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3,091,022 COLD-FORMABLE PREDOMINANTLY COBALT ALLOYS

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This invention relates to predominantly cobalt-base alloys that are capable of being cold-formed.

Cobalt-base alloys have a wide application in industry as structural materials, as heat and corrosion resistant materials, in magnets, in hard facing and abrasion resistant materials, and in many other applications. Cobalt and alloys containing predominantly cobalt are generally used only in the cast form, however, due to their poor workability. The difficulty in fabricating cold-wrought products from cobalt and high cobalt-base alloys constitutes a serious limitation on the use of this otherwise versatile metal.

The inability of cobalt and high-cobalt base alloys to undergo cold-forming is due to a work-hardening of the metal which decreases the ductility and prohibits further cold-forming until a stress-relieving heat treatment is applied to the metal parts. Cobalt has normally a close-packed hexagonal crystal structure at room temperatures and it is well known that the cold-forming of a metal having such a crystal structure produces a work-hardening or build-up of internal stresses. Actually at temperatures above 780° F. cobalt has a face-centered cubic crystal structure which would favorably permit cold-forming if this crystal structure existed at room temperatures; but an allotropic transformation in crystal structure from the cubic form to the hexagonal form takes place at about 780° F.

The stresses built up by cold-working of cobalt can be relieved only by an annealing heat treatment. Therefore, the production of cobalt cold-formed sheet or wire is a complex and expensive process, involving many small increments in reduction by rolling or drawing with intermediate annealing heat treatments necessary between each pass to eliminate the work-hardened condition and to soften the alloy for the next working operation.

An example of an industrial need for cold-formable cobalt and cobalt-base alloys is found in the production of composite tube welding rods wherein a tubular sheath containing alloy elements within the tube is fabricated. The inability of cobalt and high-cobalt base alloys to be cold-formed into such tubular sheaths unfortunately prevents the use of cobalt in this form even though cobalt is recognized to be an excellent material for use in such welding operations.

It is the primary object of this invention, therefore, to provide predominantly cobalt alloys that can be easily cold-formed into such products as thin sheet, wire and tubing.

It is another object of this invention to provide a cold-formable predominantly cobalt alloy capable of being fabricated into thin-walled tubular sheaths for use as composite tube welding rods.

It is also an object of this invention to provide cold-formable predominantly cobalt alloys that may be substituted for unalloyed cobalt in some particular applications.

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Other aims and objectives of the invention will be apparent from the following description and appended claims.

In accordance with the present invention a predominantly cobalt alloy is provided containing from about 70 to about 99.5 percent by weight cobalt and at least one element from the group consisting of iron, carbon and nickel in amounts effective to retard the formation of the close-packed hexagonal crystal structure at room temperatures.

Specifically it has been found that 0.5 percent by weight carbon additions to cobalt are sufficient to suppress or retard the allotropic transformation from the cubic to the hexagonal crystal structure. It has also been found that 6 percent iron is effective in retaining the cubic structure in cobalt. With regards to nickel, at least 24 percent by weight of this element is required to produce the desired effect when it is the only element added to cobalt; but when nickel and iron are both added, it has been found that lesser amounts of nickel are required. Thus it is not necessary to add 12 percent nickel or 0.25 percent carbon to 3 percent iron to form the equivalent of 6 percent iron, for lesser amounts are found to be equivalent due to a synergistic effect. Specifically when iron and nickel are both added to cobalt, the minimum amount required is defined by the following equation,

$$\text{Fe} + \sqrt{\text{Ni}} = 4.7$$

where Fe equals the percent by weight iron and Ni equals the percent by weight nickel, and where at least one of said elements is present in amounts of at least one percent. The maximum amount of these elements which should be added to cobalt are a maximum of 0.75 percent carbon, a maximum of 11 percent iron, and a maximum of 30 percent nickel.

Alloys produced in accordance with the specifications set forth above will exhibit cold-formable characteristics allowing their use in many operations for which cobalt and other cobalt base alloys are unsuited.

The work-hardening tendency of cobalt under cold-forming operations is due to its close-packed hexagonal crystal structure. But while cobalt has this type of crystal structure at room temperatures, at temperatures above 780° F. cobalt possesses a face-centered cubic crystal structure. It is well known in the art that metals possessing face-centered cubic structures are quite ductile and amenable to cold-forming.

