TRANSFORMATION ZONE VS. PER CENT
COBALT IN ALLOY OF 10% Mo, 20% Cr,
0.5% Si, BALANCE Ni
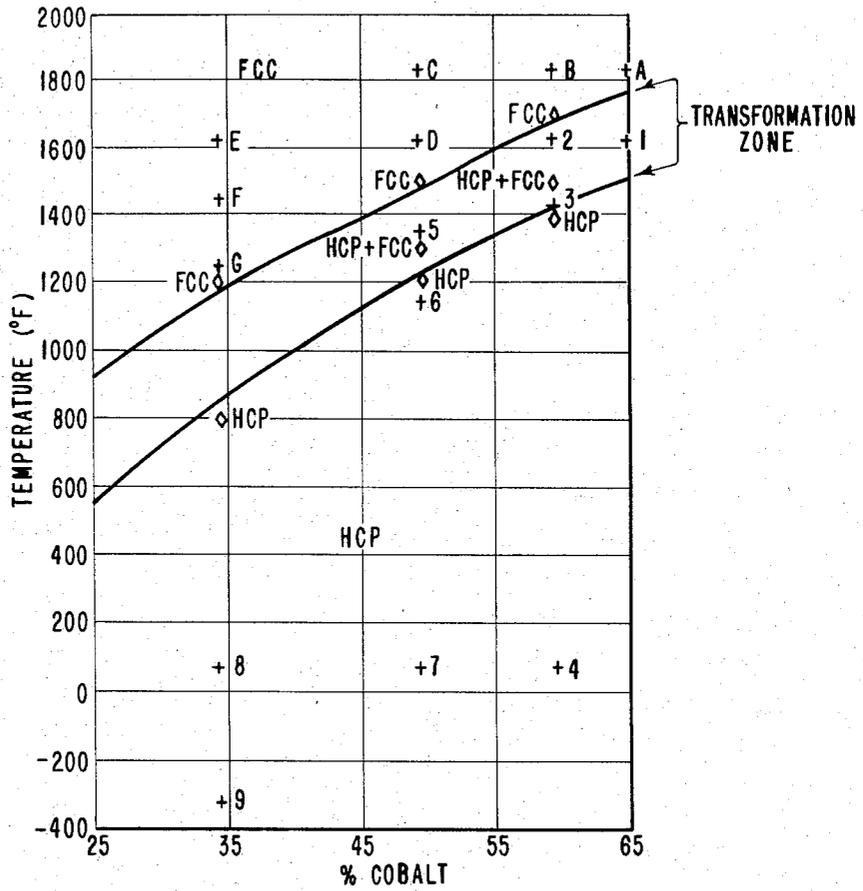
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ABSTRACT OF THE DISCLOSURE

Corrosion-resistant alloys which can be work-strengthened to have very high ultimate tensile and yield strengths, the alloys containing as essential elements, by weight, 5 to 45% nickel, 7 to 16% molybdenum, 13 to 25% chromium, and optionally minor amounts of other specified elements, the balance being cobalt in the proportion of at least 25%, the sum of cobalt and nickel being 62 to 80% and said sum divided by the percent chromium being at least 2.6.

Cross references to related applications

This application is a continuation-in-part of my copending application Ser. No. 584,029 filed Aug. 18, 1966, now abandoned, and is also a continuation-in-part of my copending application Ser. No. 565,088, filed July 14, 1966, now abandoned, both of said prior applications being 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.

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.

Cobalt- and nickel-base alloys heretofore available have 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 has not been evident how such brittleness could be avoided while retaining very high or enhanced strengths.

There has also been a need for ductile, strong alloys of the type just described which, additionally, have 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.

Summary

Now according to the present invention the above-discussed problems of the prior art are solved by the herein-described novel alloys which in their broadest aspects are strong and adequately ductile, and are highly resist-

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ant 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. Preferable 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%.

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 160,000 p.s.i. and ductility, as measured by reduction in area, of greater than 3%.

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 925° 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-strengthenable 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%.

Brief description of the drawing

FIGURE 1 of the drawing is a graphic representation of the transformation zone, between the face-centered cubic (FCC) crystal system and the hexagonal-close-packed (HCP) crystal system, for an alloy composition of the invention containing 10% molybdenum, 20% chromium, 0.5% Si, the balance being nickel except for the cobalt, the percentage of which is plotted vs. the temperature in ° F. The "transformation zone," as used herein, refers to a zone of temperature above which a face-centered-cubic crystal form of the cobalt-base alloy is stable and below the upper temperature of which the face-centered cubic form, under strain, transforms into the hexagonal-close-packed form. For the alloys of FIG. 1 the upper limit of the transformation zone ranges from about 925° F. for 25% cobalt, to about 1750° F. for 65% cobalt, and the lower limit ranges from about 550° F. for

25% cobalt to about 1500° F. for 65% cobalt. A method by which this zone may be determined is described hereinbelow.

