ABSTRACT OF THE DISCLOSURE

Alloy having as metal components, by weight, 10 to 40% of chromium and/or molybdenum and/or tungsten, the maximum of chromium being 35% and of molybdenum plus tungsten 22%, the balance of the metal components being cobalt and/or nickel in the proportion of at least 60%, the alloy being dispersion-modified with up to 6% by volume of refractory metal oxide particles having an average size less than 100 micrometers, and being characterized by containing a substantial proportion of anisodiametric grains with a length-to-thickness ratio greater than 3.

This invention relates to novel processes for producing alloys of nickel and chromium in which there is dispersed a particulate refractory metal oxide and to the products so produced. More particularly the invention is directed to such processes comprising the steps of forming by powder metallurgy a consolidated body having the chemical composition desired in the final alloy and containing the refractory oxide particles dispersed in the metal components, working said consolidated body at a temperature of up to 1800°F. to densify it substantially to 100% density and to store energy therein sufficient to permit subsequent recrystallization, heat-treating said worked body by heating it to a temperature in the range of 1900 to 2500°F., working the body to at least 50% reduction in cross section area at a temperature in the range from 1300 to 1800°F. The invention is further particularly directed to novel alloy compositions which can be prepared by said processes and which are dispersion-modified alloys comprising, as metallic components, from about 10 to 40% of at least one alloying metal selected from the group consisting of chromium, molybdenum and tungsten, the maximum concentration of chromium being 35 percent, and the maximum concentration of molybdenum plus tungsten being 22 percent, and at least 60 percent of cobalt, nickel, or a mixture of cobalt and nickel, there being pervasively dispersed in said metallic components up to 6 percent by volume of refractory metal oxide particles having an average size less than 100 micrometers, said metal oxide having a free energy of formation at 100°C. greater than 106 kilocalories per gram atom of oxygen, and said alloy, upon metallographic examination, showing a substantial proportion of anisodiametric grains having a length-to-thickness ratio greater than 3 and preferably greater than 10.

In the drawings:
FIGURE 1 is a line drawing of a photomicrograph at 500 times magnification of the product of Example 1, and
FIGURE 2 is a line drawing of a photomicrograph at 100 times magnification of the product of Example 2.

The lines in both of these figures represent grain boundaries, although some of the lines in FIGURE 1 are twin boundaries.

In United States Patent 2,972,529, there has been described certain novel compositions and processes for making them, the compositions comprising a chromium alloy of iron, cobalt or nickel dispersion-hardened with a particulate refractory metal oxide of high free energy of formation. This patent describes the preparation of these compositions in powder form and the consolidation of such powders to useful solid metallic bodies by such processes as hot extrusion, swaging or forging. The products obtained are described as fine grained, the grain size being less than 10 microns, and the grains are substantially isodiametric—that is, being substantially equiaxial. These are strong, useful compositions and alloys. It has now been found, however, that by the processes of the present invention stronger, more creep-resistant, more ductile products can be produced than those described in the prior patent.

In U.S. Patent 3,159,908, there has been described processes for working oxide-dispersion-hardened metals at low temperatures, i.e., below half of the absolute melting point of the metal, in which case nickel base alloys is below about 1100°F.

It has now been found that, in the case of chromium-containing alloys, highest strength properties are obtained when the dispersion-modified alloy has undergone a particular heat treating and working sequence, namely, the dispersion-modified alloy powder is consolidated in such a manner as to leave stored energy in the body, and thereafter, this material is heated to the range of 2100 to 2500°F. and worked to at least 50 percent reduction in the temperature range of 1300 to 2200°F.

The powder used in the processes of the invention is broadly described in U.S. 2,972,529. Preferred powders are prepared as follows: nickel oxide-chromium oxide-thoria is prepared from the respective nitrates by co-precipitation with (NH₄)₂CO₃ in aqueous solutions. The oxide is dried at 300°C., blended with low sulfur for the present invention stronger, more creep-resistant, more ductile products can be produced than those described in the prior patent. The resulting powder is consolidated by powder metallurgy, for example by compacting, sintering in hydrogen at 900-1000°C., and extruding to a bar at about 1000°C. This consolidates the powder to a metallurgical workpiece of greater than 99% of theoretical density.

