cause such embrittlement as to make the work-strengthening non-operable. It is particularly preferred to maintain the carbon content below 0.015% to insure adequate workability and in an amount effective to provide at least some carbide precipitation upon heat treatment.

In the powder metallurgy method of preparing the consolidated alloy body one first premelts the components together, then converts the resulting alloy to a powder, and finally converts the powder to the desired shaped article. The premelting step may involve arc melting and induction melting. The molten composition can be atomized to form the particulate material. The particle size of the powders can be further reduced by grinding in steel or tungsten carbide-lined equipment. The resulting powders can be readily shaped by cold pressing in steel dies at pressures ranging from about 10 to 50 tons per square inch. It is preferred to sinter the cold-pressed objects at temperatures between 1800° F. and 2500° F. for a period of 15 minutes to six hours in the presence of an inert gas or hydrogen or in a vacuum furnace atmosphere. The powders can also be hot pressed in graphite dies at temperatures between 2000° F. and 2400° F. using pressures of 1000 pounds per square inch or higher.

After the alloy body has been consolidated by casting, pressing or otherwise, the material is work-strengthened. The work-strengthening process involves reducing the cross-sectional area of the article by at least 5%, preferably not more than 90%, more preferably 10% to 80%, at a temperature below the upper temperature of the transformation zone. To reduce the area or to deform the body, any of the conventional metal working techniques

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can be employed. Such techniques include forging, swaging, extruding, rolling, tube reducing, coining, drawing, pressing, explosive treatment, and impact loading. A convenient method of deforming the article is the swaging process. The swaging machine unit may be a two-hammer, 30 horsepower machine with each set of swaging dies producing a 12–20% reduction in area.

Although the work-strengthening step can be performed directly on the article as cast or pressed, it is preferred to at least partially homogenize the cast alloy prior to the work-strengthening step, by heating the shaped article to a temperature which is between the upper temperature of the transformation zone and the melting temperature. This heating step may be accompanied by working the article while it is maintained at a temperature within the aforementioned range by swaging, rolling, forging, extruding, etc. to the extent of reducing its cross-sectional area by at least 5%, preferably 10–80%. The product, after this heating step and prior to the work-strengthening step, is quite ductile, having an elongation of 40–80%. This intermediate heating step makes it easier to attain yield strengths of at least 240,000 p.s.i. (measured at 0.2% offset), and ultimate tensile strength greater than 260,000 p.s.i., after the work-strengthening step.

The "transformation zone" is dependent to some extent on the particular alloy used and ranges from about 850–925° F. minimum to about 1175–1250° F. maximum for alloys of this invention. Therefore, it is apparent that the work-strengthening step, which must be performed below the upper temperature of the transformation zone, preferably below the transformation zone, can safely be performed on the specified compositions at temperatures below 850° F. to achieve the results of this invention. However, higher temperatures that are still below the upper temperature of the transformation zone will permit greater reductions in area for any specified applied force. Hence, it may be desirable to work-strengthen at elevated temperatures. In fact, working can start while the material is at a temperature above the transformation zone and is being permitted to cool, provided at least 5% area reduction occurs while the temperature of the material is below the upper temperature of the transformation zone. It should be understood that it is not always possible to reduce the cross-sectional area up to 90% for all the compositions falling within the specified range at a particular temperature, particularly at the lower temperatures. For the purposes of this invention, work-strengthening to accomplish an area reduction of at least 5% is critical.

As mentioned previously, the final work-strengthened product consists essentially of two phases, an fcc matrix phase and 5–70 volume percent of the second phase of fine hcp platelets, the second phase being distributed on the [111] planes of the crystals of the matrix phase. To determine the presence of these phases, the amounts thereof, and their location, techniques known to metallurgists and described in "Transmission Electron Microscopy of Metals," G. Thomas (1962), John Wiley, New York, may be used.