By the addition of the elements listed above to a cobalt base, the allotropic transformation from a cubic structure to the close-packed hexagonal structure that ordinarily takes place at 780° F. is suppressed to a point below room temperature with the result that the predominantly cobalt alloys of this invention possess a cubic crystal structure at room temperature. These cobalt alloys by virtue of their cubic crystal structure will withstand moderate to large amounts of cold-forming without severe loss of ductility or detrimental increases in hardness. Furthermore, while possessing a cubic structure not found in pure cobalt at room temperatures, these alloys still have such similar physical and mechanical properties as pure cobalt, that they are substitutable for pure cobalt in many applications.

In Table A, a number of alloy compositions are shown in comparison to their predominant crystal structure at

room temperatures and their cold formability characteristics.

TABLE A

Alloy	Nominal Composition, Percent by weight						Crystal Structure	Cold Workability
	Mo	Cr	Fe	Ni	C	Co		
A	-----	-----	-----	-----	0.3	100	HCP ¹	Poor.
B	-----	-----	-----	-----	0.6	99.7	HCP	Poor.
C	-----	-----	-----	-----	0.6	99.4	FCC ²	Good.
D	-----	-----	2.5	-----	0.6	96.9	FCC	Good.
E	-----	-----	4.0	-----	-----	96	HCP	Poor.
F	1	4	-----	-----	-----	95	HCP	Poor.
G	-----	-----	4	4	-----	92	FCC	Good.
H	-----	-----	4	4	0.1	91.9	FCC	Good.
I	-----	-----	6	-----	-----	76	FCC	Good.
J	-----	-----	-----	24	-----	76	FCC	Good.

¹ HCP means hexagonal close-packed crystal structure.
² FCC means face-centered cubic crystal structure.

It is evident from inspection of Table A that the addition of carbon, iron and nickel to cobalt has lowered the allotropic transformation point of cobalt to a point below room temperature. It is the addition of these elements in effective amounts that causes the existence of a face-centered cubic structure at room temperature.

Although commercially available cobalt may contain a small amount of nickel, iron, carbon or other impurities which cannot be avoided during refinement of the metal, these metals are not present in sufficient amounts nor in the proper proportions required to retain a face-centered cubic structure at room temperature.

The ductility of some of these alloys after a cold-working operation was determined by means of hardness tests and bending tests. These tests were performed on ordinary cobalt alloys and the predominantly cobalt alloys of this invention. The bending tests were performed on sheets of the alloy compositions indicated by bending the sheets and noting the angle at which rupture occurs on the convex surface of the bend. Materials which can undergo a 180° bend without rupture possess high ductility. The results of these tests are shown in Table B where the alloy compositions "C," "D," etc., refer to the alloys listed in Table A.

TABLE B

Remanent Ductility After Cold Working

Alloy Composition	Condition after cold working	Hardness, Standard Rockwell "B" Test	Angle of Bend Before Rupture, degrees
C	annealed to relieve internal stresses	80	180
C	cold reduced 10%, no anneal	91	160
D	annealed to relieve internal stresses	74	180
D	cold reduced 10%, no anneal	91	180
E	annealed to relieve internal stresses	83	180
E	cold reduced 10%, no anneal	² Rc=24	90
H	annealed to relieve internal stresses	50	180
H	cold reduced 10%, no anneal	75	180
H	cold reduced 30%, no anneal	79	180

¹ Indicates that samples were flattened back on themselves without fracture.
² Corresponds to a Rockwell "B" reading of 101.

Since relatively small amounts of carbon, iron or nickel can produce the face-centered cubic structure in cobalt at room temperatures, the resulting alloy is predominantly cobalt and exhibits many of the properties of pure cobalt with the improvement in workability over pure cobalt. Table C compares some physical and mechanical properties of several of the alloys mentioned in this specification with those of pure cobalt.

TABLE C

Properties of Some Typical Alloys

Property	Alloy				
	A	C	D	E	H
Hardness, Rockwell B	179	79	76	92	83
Curie Temperature, ° F	12,040	2,030	2,000	-----	1,865
Tensile Strength, p.s.i.	286,000	105,000	115,000	-----	87,000
Erichsen value, mm. ³	-----	6.0	6.45	3.5	6.5
Predominant Crystal Structure	HCP	FCC	FCC	HCP	FCC
Density, grams per cc.	8.9	8.9	8.7	8.7	8.5

¹ Represent cast cobalt as given in "Cobalt," R. S. Young, Reinhold Publishing Corp., 1948, p. 66.