The solid metal product is heated until it recrystallizes. As-extruded the bar consists of a fine grained material. On heating to a temperature in the range of 1900 to 2500°F., the grains grow, the resulting grains being anisodiametric and elongated in the direction of working.

The product after extrusion is also warm-worked. The term "work" generically is defined as being a process for reducing bar diameters, such as bar-rolling, swaging, drawing, forging, and other similar, conventional metalurgical processes. Warm-working temperatures are in the range of 1300 to 1800°F., work can be to at least 50 percent reduction in area.

It will be understood that the above-described recrystallization heating and warm-working steps can be carried out in either order. In one specific aspect of the invention the consolidated piece is warm-worked and then heat treated. In this sequence, the optimum working temperature is about 1500°F. and must be in the range 1300 to 1800°F. In another specific, preferred aspect, the consolidated, warm-worked piece is heat-treated and thereafter hot-worked. In this case the hot-working temperature should be in the range 1800-2200°F. Working can be done in air, as can heat treating. The material is so oxidation-resistant that scale formation is negligible. In a further specific aspect the consolidated piece is first
heat-treated to effect recrystallization and is thereafter work-hardened. The products of invention are essentially nickel or cobalt base alloys, containing at least 60 percent by weight of these elements. They contain about from 10 to 40 percent of at least one alloying metal selected from the group consisting of chromium, molybdenum and tungsten, the maximum concentration of chromium being 35 percent, and the maximum concentration of molybdenum plus tungsten being 22 percent. Said alloys optionally may contain minor amounts of other metals such as up to 15 percent manganese, and up to 20 percent iron. They can also contain up to 1 percent of zirconium, hafnium or magnesium.

Preparations of the invention contain dispersed refractory oxides, the average diameter of which is less than 100 millimicrons and preferably less than 30 millimicrons. Such oxides must have a free energy of formation at 1000°C above 106 kilocalories per gram atom of oxygen in the oxide. Typical of such oxides are Y₂O₃, CaO, LaO, ThO₂, BeO, and MgO. The proportion of refractory oxide can be up to 6 percent by volume, 0.1 to 3 percent being a preferred range.

The particle diameter of the refractory oxide filler particles can be calculated from a measurement of their surface area. The metal component of a powder product of the invention is dissolved in an acid, or in bromine-methanol, leaving the filler oxide particles, which are recovered by coagulating, centrifuging, washing and drying.

The Br₂-CH₃OH extraction procedure is as follows: Calculate the weight of metal for extraction required to give approximately 0.2 gm. ThO₂ residue. Thus, 10 gm. of a metal containing 2 percent ThO₂ are required. For each 10 gram portion of metal, prepare 500 ml. of solution containing 5.3 percent Br₂ by volume in dry methanol. Subdivide the metal. If dense, machine to chips. Add the metal slowly with stirring to the Br₂-CH₃OH solution. Place the solution in a water bath, and cool during the extraction. (Temperature should be <35°C.) Avoid frothing caused by excessive gas evolution. After all the metal is added, remove the solution from the water bath, and allow to stand 24 hours with occasional stirring. Allow the residue to settle. Carefully decant the clear supernatant. Centrifuge the remaining residue. Wash and centrifuge the solid residue repeatedly with dry methanol until the supernatant liquor is colorless. Retain all decants and washings for 24 hours to see if additional residue settles out. If so, repeat the centrifuging and washing procedure so as to include this material with the original residue. If, during washing, the ThO₂ residue begins to peptize, float the material by adding 2 to 3 drops of concentrated HNO₃, then continue centrifuging. Dry the final, washed residue and weigh.

The surface area of the recovered oxide from the above-described process is then measured by the conventional BET method or its equivalent. (P. H. Emmett in “Symposium on New Methods for Particle Size Determination in the Subsieve Range,” Philadelphia: ASTM, 1941, p. 95.) From this surface area measurement, the mean particle diameter, D, is calculated from the expression:

$$D = \frac{6000}{f \sqrt{A_t}}$$

where \(f\) is the absolute density of the filler oxide particles in grams per milliliter and \(A_t\) is their surface area in square meters per gram.

