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## COBALT ALLOYS

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This invention relates to cobalt alloy compositions and to metal objects produced therefrom. More particularly, this invention relates to cobalt base alloy compositions containing substantial amounts of molybdenum and silicon and to high temperature-resistant articles of manufacture (i.e., shaped objects) prepared from such alloys.

In recent years there has developed a considerable demand for structural materials capable of withstanding temperatures up to 2000–2400° F.; i.e., 200–600° G. higher than presently used iron, cobalt, and nickel base alloys can practically be utilized. Such materials would find use, for example, in the fabrication of turbine blades and nozzles for jet engines, gas turbines, and the like, as well as in extrusion dies and forging and other tools for hot working of metals. It is known that improved high-temperature properties may result from elemental additions to cobalt of refractory metals, such as molybdenum and tungsten. It is also known that these refractory metals are very susceptible to high-temperature oxidation and that either coatings or alloys must be perfected to make the refractory metal-containing alloys useful. Despite the fact that many alloys have been investigated, need remains for specific superior property combinations.

It is a primary object of the present invention to provide strong, tough, heat-resistant alloys consisting essentially of cobalt, molybdenum, and silicon in the proportions by weight of 50–70% cobalt, 25–48% molybdenum, and 2–10% silicon and shaped objects comprising such alloys.

Alloy objects of the invention are prepared either by melting and casting compositions consisting essentially of cobalt, molybdenum, and silicon in the same proportions by weight using temperatures 400–800° F. above the solidus temperature or by first prereacting such compositions of cobalt, molybdenum, and silicon, reducing the reaction product to powder size and converting the powders to objects by cold pressing followed by partial melting, by hot pressing at elevated pressures, or by melting and casting.

Alloys of cobalt-molybdenum-silicon falling within the composition ranges cited above are found to exhibit a number of outstanding and surprising properties. These alloys are strong at room temperature and maintain high transverse rupture strength at temperatures up to 2200° F. These alloys break with no measurable elongation below 1800° F. but can fail plastically at higher temperatures. Furthermore, these alloys exhibit high impact strength and are resistant to thermal stress and to degradation by heat and air. These properties make these alloys suitable for various critical service structural components such as gas turbine blades, forging dies, extrusion dies, gasoline and diesel exhaust valves, and furnace fixtures. Shaped objects of these alloys can be fabricated to close dimensional tolerances.

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Alloys outside the above-defined ranges are found to be significantly deficient in one or more of the above desired properties for the alloys of the invention. Alloys containing less than 25% by weight molybdenum have strengths which diminish rapidly above 1600° F. It is found that alloys containing more than 48% by weight molybdenum exhibit very poor mechanical properties. The use of less than 2% by weight silicon leads to highly inferior oxidation resistance at elevated temperatures. Alloys containing more than 10% by weight silicon possess inferior mechanical properties.

Other elements may be added to the cobalt-molybdenum-silicon alloys of the invention provided they do not have a substantial adverse effect upon one or more of the properties: high transfer rupture strength at elevated temperatures; good impact strength; and excellent oxidation resistance. There, of course, may be added such amounts of other elements which will impart to the alloys of the invention, in an anticipated manner, various properties that are desirable for special application without substantially affecting their inherent attributes as structural materials. The presence of nonmetals such as carbon, sulphur, boron, oxygen, and nitrogen, can be tolerated in small amounts but the total should not be allowed to exceed about 0.1 weight percent of the alloy composition.

Examination of alloys of the invention by metallographic techniques shows that on the basis of microstructure the alloys consist of about 20–85 volume percent of a Laves phase of the  $MgZn_2$  type structure and from about 15–80 volume percent of a matrix composed of at least one or both of the intermetallic compounds  $Co_2Si$  or  $Co_7Mo_6$ .  $Co_2Si$  or  $Co_7Mo_6$  co-exist with the Laves phase in the liquidus-solidus temperature range of the composition of this invention. Total trace volume fractions of something less than about 5 volume percent of the following phases may be present in a microstructure of these alloys as impurities: Co,  $Co_3Mo$ ,  $CoSi$ ,  $Mo_3Si$ , and  $Mo_3Si_2$ .

In preparing the compositions of cobalt-molybdenum-silicon from which alloy objects of the invention are formed, it is preferred to use commercially pure elements. It is to be understood that minor changes in the relative proportions of the essential elements will occur when the untreated compositions are converted to alloy objects due to the elimination of expendable impurities in the starting materials. However, for simplicity of expression and ease of understanding, the proportions of essential elements in the untreated compositions and in the alloy compositions and shaped objects are hereafter referred to in terms of the same numerical values.

The preferred mode of forming shaped objects comprising alloys of the invention is to first premelt the cobalt-molybdenum-silicon compositions, then reduce the alloy to a powder and convert the powder to a shaped object. Pre-melting of the essential elements insures uniformity of composition and structure in the final alloy objects. The premelting step involves the arc-melting or induction-melting of the untreated composition of cobalt, molybdenum, and silicon and then casting the melt into buttons or ingots.

The buttons or ingots are then broken up preferably



in steel or tungsten carbide-lined equipment to a fine particle size, e.g., 95% of which will pass a —240 mesh screen. The powders are preferably stored in airtight containers maintained at slightly elevated temperatures in order to prevent moisture pickup until used in producing shaped objects.