² Represents wrought annealed material as given in "Metals Reference Book," C. J. Smithells, Interscience Publisher, Inc., 1955, vol. 2, p. 803.

³ Erichsen value is the depth of a cup which can be formed in sheet material without rupture with a standard mandrol and die.

The substantial similarity in properties of these predominantly cobalt alloys with pure cobalt allows the substitution of the workable predominantly cobalt alloys of this invention for pure cobalt in many applications. For example in the production of magnets containing cobalt, the fabrication of the magnets is complicated by the poor workability of pure cobalt. The highly workable alloys of this invention, because they possess similar magnetic properties, are substitutable for pure cobalt in this application.

Pure cobalt has many other unique properties, for example, radio-active, electrical and thermal properties, which are essentially unaffected by the alloying procedures of the present invention which yield a cold-formable cobalt material.

In addition to nickel, iron, and carbon, there are other elements which also stabilize the face-centered cubic crystal structure. These elements include those in the group containing boron, manganese, aluminum, titanium, copper and tin and they can be substituted in whole or in part for the nickel, iron and carbon in the alloy.

There are other substances which instead of suppressing the allotropic transformation from cubic to hexagonal structure, will actually stabilize the hexagonal structure. This group includes chromium, tungsten, molybdenum, phosphorus, sulfur and silicon. Table D shows several addition alloy compositions having varying amounts of these impurities.

TABLE D

Alloy Composition	Mo	Cr	Fe	Ni	C	Mn	Si	S	P	Co
K	-----	-----	4.2	4.2	0.1	-----	-----	0.01	-----	balance.
L	2	5	4	4	0.15	-----	-----	0.008	0.008	Do.
M	-----	1	5	5	0.90	0.8	0.8	-----	-----	Do.

The amounts of these elements that may be tolerated in alloys of this invention will be governed by the degree to which they stabilize the hexagonal crystal structure or impair workability. For example alloy "F" of Table A, containing 1 percent molybdenum and 4 percent chromium in a cobalt base, possesses the hexagonal structure of pure cobalt at room temperature and exhibits poor workability. On the other hand, the presence of 5 percent chromium and 2 percent molybdenum in alloy "L" of Table D is not sufficient to stabilize the hexagonal structure against the action of the stronger

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cubic formers 4 percent iron, 4 percent nickel and 0.15 percent carbon.

The alloys may be melted by standard furnacing procedures. Vacuum melting is preferred when a minimum amount of oxides and gas inclusions is desired. To insure good hot-working characteristics of the alloy, it has been found that sulfur and phosphorous contents should be kept as low as possible, since these elements severely impair workability.

These alloys may be hot-worked, or they may be cold-worked by well-known methods to produce sheet, tubing, wire, strip, etc. An example of the need for a cold-formable material of a predominantly cobalt composition is found in the production of a composite tube welding rod. A composite tube welding rod consists of a tubular sheath which contains alloy elements within the tube such that the deposition of such a material by ordinary welding techniques will produce an alloy deposit having a composition including the metal composing the tubular sheath and the elements contained in the sheath. Typical elements contained in these tubes are carbon, nickel, cobalt, tungsten, molybdenum, or other alloy ingredients.

The use of such composite tube welding rods for producing iron-base or nickel-base weld deposits is quite common in industry since both these metals are easily cold-formed into thin-walled small-diameter tubular sheaths. However, the difficulty of forming high cobalt alloys into thin-walled small-diameter tubing has precluded the practical and economic production of cobalt-base welding rods of this type. At present cast and wrought cobalt-base alloy welding rods are manufactured in solid rod form. They are used to produce hard surfacing deposits which are wear-resistant and/or corrosion resistant. By means of an alloy of the present invention, it is now commercially practical to produce cobalt-base composite tube welding rods having cold-formable cobalt alloys of this invention as the sheath material. These composite tube welding rods can now be produced in continuous coils of the harder and more wear-resistant grades of cobalt-base hard surfacing alloy, previously made only in short cast lengths.

As an example a composite tube welding rod having a tubular sheath made of a ductile cobalt alloy of this invention could contain a filler material having the following composition: 72 percent chromium, 14 percent tungsten, 1 percent iron, 3.5 percent carbon, and 3.5 percent cobalt. A tubular rod of this type produced a weld deposit similar to those previously obtainable only from cast weld rods.