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 160,000 p.s.i. and ranges to about 350,000 p.s.i. Their ductility, as defined by reduction in area, is at least 3% 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. Any other alloy additions can also be made at this time. Thus, calcium-silicon, ferro-silicon, or ferro-manganese may be added to deoxidize the alloy or the conventional hot-topping compounds may be used to minimize porosity and pipe in the articles cast. The molybdenum and chromium may be added in the form of ferro-molybdenum and ferro-chromium alloys; however, the total iron, which can substitute for part of the required nickel or cobalt, should not exceed 6%. More than 6% iron results in serious reduction in product properties, particularly stress-rupture properties and aqueous acid corrosion resistance.

As disclosed hereinabove, the percentages of components in the final composition should be as follows: 5–45% nickel, 7–16% molybdenum, 13–25% chromium and at least 25% cobalt. If silicon is used, the amount remaining after deoxidizing must be no more than 0.5%. In the preferred composition, the amount of silicon remaining after deoxidation should be no more than 0.1%. 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 and products the alloy must contain, as principal components, 7–16% molybdenum, 13–25% chromium, the remainder being essentially cobalt and nickel with the cobalt being no greater than 75%, preferably less than 60%. The percentages of nickel, cobalt and chromium are so interrelated that the sum of the percent nickel and percent cobalt when divided by the percent chromium is a number greater than 2.6. However, this number may be as low as 2.5 when aluminum, titanium, zirconium, and/or iron are present.

It is critically important that the alloy composition contain no more than 0.05% of carbon, boron, oxygen, nitrogen or beryllium, 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

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to maintain the carbon content below 0.015% to insure adequate workability.

The presence of aluminum, titanium and zirconium should be limited to no more than 2% each and to a total of no more than 4%. The presence of these elements up to the specified limits may impart some additional strengthening; amounts above those specified will not only affect the properties of the final product adversely, but may lower processability through such mechanisms as interstitial embrittlement and grain boundary second phase formation.

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 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 200,000 p.s.i. (measured at 0.2% offset), and ultimate tensile strength greater than 220,000 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 575° F. to about 1750° F. 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 575° 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

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elevated temperatures. In fact, working can start while the material is at a temperature above the transformation zone and is being permmitted 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.

The data used in plotting the points in the transformation zone of FIGURE 1 are shown in Table A, hereinbelow. These alloys were treated in accordance with the procedure described for Examples 1–3. Specifically, the transformation zone was determined by an X-ray diffraction technique. Alloys were severely deformed at 70° F. and then heat-treated at temperatures ranging from 700 to 1900° F. for times ranging from 24 to 100 hours. X-ray diffractometer patterns were taken with filtered CrK_a raditation before and after each heat treatment. The ratio (I_r) of the intensity of the (101) HCP peak to the (200) FCC peak was determined from the diffractometer patterns. An increase in the ratio I_r is indicative of growth of the HCP phase at the expense of the FCC phase; whereas a decrease in the ratio I_r is indicative of growth of the FCC phase at the expense of the HCP phase. Where the letters (HCP) appear near a point in FIGURE 1 for a particular alloy they signify that the intensity ratio increases during heat treatment at the indicated temperature (i.e., the HCP phase is the stable phase). Where the letters (FCC) appear near a point for a particular alloy they signify that the intensity ratio approaches zero during heat treatment at the indicated temperature (i.e., the FCC phase is the stable phase). The letters (HCP+FCC) near a point indicate that the intensity ratio remains essentially constant during heat treatment (i.e., both the FCC phase and the HCP phase are stable).

The data in Table A show that the yield strength of alloys worked at temperatures in the vicinity of or below the transformation zone is increased to above 160,000 p.s.i., which is approximately four times the yield strength of as-cast alloys. The coded data points in Table A are plotted at their respective deformation temperatures on FIGURE 1. In controlled working experiments at elevated temperatures, the temperature of bars with an initial diameter of 0.4 inch was measured before and after swaging. The deformation temperature (Td) is defined as the arithmetic mean of the temperature before swaging and the temperature after swaging.