The grains in the products of invention are anisometric. At least 25 percent of the grain structure consists of grains which have a length-to-thickness ratio greater than about 3:1. Preferably up to 60 percent or more of the grains are in this category, i.e., having a length-to-thickness ratio above 3. The length-to-thickness ratio of the grains is greater than 3 and preferably greater than 10. In the most preferred instances the ratio can be up to 25 or even greater. It will be evident that these grains can be in the form of needles or platelets and as observed in the metallographic examination this will depend on whether viewed in the longitudinal or transverse direction. This can be determined by viewing the product in both the longitudinal and transverse direction.

It has been noticed in particular that some of the grains have sharp apexes at the ends—that is the grains seem to be pointed when viewed in a longitudinal direction. This seems to be associated with good strength of the product.

When a product is referred to as "strong" in this application this refers to the 2000° F. properties of tensile strength and stress rupture. In particular, a stress-rupture life in excess of 20 hours at 6 K. s. i. at 2000° F. is strong.

Preferred limits on products of the invention are:

1. Excess oxygen—less than 100 p.p.m.—most preferred under 200 p.p.m.
2. Carbon less than 100 p.p.m. Present as incidental impurities.
3. Sulfur less than 50 p.p.m.
4. Nitrogen less than 200 p.p.m.

The invention will be better understood by reference to the following illustrative examples:

**Example 1**

A coprecipitated nickel oxide-chromium oxide-thoria gel was prepared by intensively mixing separate aqueous solutions made by (a) dissolving 600 lb. of ammonium hydroxide containing 28.0 percent free ammonia, and (b) dissolving 800 lb. of Ni(NO₃)₂·6H₂O in 420 lb. of water. The solutions were mixed in a tank initially charged with about 6 gallons of liquor from the filtration of a previously prepared gel, the rates of addition being controlled so as to maintain the pH of the solution in the tank at about 7.0 and to complete the additions in 3½ hours.

The precipitate was filtered, washed with water, and dried at about 110°C. for 16 hours. The temperature was then increased to 450°C., for 4 hours to remove residual nitrates and carbonate and convert the product entirely to an oxide mixture. The dried product was pulv erized in a hammer-mill.

A portion of the oxide product was blended with 12 parts carbon black per 100 parts oxide and the blended mixture was heated to about 425°C. for about 4 hours with hydrogen gas passing over it. The hydrogen gas has previously been carefully freed of oxygen, sulfur, nitrogen, and moisture. The hydrogen flow was then replaced with argon at a flow rate of about 5 linear feet per minute. The temperature was raised to about 975°C., argon was replaced with hydrogen, and the temperature was held at 975°C. for 20 hours. The temperature was then raised to 1100°C., where it was held for 5 hours after which time the furnace was cooled to 925°C. under hydrogen for 30 hours to remove the excess carbon as methane and then to room temperature. The sintered product was recovered, ground, and passed through a 60-mesh screen.

The product thus obtained was a fine powder containing thoria at a volume loading of 2 percent uniformly dispersed in an alloy matrix of nickel and chromium combined in the ratio of 80 percent Ni-20 percent Cr by weight. Oxygen analyses of the reduced material showed that there was less than 0.01 percent oxygen present in excess of the oxygen in the ThO₂, and the residual carbon analysis was 151 parts per million. Sulfur was 30 p.p.m. ThO₂ size by X-ray line broadening was 50 mₜ, and the BET method was 35 mₜ.

The Ni-Cr-ThO₂ powder so produced was compacted hydrostatically at 60,000 p.s.i., the compacted billet ma-
chined to 5.57" diameter by about 8" long, canned, and thereafter treated with pure dry hydrogen at 1700° F. It was then extruded at 1700° F. at 10:1 ratio to a bar. Analytical data on this bar were: Nitrogen 215 p.p.m., sulfur 31 p.p.m., carbon 170 p.p.m., chromium 20.4 percent, iron less than 100 p.p.m., ThO₂ size (by bromine-methanol extraction and surface area) 30 millimicrons.