The presence of hcp phase is detected, for example, by the extremely sensitive techniques of electron transmission microscopy and electron transmission diffraction. These techniques can be used to detect the strain-induced formation in all alloys covered by this invention. Specimens can be electrolytically thinned to permit transmission of the electron beam by the "window method" as described by G. Thomas on pp. 153–155 of his above-identified book or by the "jet cupping" method described by P. R. Strutt.¹

Electron transmission micrographs and electron transmission diffraction patterns were taken of small regions in the center of grains of severely deformed alloys. The electron transmission diffraction patterns consisted of the

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single crystal pattern for the fcc grain plus the single crystal pattern for the hcp platelets on one or more of the four sets of [111] planes of the fcc grain. The diffraction patterns also indicated the presence of mechanical twins within many of the hcp platelets, the principal slip-planes of the twins being approximately at right angles to the principal slip planes of the untwinned regions.

Measurements of the thickness of the hcp platelets and of the average distance of separation between platelets were obtained from the electron transmission micrographs. The volume percent of the hcp phase formed by the strain-induced transformation was determined by areal analysis of the electron transmission micrographs. For example, an alloy containing 34.5% Co, 35% Ni, 20% Cr, 10% Mo, and 0.5% Si was rolled 80% at room temperature. Areal analysis of electron micrographs of a sample from this alloy indicated the presence of approximately 30 volume percent hcp phase. The average thickness of the hcp platelets was 300 angstrom units, and the average distance of separation between platelets was 1400 angstrom units. The work-strengthened plural phase alloys of this invention are found to contain from 5 to 70 volume percent of hcp platelets.

The following illustrative example constitutes a specific embodiment of the processes of this invention and is not intended to be limitative. In this example, various property data are reported. The test methods by which these data are obtained are, unless otherwise stated, the standard ASTM test methods using standard ASTM specimens.

EXAMPLE

A heat of approximately 2,000 pounds was made up having the following chemical composition by weight as determined by ladle analysis: 34.56% nickel, 9.53% molybdenum, 19.7% chromium, 0.04% silicon, 0.018% carbon, balance cobalt plus minor impurities. This heat was vacuum-melted and cast into ingots of varying weights and sizes. One of the ingots, 8" diameter by 320 pounds, was turned to 7.6" diameter by 19" length, canned in a mild steel jacket of 1/8" thickness, and extruded to 1.9" diameter using an ingot preheat temperature of 2300° F. The extruded product was cropped, sandblasted, and pickled to yield sound bar conditioned for swaging.

The bar was swaged to 1.08" diameter with 2-hour anneals at 2,000° F. at 1.45" diameter and 1.08" diameter. The bar was then pointed, lubricated, and drawn 49.5% reduction in area to 0.77" diameter. The resultant bar was aged for 4 hours at 900° F. The tensile and ductility properties were as follows:

282,500 p.s.i. ultimate tensile strength
272,300 p.s.i. 0.2% yield strength
10.4% elongation
48.5% reduction in cross-sectional area.

I claim:

1. In a process for producing an intermediate material capable of being work-strengthened to give a ductile, high-strength alloy, the steps comprising (1) preparing a body of metal consisting essentially of, by weight, 33 to 37 percent nickel, 7 to 10.5 percent molybdenum, 19 to 21 percent chromium, carbon in a maximum amount of 0.025 percent, the balance being cobalt in the proportion of at least 33 percent, the sum of the cobalt and nickel being in the range of 66 to 74 percent and the sum of the percents of cobalt and nickel divided by the percent chromium being from 3.1 to 3.9, and (2) thereafter working said body at a temperature between its melting temperature and the upper temperature of its transformation zone, said temperature being at least about 1175° F. to 1250° F., until its cross-sectional area has been reduced at least 5 percent.

2. In a process for producing an intermediate material capable of being work-strengthened to give a ductile, high-strength alloy, the steps comprising (1) preparing a body of metal consisting essentially of, by weight, 33 to 37

¹ P. R. Strutt, Res. Sci. Inst. 32, 411, 1961.