TABLE A

Point	Percent Co	Deformation Temp. (° F.)	Percent Deformation	0.2% Yield Strength (× 10³ p.s.i.)
A	65.0	1,825	60	106
1	65.0	1,625	60	193
B	59.5	1,825	60	76
2	59.5	1,625	60	192
3	59.5	1,425	20	193
4	59.5	70	40	268
C	49.5	1,825	60	76
D	49.5	1,625	60	158
5	49.5	1,350	40	190
6	49.5	1,175	40	224
7	49.5	70	40	254
E	34.5	1,625	60	118
F	34.5	1,450	60	138
G	34.5	1,250	60	136
8	34.5	70	60	221
9	34.5	−320	60	255

As mentioned previously, the final 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. Thus, one may use conventional analysis of X-ray diffraction patterns with alloys containing no more than about 20% nickel or electron micrography coupled with electron diffraction on the same samples, the samples having been electrolytically thinned to permit transmission of the electron beam through the samples.

Specifically, for alloys containing more than about 45% cobalt, the strain-induced formation of HCP platelets at room temperature can be monitored by conventional X-ray diffraction techniques. The ratio (I_r) of the intensity of the (101) HCP diffraction peak to that of the (200) FCC diffraction peak is a quantitative indication of the amount of HCP phase formed in a deformed alloy. The data in Table B show that the increase in a 0.2% yield strength of an alloy during deformation at room temperature is accompanied by an abrupt increase in the amount of HCP phase formed as measured by the intensity ratio (I_r). The intensities used to calculate the values for I_r reported in Table B were measured on X-ray diffractometer patterns taken with filtered CrK_a radiation.

For alloys with less than about 45% cobalt, the presence of HCP phase is detected 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 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 mechanical properties of the bulk specimen were as follows:

Ultimate tensile strength _____p.s.i__ 250,000
0.2% yield strength _____p.s.i__ 227,000
Reduction in area _____percent__ 57
Elongation _____do____ 7.7

The work-strengthened multiphase alloys of this invention are found to contain from 5 to 70 volume percent of HCP platelets.

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

TABLE B.—CORRELATION OF WORK STRENGTHENING WITH STRAIN-INDUCED FORMATION OF HCP-PHASE BY DEFORMATION AT 70° F.

[Alloy composition: 49.5% Co, 20% Ni, 20% Cr, 10% Mo, 0.5% Si; history prior to deformation at 70° F.: Swaged 60% at 1,625° F.]

Percent Deformation by Swaging at 70° F.	0.2% Yield Strength (K s.i.)	Intensity Ratio $I_{(101)}$ HCP/$I_{(200)}$FCC
0	158	<0.02
15	191	0.15
22	224	0.30
37	246	0.50

The following illustrative examples constitute specific embodiments of the process of this invention and are not intended to be limitative. In these examples, 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 1

A 55 pound heat of 49.5% Co, 10% Mo, 20% Cr, 0.5% Si, 20% Ni is air melted in a carbon arc furnace (silica liner) and poured into a cast iron mold (4" square) at the top tapering to 2½" square at the bottom (9" length) which has a sand riser of approximately 4" height. The cobalt and nickel are initially melted and the chromium, molybdenum, one-half of the silicon, and 1½ ounces each of ferro-manganese, and ferro-silicon are added. The final percentage of silicon is added just prior to pouring the metal directly into the mold. Pouring temperature is 2980° F. Chemical analysis shows the Co, Ni, Mo, and Cr to be within 2% of the amount added. The final silicon content is 0.3%. The ingot is sufficiently cool to remove from the mold in one-half hour, after which it is water quenched.

An extrusion billet (2" diameter x 4.5" long) is machined from the bottom of the ingot, using conventional carbide tooling for interrupted cutting, and extruded in a 360 ton press using a billet temperature of 2300° F. and an 8 to 1 reduction ratio. Quartz glass is used as the extrusion lubricant. The extrusion is further homogenized by heat treating for approximately one hour at 2200° F. At the end of the heat treating period the rod is deformed 60% by swaging. The swaging unit is a two-hammer, 30 horsepower machine. The deformed rod is water quenched after the final pass through the swaging machine. Grain size of the homogenized rod is found to be within the ASTM (grain size measurement) numbers 10 to 8.

Work-strengthening is then accomplished by heating ground, six-inch long rods (diameter from 0.500" to 0.875") to the temperature set forth in Table I in an electric furnace, followed by swaging. Each set of swaging dies permits 12% to 20% reduction in area. During die changes, the rod is placed in the furnace. The rod is water quenched to room temperature after the final reduction.