A piece of this bar was heat treated at 2100° F. for one hour, whereupon it recrystallized. The recrystallized bar was swaged at 1800° F. from 1.5 to 1.0 inches diameter. This bar is an example of the products of the invention.

The appearance of the microstructure of this swaged bar remained unchanged after heating to 2400° F. for one hour. X-ray back reflection patterns confirmed that the as-swaged bar was cold-worked and that this cold-work was retained after the heating at 2400° F. The 2000° F. strength properties were identical in the as-swaged and one hour/2400° F. heat treated pieces. These were: U.T.S.—17,000 p.s.i., 0.2 percent Y.S.—16,000 p.s.i., elongation 15 percent, reduction in area 13 percent. Stress rupture at 2000° F. on a bar step-loaded from 6,000 p.s.i. was greater than 90 hours at 11,000 p.s.i.

The microstructure of this bar consisted of a mixture of various types of grains. A striking feature was the presence of many extremely thin needle-like grains typically .025 mm. long by .001 mm.

The indenter test on a longitudinal section from this bar showed a cubic impression, i.e., a square shaped impression with sides parallel and perpendicular to the bar axis. This was identical in as-swaged or in one hour/2400° F. heat treated bar.

Example 2

Another bar was made from the extrusion in Example 1 as follows: The 1.5" bar was swaged 1500° F. to 0.5" diameter. This was accomplished in 5 passes with 10 minute re heats between passes. The .5" diameter bar was recrystallized by a one hour/2400° F./air heat treatment.

Tensile properties of the recrystallized bar at 2000° F. were:

U.T.S. 14.0–17.5
0.2% Y.S. 14.0–17.5
Elongation – percent 7
R.A. do 3

A 2000° F. stress-rupture test was carried out on the same material, it was loaded at 6 K s.i. (6,000 p.s.i.) for 20 hours, then step-loaded to 16 K s.i. where failure occurred after a total time of 49 hours. The room temperature hardness of the recrystallized bar was R₆₉ 24. Microstructural features of this bar were:

1. Most of the structure consisted of very elongated grains 0.10–0.25 mm. wide. L/W ratio of these grains was up to 20. L/W of 10 was common.
2. The elongated grains tended to have sharper apaxes and had less serrated grain-boundaries than in weaker material.
3. There was preferred orientation in the structure as indicated by the R₆₉ indenter test. This round indenter gave a square shaped impression in a longitudinal section. The diagonal of the square is oriented parallel to the bar axis.

Example 3

This example is like the previous examples except as hereafter noted:

A rod was prepared from a powder composition like that of Example 1, containing 30 ma thorium, by compacting the powder, sintering, extruding 8:1 at 1700° F. and then swaging about 70 percent reduction in area in approximately 12 percent steps heating before each pass to 1600° F ± 100° F. The resultant rod was exposed to 2000° F. and recrystallized to coarse grains. The grains were anisodiametric, and about 20 to 200 microns in length.

Example 4

A thoriated nickel 15 percent chromium, 11 percent molybdenum alloy powder was prepared by a process similar to that used in Example 1. More specifically, a nickel-chromium hydroxycarbonate-thoria coprecipitate was prepared. The precipitate was separated by filtration and was washed with water. The precipitate was then slurried in water, and a solution of ammonium molybdate was added. Most of the molybdate absorbed onto the precipitate which was then recovered by filtration. The filter cake was dried and the nickel-chromium and molybdate values were reduced to metal by a procedure similar to that in Example 1. The chemical composition of the thoriated nickel-chromium-molybdenum alloy powder was, by weight: 4.52% ThO₂, 11.16% Mo, 15.2% Cr, 0.0046% C, balance Ni. Three-tenths percent by weight of zirconium hydride powder having an average particle size less than 10 microns was cone-blended for 2 hours with the minus 200 mesh fraction of the thoriated alloy powder.