Another application for a cold-formable predominantly cobalt alloy would be its use as a sheath for a composite tube welding rod in which the filler material is tungsten carbide. A filler material composed of about 8 percent chromium and 92 percent tungsten carbide was placed in a predominantly cobalt tubular sheath. Such a material would be useful for producing wear-resistant hard-surfacing deposits. During deposition, the molten cobalt alloy sheath dissolved some of the tungsten carbide and, upon cooling, rejected a precipitate in the solid state, thus producing a deposit having large particles of unmelted tungsten carbide retained in a cobalt-rich matrix. This deposit had excellent wear-resistant properties.

The filler material may be in the form of a pre-alloyed powder or elemental particles may be used. The compositions listed above do not represent limits. Other compositions may be used to produce almost any composition in the final weld deposit.

What is claimed is:

1. A cold-formable cobalt alloy having a predominantly face-centered cubic crystal structure at room temperature consisting essentially of about 3 percent by weight iron, 75

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3 percent by weight nickel and the balance cobalt and incidental impurities.

2. A welding rod comprising a tubular sheath containing a filler material alloying with said tubular sheath upon melting in a welding operation, said tubular sheath being composed of a cold-formable, cobalt alloy consisting essentially of at least one element selected from the group consisting of carbon in amounts from 0.5 to 0.75 percent by weight, iron in amounts from 6 to 11 percent by weight, and nickel in amounts from 24 to 30 percent by weight, said elements being present in equivalent amounts when more than one of said elements is selected, and the balance cobalt in a minimum amount of 70 percent by weight and incidental impurities.

3. A cold-formable cobalt alloy having a predominantly face-centered cubic crystal structure at room temperature, said alloy consisting essentially of cobalt together with iron and nickel, the minimum amounts of iron and nickel being defined by the following equation:

$$Fe + \sqrt{Ni} = 4.7$$

where Fe equals the percent by weight iron and Ni equals the percent by weight nickel, at least one of said elements being present in an amount of at least one percent, and up to a maximum amount of iron equal to 11 percent by weight and a maximum amount of nickel equal to 30 percent by weight, and the balance cobalt in a minimum amount of 70 percent by weight and incidental impurities.

4. A welding rod comprising a tubular sheath containing a filler material alloying with said tubular sheath upon melting in a welding operation, said tubular sheath being composed of a cold-formable cobalt alloy consisting essentially of at least one element selected from the group consisting of carbon in amounts from 0.5 to 0.75 percent by weight, iron in amounts from 6 to 11 percent by weight, and nickel in amounts from 24 to 30 percent by weight, said elements being present in equivalent amounts when more than one of said elements is selected, and the balance cobalt in a minimum amount of 70 percent by weight and incidental impurities, and said filler material consisting essentially of about 14 percent by weight tungsten, about 1 percent by weight iron, about 3.5 percent by weight carbon, about 9.5 percent by weight cobalt, and the balance chromium and incidental impurities.

5. A welding rod comprising a tubular sheath containing a filler material alloying with said tubular sheath upon melting in a welding operation, said tubular sheath being composed of a cold-formable cobalt alloy consisting essentially of at least one element selected from the group consisting of carbon in amounts from 0.5 to 0.75 percent by weight, iron in amounts from 6 to 11 percent by weight, and nickel in amounts from 24 to 30 percent by weight, said elements being present in equivalent amounts when more than one of said elements is selected, and the balance cobalt in a minimum amount of 70 percent by weight and incidental impurities, and said filler material consisting essentially of about 8 percent by weight chromium and the balance tungsten carbide and incidental impurities.

6. A cold-formed article of manufacture in the form of sheet, tube, wire and the like having substantially the properties of pure cobalt and consisting essentially of cobalt together with iron and nickel, the minimum amounts of iron and nickel being defined by the following equation:

$$Fe + \sqrt{Ni} = 4.7$$

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where Fe equals the percent by weight iron and Ni equals the percent by weight nickel, at least one of said elements being present in an amount of at least one percent, and up to a maximum amount of iron equal to 11 percent by weight and a maximum amount of nickel equal to 30 percent by weight, and the balance cobalt in a minimum amount of 70 percent by weight and incidental impurities.

7. A cold-formable cobalt alloy having a predominantly face-centered cubic crystal structure at room temperature consisting essentially of about 4 percent by weight iron,

4 percent by weight nickel, about 0.1 percent carbon, and the balance cobalt and incidental impurities.

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