The rod is then cut and ground into tensile test specimens, and 0.2% yield strength, ultimate tensile strength, and reduction in area data obtained. The resulting room temperature properties and the amounts of deformation at various deformation temperatures compared to the properties of the as-cast material and the properties of specimens worked at a temperature above the transformation zone are presented in Table I. It should be noted that the specimens prior to work-strengthening display elongations of 40 to 80% at room temperature.

Example 2

The procedure of Example 1 is repeated using a 55 pound heat of 34.5% Co, 10% Mo, 20% Cr, 0.5% Si and 35% Ni. The resulting data are presented in Table II.

Example 3

The procedure of Example 1 is repeated using a 55 pound heat of 59.5% Co, 10% Mo, 20% Cr, 0.5% Si and 10% Ni. The resulting data are presented in Table III.

TABLE I

[Alloy composition: 49.5 Co, 10 Mo, 20 Cr, 0.5 Si, 20 Ni]

Deformation Temperature [1] and Percent Deformation	0.2% Yield Strength ($\times 10^3$ p.s.i.)	Ultimate Tensile Strength ($\times 10^3$ p.s.i.)	Reduction in Area (Percent)
As-Cast [2]	45	74	34
70° F.:			
10%	172	197	28
20%	214	244	29
40%	254	281	13
60%	269	346	8
1,000° F. (1,200):			
20%	167	191	36
40%	218	236	10
46%	224	255	16
1,175° F. (1,400):			
20%	164	186	36 [3]
40%	224	237	16 [3]
52%	222	249	16 [3]
1,350° F. (1,600):			
20%	176	200	24 [3]
40%	190	224	10 [3]
60%	191	204	14 [3]
1,450° F. (1,750):			
10%	163	180	25
20%	198	208	24
40%	184	202	21
60% [2]	216	229	41
80%	242	259	15
1,625° F. (1,950): 60%	158	189	26
1,825° F. [4] (2,200): 60%	76	152	54

[1] Number in parentheses is temperature (° F.) prior to deformation.
[2] Heat-treated at 2,200° F. for one hour and water-quenched.
[3] Also heat-treated at 800° F. for three hours.
[4] Above the transformation zone.

TABLE II

[Alloy composition: 34.5 Co, 10 Mo, 20 Cr, 0.5 Si, 35 Ni]

Deformation Temperature [1] and Percent Deformation	0.2% Yield Strength ($\times 10^3$ p.s.i.)	Ultimate Tensile Strength ($\times 10^3$ p.s.i.)	Reduction in Area (Percent)
As-Cast	39	94	61
−320° F.:			
40%	238	250	28
60%	255	268	31
80%	264	290	4
70° F.:			
10%	160	170	18
32%	170	196	30
40%	197	211	44
60%	221	239	40
75%	220	240	40
80%	234	250	56
1,250° F. (1,500): 60%	136	150	17
1,450° F. (1,750):			
40%	103	154	56
60%	138	191	17
1,625° F. [2] (1,950): 60%	118	152	53

TABLE III

[Alloy composition: 59.5 Co, 10 Mo, 20 Cr, 0.5 Si, 10 Ni]

Deformation Temperature [1] and Percent Deformation	0.2% Yield Strength ($\times 10^3$ p.s.i.)	Ultimate Tensile Strength ($\times 10^3$ p.s.i.)	Reduction in Area (Percent)
As-Cast	47	66	30
70° F.:			
10%	234	269	4
20%	251	282	5.5
40%	266	334	5.5
1,425° F. [3] (1,700): 20%	193	215	39
1,625° F. (1,950):			
25%	120	165	20
60%	192	212	25
1,825° F. [2] (2,200): 60%	76	160	38

[1] Number in parentheses is temperature (° F.) prior to deformation.
[2] Above the transformation zone.
[3] Swaged 60% at 1,825° F. prior to deformation at 1,425° F.

Example 4

The composition of Example 1 (49.5% Co, 10% Mo, 20% Cr, 0.5% Si and 20% Ni) is melted in an arc furnace in air and cast into sand molds to form rods 1¼″ diameter

x 6″ long. The rods are machined to ½″ diameter x 6″ long. The rods are swaged at 1625° F. (the temperature prior to deformation being 1950° F.), reducing the area by 60%, and then at room temperature (70° F.) to reduce the area by 60%, using a 30 horsepower swaging machine.