A billet was prepared by hydrostatically compacting the resulting powder blend at 60,000 p.s.i. The billet was machined to a right circular cylinder and was welded into a mild steel containing entrance and exit tubes for passing hydrogen through the billet and for evacuation. The canned billet was evacuated at room temperature to a pressure of less than about 50 microns and back-filled with pure, dry hydrogen. The billet was heated slowly to 580° F. under a flow of about 7 cubic feet per hour of said hydrogen. After about 16 hours at 380° F. the temperature was increased to 680° F., held there for about 1½ hours, raised to 930° F. for 1 hour, and finally raised to 1700° F. After about 2 hours at 1700° F., hydrogen flow was terminated, and the canned billet was evacuated at temperature. After about 2 hours at temperature under vacuum an ultimate pressure of about 10 microns was attained.

The canned billet was then cooled to ambient temperature under vacuum, and the exit and entrance tubes were forge-welded shut. The canned billet was extruded at 1700° F. to a reduction ratio of 8:1. After extrusion the mild steel can was removed by pickling.

The thoriated nickel-chromium-molybdenum alloy bar was then canned in stainless steel tubing, heated to 1500° F., and swaged, with reheating after each pass, to a reduction of 67.8 percent in cross-sectional area. After swaging the stainless steel can was removed by pickling. Hardness of the swaged bar was approximately 484 D.P.H.

The swaged bar was annealed at 2200° F. for 2 hours. Hardness of the annealed bar was about 377 Diamond Pyramid Hardness. Metallographic examination of the annealed bar revealed a relatively uniform, recrystallized grain structure, a substantial portion of the structure being composed of anisodiametric grains having a length/thickness ratio greater than about 5.

Stress rupture properties of samples cut from the annealed bar were:

<table>
<thead>
<tr>
<th>Test Temperature, °F</th>
<th>Stress, p.s.i.</th>
<th>Life, hrs.</th>
<th>Elongation, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,400</td>
<td>35,000</td>
<td>6.6</td>
<td>2.0</td>
</tr>
<tr>
<td>1,400</td>
<td>30,000</td>
<td>9.2</td>
<td>6.0</td>
</tr>
<tr>
<td>2,000</td>
<td>10,000</td>
<td>2.7</td>
<td>2.0</td>
</tr>
<tr>
<td>2,000</td>
<td>5,000</td>
<td>26.7</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Example 5

A thoriated nickel-19 percent chromium-6 percent molybdenum alloy powder was prepared by a process similar to that used in Example 4. The chemical composition of the thoriated nickel-chromium-molybdenum alloy powder
was, by weight: 4.88% ThO₂, 5.90% Mo, 19.34% Cr, balance Ni. Three-tenths percent by weight of zirconium hydride powder having an average particle size less than 10 microns, was const-bled for 2 hours with the minus 200 mesh fraction of the thoriated alloy powder.

A billet was prepared by hydrostatically compacting the resulting powder blend at 60,000 p.s.i. The billet was machined to a right circular cylinder and was welded into a mild steel can containing entrance and exit tubes for passing hydrogen over the billet and for evacuation. The canned billet was evacuated at room temperature to a pressure of less than about 50 microns and back-filled with pure, dry hydrogen. The billet was heated slowly to 525° F., under a flow of about 7 cubic feet per hour of said hydrogen. After about 9½ hours at 525° F., the temperature was increased to 700° F., held there for about 2 hours, raised to 815° F. and finally to 1625° F. After 1¾ hours at 1625° F., hydrogen flow was terminated, and the canned billet was evacuated at temperature. After about 8 hours at temperature under vacuum an ultimate pressure of about 75 microns was attained.

The canned billet was then cooled to ambient temperature under vacuum, and the exit and entrance tubes were forge-welded shut. The canned billet was extruded at 1700° F. to a reduction ratio of 8:1. After extrusion the mild steel can was removed by pickling.

The thoriated nickel-chromium-molybdenum alloy bar was then canned in stainless steel tubing, heated to 1500° F. and swaged, with reheating after each pass, to a reduction of 64.3 percent in cross-sectional area. After swaging the stainless steel can was removed by pickling. Hardness of the swaged bar was approximately 451 D.P.H.