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percent nickel, 7 to 10.5 percent molybdenum, 19 to 21 percent chromium, carbon in a maximum amount of 0.025 percent, the balance being cobalt in the proportion of at least 33 percent, the sum of the cobalt and nickel being in the range of 66 to 74 percent and the sum of the percents of cobalt and nickel divided by the percent chromium being from 3.1 to 3.9, and (2) heat-treating said body at a temperature above 1950° F. until it is substantially homogenized, whereby the body has sufficient ductility that its cross-sectional area can be reduced at least 40 percent at about 68° F.

3. In a process for producing a work-strengthened alloy, the steps comprising (1) preparing a body of metal consisting essentially of, by weight, 33 to 37 percent nickel, 7 to 10.5 percent molybdenum, 19 to 21 percent chromium, carbon in a maximum amount of 0.025 percent, the balance being cobalt in the proportion of at least 33 percent, the sum of the cobalt and nickel being in the range of 66 to 74 percent and the sum of the percents of cobalt and nickel divided by the percent chromium being from 3.1 to 3.9, and (2) thereafter working said body at a temperature below the upper temperature of its transformation zone until its cross-sectional area has been reduced at least 5 percent.

4. An alloy body consisting essentially of, by weight, 33 to 37 percent nickel, 7 to 10.5 percent molybdenum, 19 to 21 percent chromium, carbon in a maximum amount of 0.025 percent, the balance being cobalt in the proportion of at least 33 percent, the sum of the cobalt and nickel being in the range of 66 to 74 percent and the sum of the percents of cobalt and nickel divided by the percent chromium being from 3.1 to 3.9, said body having been worked at a temperature between its melting temperature and the upper temperature of its transformation zone, said temperature being at least 1175° F., until its cross-sectional area has been reduced by at least 5 percent, and being further characterized by containing substantially no hexagonal close-packed phase.

5. An alloy body as in claim 4, wherein carbon is present in an amount less than 0.015 percent.

6. An alloy body consisting essentially of, by weight, 33 to 37 percent nickel, 7 to 10.5 percent molybdenum, 19 to 21 percent chromium, carbon in a maximum amount of 0.025 percent, the balance being cobalt in the proportion of at least 33 percent, the sum of cobalt and nickel being in the range of 66 to 74 percent and the sum of the percents of cobalt and nickel divided by the percent

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chromium being from 3.1 to 3.9, said body having been heat-treated above 1950° F. until substantially homogeneous, and being characterized by having sufficient ductility that its cross-sectional area can be reduced at least 40 percent at about 68° F., and by containing substantially no hexagonal close-packed phase.

7. An alloy body as in claim 6 wherein carbon is present in an amount less than 0.015 percent.

8. A work-strengthened alloy consisting essentially of a matrix phase having dispersed therein at least 5 volume percent of a platelet phase, said matrix phase having a face-centered-cubic crystal structure and being a solid solution of an alloy consisting essentially of, by weight, 33 to 37 percent nickel, 7 to 10.5 percent molybdenum, 19 to 21 percent chromium, carbon in a maximum amount of 0.025 percent, the balance being cobalt in the proportion of at least 33 percent, the sum of the cobalt and nickel being in the range of 66 to 74 percent and the sum of the percents of cobalt and nickel divided by the percent chromium being from 3.1 to 3.9, said platelet phase being a solid solution of the same alloy composition but having a hexagonal-close-packed crystal structure, the platelets being about from 20 to 1000 A. thick and being distributed substantially on the [111] planes of the matrix-phase crystals, said work-strengthened alloy being characterized by having, in a tensile test at 68° F., an ultimate tensile greater than 260,000 p.s.i., a 0.2 percent yield strength of greater than 240,000 p.s.i., and a ductility, as measured by reduction in area, greater than 40 percent.

9. A work-strengthened alloy as in claim 8 which has been aged at least 0.5 hours at 600° F. to 1200° F.

10. A work-strengthened alloy as in claim 8 wherein carbon is present in said alloy composition in an amount less than 0.015 percent.

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