The resulting rods are cut into specimens, for exposure to 700° F., 800° F., and 1200° F. for lengths of time up to 100 hours, and tested at room temperature. The ability of the articles of the invention to retain their room temperature strength to a substantial extent is shown in Table IV. The fact that the X-ray intensity ratio remains essentially constant during prolonged heat treatments at 700° F. and 800° F. indicates that there is no significant growth of HCP phase in this alloy even though the stable structure at these temperatures is 100% HCP phase. In the microstructure of specimens that have been severely deformed at room temperature, the platelet shape is maintained as the predominant shape after prolonged exposure to temperatures below 1200° F. At 700° and 800° F. the platelet form is retained for at least 100 hrs. of exposure in the alloy whose properties are reported in Table IV. At 1200° F. the platelet form is retained for more than 10 hrs. but less than 100 hrs. in an alloy worked 60% at room temperature.

As long as the platelet form is maintained the strength of the alloy is not diminished. When there is excessive growth of the HCP phase during exposure to elevated temperatures, as indicated by a substantial increase in the intensity ratio, the platelets spheroidize and new equiaxial grains of the HCP phase are formed. For the alloy whose properties are reported in Table IV, the disappearance of the platelets due to spheroidization and the growth of equiaxial grains is accompanied by a decrease in the yield strength from approximately 300,000 p.s.i. to 200,000 p.s.i. after 100 hours of exposure.

TABLE IV

[Alloy composition: 49.5 Co, 10 Mo, 20 Cr, 0.5 Si, 20 Ni]

Exposure Conditions		0.2% Yield Strength ($\times 10^3$ p.s.i.)	Ultimate Tensile Strength ($\times 10^3$ p.s.i.)	X-Ray Intensity Ratio $I_{(101)}HCP/I_{(200)}FCC$
Temperature (° F.)	Time (hours)			
700	1	323	324	3.3 [1]
700	10	338	340	3.1 [1]
700	100	346	346	3.2 [1]
800	1	320	320	3.9 [1]
800	10	349	350	3.4 [1]
800	100	347	348	3.6 [1]
1,200	1	300	323	4.2 [1]
1,200	10	326	334	6.2 [1]
1,200	100	197	208	470.0 [2]

[1] Striations in FCC grains due to strain-induced formation of HCP platelets during deformation at room temperature are still present in optical microstructure after heat treatment.
[2] Spheroidization of the HCP platelets and growth of equiaxial HCP grains evident in the optical microstructure.

Example 5

The composition of Example 2 (34.5% Co, 10% Mo, 20% Cr, 0.5% Si and 35% Ni) is melted in an arc furnace in air and cast into sand molds to form rods 1¼″ diameter x 6″ long. The rods are machined to 1″ diameter x 6″ long. The rods are swaged at 1625° F., to reduce the area by 60%, and then at room temperature, to reduce the area by 60%, using a 30-horsepower swaging machine.

The resulting rods are cut into specimens for exposure to 700° F., 800° F., and 1200° F. for lengths of time up to 100 hours, and tested. The ability of the articles of the invention to retain their room temperature and 1250° F. strengths to a substantial extent is shown in Table V.

Examples 6–21

Examples 6–21 are summarized in Tables VI and VII. All the compositions were first cast as in Example 1. They were formed into consolidated bodies and then processed in accordance with a process of the invention and tested as in Example 1. Table VI presents the alloying composi-

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tions for each example and the processing imposed on the articles subsequent to casting. Table VII presents the physical properties measured at room temperature of the work-strengthened articles compared to the as-cast articles. Thus, Example 6 would apply to the work-strengthened article, whereas Example 6A would apply to the control, the as-cast article.

TABLE V

[Alloy composition: 34.5 Co, 10 Mo, 20 Cr, 0.5 Si, 35 Ni]

Exposure Conditions		Room Temperature		1,250° F.	
Temper- ature (° F.)	Time (hours)	0.2% Yield Strength (×10³ p.s.i.)	Ultimate Tensile Strength (×10³ p.s.i.)	0.2% Yield Strength (×10³ p.s.i.)	Ultimate Tensile Strength (×10³ p.s.i.)
700	1	265	270	126	182
700	10	280	286	126	172
700	100	286	291	128	189
800	1	282	288	138	184
800	10	293	300	127	190
800	100	316	318	130	179
1,200	1	254	255	135	189
1,200	10	273	276	123	190
1,200	100	240	250	87	142