The swaged bar was annealed at 2200° F. for 2 hours. Hardness of the annealed bar was about 380 Diamond Pyramid Hardness. Metallographic examination of the annealed bar revealed a relatively uniform, recrystallized grain structure, a substantial portion of the structure being composed of anisodiamic grains having a length/thickness ratio greater than about 5.

Stress rupture properties of samples cut from the annealed bar were:

<table>
<thead>
<tr>
<th>Test Temperature, ° F.</th>
<th>Stress, p.s.i.</th>
<th>Life, hrs.</th>
<th>Elongation, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,400</td>
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<td>22.4</td>
<td>4</td>
</tr>
<tr>
<td>1,400</td>
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<td>47.1</td>
<td>2</td>
</tr>
<tr>
<td>2,000</td>
<td>10,000</td>
<td>204.5</td>
<td>2</td>
</tr>
<tr>
<td>1,400</td>
<td>11,000</td>
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</tr>
<tr>
<td>1,400</td>
<td>13,000</td>
<td>24.3</td>
<td>6.0</td>
</tr>
</tbody>
</table>

We claim:

1. A dispersion-modified sintered alloy consisting essentially of metallic components, by weight, about from 10 to 40 percent of at least one alloying metal selected from the group consisting of chromium, molybdenum and tungsten, the maximum concentration of molybdenum being 35 percent, and the maximum concentration of molybdenum plus tungsten being 22 percent, up to 15 percent manganese, up to 20 percent iron, and up to 1 percent of a metal selected from the group consisting of zirconium, hafnium and magnesium, the balance of metallic components being substantially all cobalt, nickel or a mixture of cobalt and nickel, in the proportion of at least 60 percent, there being pervasively dispersed in said metallic components up to 6 percent by volume of refractory metal oxide particles having an average size less than 100 micrometers, said metal oxide having a free energy of formation at 100° C. greater than 106 kilocalories per gram atom of oxygen, and said alloy containing a substantial proportion of anisodiamic grains having a length-to-thickness ratio greater than about 3.

2. A dispersion-modified sintered alloy consisting essentially of metallic components, by weight, about from 10 to 40 percent of at least one alloying metal selected from the group consisting of chromium, molybdenum and tungsten, the maximum concentration of chromium being 35 percent, and the maximum concentration of molybdenum plus tungsten being 22 percent, up to 15 percent manganese, up to 20 percent iron, and up to 1 percent of a metal selected from the group consisting of zirconium, hafnium and magnesium, the balance of metallic components being substantially all cobalt, nickel, or a mixture of cobalt and nickel, in the proportion of at least 60 percent, there being pervasively dispersed in said metallic components up to 6 percent by volume of refractory metal oxide particles having an average size less than 100 micrometers, said metal oxide having a free energy of formation at 100° C. greater than 106 kilocalories per gram atom of oxygen, and said alloy containing a substantial proportion of anisodiamic grains having a length-to-thickness ratio greater than about 5.

3. A composition of claim 2 in which the metallic components consist essentially of about from 10 to 25 percent by weight of chromium and the balance substantially nickel.

4. A composition of claim 2 in the form of a bar in which the metallic components consist essentially of 20 percent by weight of chromium and the balance substantially nickel.

5. A composition of claim 2 in which the length-to-thickness ratio is greater than 10.

6. A composition of claim 2 having a recrystallized structure.

7. A composition of claim 2 having a stable, cold-worked structure.

8. A composition of claim 2 in which the metallic components consist essentially of, by weight, about 14 to 25 percent of chromium, 5 to 12 percent of molybdenum, 0.1 to 0.4 percent of zirconium and the balance substantially nickel, at least 0.04 percent, based on the total composition of said zirconium being present in solid solution and nickel-zirconium type intermetallic compounds.

References Cited

UNITED STATES PATENTS

2,972,529 2/1961 Alexander.
3,026,200 3/1962 Gregory ---- 75—206 X
3,087,234 4/1963 Alexander ---- 75—164 X
3,152,399 7/1964 Alexander ---- 75—206 X
3,166,416 1/1965 Worn ---- 29—182.5 X

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