TABLE VI

Ex.	Nomiral Alloy Composition					Temperature Prior to Deformation (° F.)	Percent Deformation
	Co	Mo	Cr	Si	Ni		
6	64.5	10	20	0.5	5	1,950	60
7	66.5	12	16	0.5	5	1,950	60
8	61.5	8	20	0.5	10	1,950	60
9 [1]	59.5	10	20	0.5	10	70	40
10	56.5	12	16	0.5	10	1,950	60
11	49.5	10	20	0.5	20	70	60
12	43.9	15.3	18.3	0.5	22	1,950	60
13	41.5	10	20	0.5	28	1,950 70	60 40
14	35	12	20	0.5	32.5	(2)	(2)
15	30	10	25	0.5	34.5	(2)	(2)
16	35	10	20	0.2	34.8	(2)	(2)
17	30	8	25	0.5	36.5	(2)	(2)
18	35	8	20	0.5	36.5	(2)	(2)
19	29.5	10	20	0.5	40	(2)	(2)
20	35	10	20	0.02	34.98	70	60
21 [3]	29.8	10	20	0.02	35	70	60

[1] Also contains 5% iron.
[2] 4 hours at 900° F.
[3] Also contains 5% copper and 0.2% zirconium.

TABLE VII

Example*	0.2% Yield Strength (×10³ p.s.i.)	Ultimate Tensile Strength (×10³ p.s.i.)	Reduction in Area (Percent)
6	193	220	19
6A	49	67	21
7	197	236	6
7A	60	80	6
8	191	232	14
8A	63	80	13
9	266	334	6
9A	47	66	20
10	196	231	8
10A	51	70	12
11	242	266	6
11A	41	87	43
12	208	219	6
12A	51	67	17
13	316	320	7
13A	41	92	55
14	306	307	4
14A	41	73	33
15	301	304	5
15A	41	75	39
16	305	306	14
16A	36	78	63
17	282	284	18
17A	40	90	51
18	284	287	19
18A	37	70	37
19	287	288	11
19A	36	82	54
20	229	233	61
20A	56	130	70
21	221	222	61
21A	52	115	71

*A signifies as-cast condition.

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Example 22

The importance of limiting the amount of carbon in the alloy composition is illustrated in this example. An alloy composition of about 34.5% cobalt, 10% molybdenum, 20% chromium, 0.5% silicon, 34.5% nickel and 0.38% carbon is air-melted in an induction furnace and poured into a graphite mold. Its as-cast Charpy V-notch is less than 5 foot-pounds. After being solution heat-treated for 4 hours at 2200° F., a billet of the alloy cracks during extrusion at 2200° F. using an 8:1 reduction ratio.

On the other hand, the alloy composition of Example 22 (34.5% Co, 10% Mo, 20% Cr, 0.5% Si, 35% Ni and only 0.04% C) is formed into a billet in the same manner. Its Charpy V-notch is over 120 foot-pounds.

Examples 23 and 24

In Example 23, an alloy composition of 35% Ni, 10% Mo, 20% Cr, 0.1% Si and a balance of Co is air cast into a cast iron mold as in Example 1. The resulting billet is swaged at 1625° F.[1] to reduce its area by 60% and then swaged 64% at room temperature. When subjected to the stress-rupture test at 1100° F., it elongates about 6% after 100 hours using a stress of 90,000 p.s.i.

In Example 24, an alloy composition of 20% Ni, 10% Mo, 20% Cr, 0.1% Si and a balance of Co is air cast into a cast iron mold as in Example 1. The resulting billet is swaged at 1625° F.[1] to reduce its area by 60% and then swaged 37% at room temperature. When subjected to the stress-rupture test at 1100° F., it elongates 10% after 100 hours using a stress of 94,000 p.s.i.

As a control, a billet of a commercial cobalt-base alloy (2% Ni, 6% Mo, 27% Cr, 0.6% Si, 0.25% C, 1% Fe, 0.6% Mn and a balance of Co) is subjected to the stress-rupture test at 1100° F. for 100 hours. It fails when subjected to a stress of only 65,000 p.s.i.

Examples 25–27

The effect on mechanical properties of an aging heat treatment of at least 0.5 hour at a temperature of 600 to 1200° F. after deformation is shown in Table VIII.

A 15 pound vacuum cast billet of an alloy of 35% Ni, 10% Mo, 20% Cr, 0.5% Si and the balance Co is extruded 8:1 at 2200° F. After being held at 2200° F. for one hour, the product is water-quenched. The quenched product is then swaged 80% at room temperature. Portions of the swaged rod are aged for four hours at a temperature of 800° F. in Example 25; 4 hours at 1000° F. in Example 26; and 4 hours at 1200° F. in Example 27.

The properties of the aged products are compared to a control that was swaged 80% and not aged. The improvement in mechanical properties, particularly the improvement in yield strength, is apparent from the table. It should be pointed out that yield strength is not increased by this aging heat treatment unless the alloy is first deformed at a temperature below its transformation zone.

TABLE VIII

Example	0.2% Yield Strength (×10³ p.s.i.)	Ultimate Tensile Strength (×10³ p.s.i.)	Reduction in Area (Percent)	Elongation (Percent)
25	306	312	45	7
26	321	327	46	7
27	312	317	16	2
Control	260	278	56	12

Example 28

The effects of aluminum and titanium additions to the alloys of this invention are shown in this example. Ten-pound castings, 2 inches in diameter by 6 inches long, were vacuum-melted and cast into cast iron molds. The alloy compositions were, by weight, 35% nickel, 10%

[1] Temperature prior to deformation is 1950° F.

molybdenum, 20% chromium, and balance cobalt except for the aluminum and titanium additions. The aluminum and titanium additions were as follows:

Alloy No.	Percent Aluminum	Percent Titanium
1	3	1
2	2	2
3	3	3
4	4	2

Because of the deoxidizing characteristics of both aluminum and titanium, no other deoxidizing agent was added. The Al and Ti additions were made to the molten heat just prior to pouring. The use of exothermic hot tops especially designed for use in vacuum ensured sound castings. The castings were heat-treated 1 hour at 2200° F., then extruded 8:1 at 2200° F. Portions of the extrusions were swaged at room temperature until failure of the bar in fracture or until the bar diameter could not be further reduced.

Alloys 1 and 2 are within the scope of this invention and possess the work strengthening previously described. Alloys 3 and 4 contain more aluminum plus titanium than the permissible 4% total, and are brittle in the as-extruded plus heat-treated condition. It is not possible to work Alloys 3 and 4 to the same extent as Alloys 1 and 2, as will be seen from the following results:

Alloy	Condition	U.T.S. (K s.i.)	0.2% Y.S. (K s.i.)	(Percent) El.	(Percent) R.A.
No. 1:					
1	As-extruded	150.3	91.7	57.0	70.0
2	Above, plus 4 hrs. at 1,000° F	173.9	117.2	36.0	38.0
3	As-extruded, plus 44% reduction by swaging	232.4	229.3	13.0	58.7
4	Above, plus 4 hrs. at 1,000 °F	256.6	251.6	10.0	32.6
No. 2:					
1	As-extruded	166.9	105.7	52.0	52.7
2	Above, plus 4 hrs. at 1,000° F	173.4	123.4	20.0	15.6
3	As-extruded, plus 39% reduction by swaging	251.6	245.2	10.0	35.7
4	Above, plus, 4 hrs. at 1,000 °F	257.0	253.8	9.0	36.9
No. 3:					
1	As-extruded	177.0	138.8	18.0	29.3
2	Above, plus 4 hrs. at 1,000° F		Brittle fracture at 157.3 K s.i.		
3	Failed to deform to equivalent reductions of Alloys Nos. 1 and 2.				
4					
No. 4:					
1	As-extruded	170.7	129.5	13.0	40.7
2	Above, plus 4 hrs. at 1,000° F		Brittle fracture at 117.8 K s.i.		
3	Failed to deform to equivalent reductions of Alloys Nos. 1 and 2.				
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Example 29

Cubic, ½″ x ½″ x ½″ specimens of the alloys of Examples 6, 8, 9, 11, 14, and 16 through 19 were solution-heat treated for 2 hours at 2200° F., water-quenched, and tested for corrosion resistance to three mineral acids. The specimens were immersed in a static environment at 122° F. for three periods (3 days, 3 days, and then 4 days) and an average corrosion rate in mils/month was determined by weight loss measurements. Results were as follows:

Alloy Example No.	Corrosion Rate (mils/month)					
	H₂SO		HCl		HNO₃	
	10%	78%	10%	37%	10%	65%
6	0.00	0.57	1.54	0.14	0.00	0.03
8	0.00	0.47	3.48	0.24	0.00	0.06
9	0.00	0.59	3.58	0.25	0.00	0.10
11	0.00	0.27	2.64	0.16	0.03	0.08
16	0.00	0.29	1.76	0.50	0.08	0.00
18	0.00	0.40	3.26	0.93	0.01	0.01
14	0.04	0.23	2.07	0.59	0.02	0.09
17	0.00	0.00	2.17	0.45	0.00	0.01
19	0.02	0.02	1.62	0.35	0.00	0.04

Example 30

Accelerated corrosion tests, to simulate sea-water corrosion, are run in aqueous solutions which provide exaggerated sea-water conditions. They are static tests in which bar samples, each having an open crevice in one face, are immersed for 10 days at 50° C. in the following solutions: (1) 10% aqueous hydrochloric acid containing ferric ion, (2) 10% aqueous sodium chloride adjusted to pH 2 with hydrogen chloride and (3) 10% aqueous ferric chloride. The depth of pitting is measured and corrosion rate is expressed as mils per year.

In these tests an alloy of the present invention containing, by weight, 35% nickel, 35% cobalt, 20% chromium and 10% molybdenum is compared with three of the better corrosion-resistant alloys available commercially— namely, 316 stainless steel; an alloy here designated "X," containing 16% chromium, 16% molybdenum, 5% iron, 4% tungsten, balance nickel; and an alloy here designated "Y," containing 21–23% chromium, 5.5–7.5% molybdenum, 1% tungsten (max.), 2.5% cobalt (max.), 1–2% manganese, 44–47% nickel, 1.75–2.5% columbium plus tantalum, balance iron. The results were as follows:

Alloy	Corrosion Rate (mils per yr.)		
	10% HCl +Fe³⁺	10% NaCl +HCl pH₂	10% FeCl₃
35 Ni, 35 Co, 10 Mo, 20 Cr	0.0	0.1	0.0
Alloy "X"	0.7	0.1	0.1
Alloy "Y"	13.0	0.1	0.1
316 Stainless Steel	>50	5.0	>50

Stress-corrosion cracking is tested by first finishing one face of the test specimen for metallographic examination; die-pressing an "O" and a superimposed "X" into this face to form an ⊗ pattern; and placing the specimens similarly prepared "controls." The specimen is examined six times over a total 192 hour test period (i.e., at the end of 4, 8, 24, 48, 72, 192 hours) to determine whether cracking occurs. In these stress-corrosion tests an alloy of this invention etches and pits without cracking, whereas Type 316 stainless steel, for example, cracks within 4 hours in the MgCl₂ solution.

Bars of an alloy of this invention were stressed by bending them into a horseshoe shape and bolting them to a sheet of inert plastic material to produce a crevice cor-

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rosion environment, and then were tested to determine their resistance to stress corrosion. Specifically, they were immersed for 12 months in sea water and examined periodically. The results are shown below in comparison with results on two Co-Ni-Cr-Mo alloys outside the scope of this invention, here-designated as Alloy "A" and Alloy "B," and on several of the best commercial metals and alloys for use in sea water. The composition of the alloy of this invention, was 45% cobalt, 35% nickel, 20% chromium and 10% molybdenum; of Alloy "A" was 14% cobalt, 50% nickel, 30% chromium and 6% molybdenum; and of Alloy "B" was 29% cobalt, 50% nickel, 15% chromium, and 6% molybdenum.

Test Alloy	Process Condition	Specimen Condition after 12 Mos.
This invention	Solution ht. treat.	No effect.
Do	60% cold-work + 1900° F./4 hrs.	Do.
Alloy "A"	Solution ht. treat.	Severe crevice corrosion.
Alloy "B"	do	Do.
Alloy "X"		No effect.
Monel		Tarnished.
Copper		Some corrosion.
Titanium		Tarnished.
316 Stainless Steel		Slightly pitted.

What is claimed is:

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 having a composition consisting 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% titanium, 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 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, 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 925° F., until its cross-sectional area has been reduced at least 5%.

2. In a process for producing a work-strengthened alloy the steps comprising (1) preparing a body of metal having a composition consisting 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% titanium, 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 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, 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%.

3. An alloy body having a composition consisting essentially of, by weight, 5 to 45% nickel, 7 to 16% molybdenum, 13 to 25% chromium, up to 0.05% carbon, up

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to 2% aluminum, up to 2% titanium, 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 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, 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 925° F., until its cross-sectional area has been reduced by at least 5%, and being further characterized by containing substantially no hexagonal close-packed phase.

4. 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 being a solid solution of a composition consisting 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% titanium, 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 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 having a face-centered-cubic crystal structure and said platelet phase being a solid solution of said 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 greater than 160,000 p.s.i. and a ductility, as measured by reduction in area, greater than 3%.

5. A work-strengthened alloy of claim 4 in which the percent of nickel is from 5 to 40, the percent of molybdenum is from 8 to 14, the percent of chromium is from 15 to 22, and the sum of the percent nickel and percent cobalt is from 65 to 75, said alloy having an ultimate tensile strength, measured at 68° F., of at least 220,000 p.s.i.

6. A work-strengthened alloy of claim 4 which has been aged at least 0.5 hour at 600 to 1200° F., said alloy being characterized by having an ultimate tensile strength, measured at 68° F., of at least 260,000 p.s.i.

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