The powders are readily shaped, for example, by cold pressing in steel dies at pressures in a range of from about 30–50 tons per square inch. The cold pressed object is then liquid phase bonded at temperatures between 2100° F. and 2500° F. for a period of time ranging from less than one minute to as much as 60 minutes. This temperature range is between the solidus and liquidus line for these alloy compositions. Inert gas, hydrogen, or vacuum furnace atmospheres are satisfactory and will yield dense, bright shaped objects.

ten pounds were converted to alloys of the invention by arc-melting. The arc-melter was designed with a tungsten electrode and a deep boat-shaped copper hearth to minimize contamination and weight losses. To insure homogeneity, each sample was arc-melted at least four times and the resulting alloy buttons were examined metallographically for property characterization. The results of examination on these alloys are reported in Table I below including the v/o of Laves phase determined, the Knoop microhardness of the Laves phase, the average grain size, the type of cast structure, and crystal structure of the matrix phase. The alloys all exhibit a Laves phase content between 20 and 85 v/o. Knoop microhardness values of the Laves phase present in the microstructure of these alloy ranges from 900 to 1443.

Table I

Composition (w/o)			Laves phase (v/o)	Laves phase (K <sub>100</sub> microhardness)	Laves phase (grain size, dia.) in microns	Composition structure type	Crystal structure of matrix phase
Co	Mo	Si					
70	28	2	20	1,039	5	Eutectic	Co <sub>7</sub> Mo <sub>8</sub>
65	25	10	50	1,039	8	Dendritic	
65	29	6	50	1,039	15	do.	
65	33	2	50	1,039	35	Eutectic+dendritic	
60	30	10	58	1,220	10	Dendritic	Co <sub>7</sub> Mo <sub>8</sub>
60	34	6	65	950	25	Dendritic+slight eutectic	
60	38	2	50	1,039	25	Eutectic+dendritic	Co <sub>7</sub> Mo <sub>8</sub>
55	35	10	80	1,231	50	Dendritic	Co <sub>2</sub> Si
55	39	6	78	1,200	30	Coarse dendritic	Co <sub>7</sub> Mo <sub>8</sub>
55	41	4	85	954	80	Coarse dendrites	Co <sub>7</sub> Mo <sub>8</sub>
55	43	2	75	900	10	Fine grain two phase	Co <sub>7</sub> Mo <sub>8</sub>
50	40	6	76	1,432	20	Coarse dendrites	Co <sub>7</sub> Mo <sub>8</sub>
50	48	2	76	1,443	15	Fine grain two phase	Co <sub>7</sub> Mo <sub>8</sub>

Shaped objects can also be made from the powders by hot pressing the powder in graphite dies at temperatures between 2100° F. and 2400° F. at 1000 pounds per square inch or higher. Atmosphere control in this operation is not critical. Soaking time at the operating temperature is dependent upon the mass of the object but will usually be limited to times in the range of about 5–20 minutes.

Shaped objects can also be made from the powders by melt casting them in air, vacuum, or inert atmospheres using molds of graphite or stable oxides, such as MgO, ZrO<sub>2</sub>, or ThO<sub>2</sub>. Graphite crucibles can be used where the cast objects may be later ground to remove the surface material contaminated by the graphite. In forming shaped objects by casting the powders, it is found that temperatures in excess of 2750° F. are preferred to obtain good fluidity.

A better understanding of the invention will be gained from the following working examples. In these examples, the starting materials employed were of conventional commercial purity. The abbreviations "w/o" and "v/o" represent "percent by weight" and "percent by volume," respectively.

## EXAMPLE 1

A series of compositions of cobalt-molybdenum-silicon falling within the cited ranges weighing between one and

A representative group of the alloy buttons of Table I were then separately ground to powder by jaw crushing to —4 mesh followed by ball milling, either dry or with benzene, in a four-quart capacity steel mill (8 inches diameter) using tungsten carbide inserts (¼" x ½" x ½"). The mill was run at 60 r.p.m. from one hour to as much as twenty-four hours to obtain at least 95% —230 mesh powder.

Solid bars (¼" x ½" x 2") were then made by cold pressing the compositions in steel dies at pressures in the range of 30 to 50 tons per square inch followed by liquid phase bonding at temperatures between 2282° and 2462° F. for approximately ten minutes. Either vacuum or controlled atmosphere furnaces were used to prevent oxidation of the particulate material prior to densification.

These bars were then tested to determine the following properties: R<sub>A</sub> hardness; transverse rupture strengths at various temperatures; impact strength as determined using unnotched Izod test specimens; oxidation resistance at various temperatures; and thermal shock. The results of these tests on the shaped objects are reported in Table II below together with information on the liquid phase sintering temperature in preparing the bars, the shrinkage occurring during the sintering step; and the bulk density of the shaped objects.



Table II

Composition (w/o)			Liquid phase sinter.		Shrink. during liquid phase sint. (percent)	Bulk dens. (g./cc.)	RA Hardness	Transverse rupture strength, 1,000 p.s.i.					Impact strength un-notched Izod test (ft.lbs./sq. in.)
Co	Mo	Si	° F.	° C.				70° F. (21° C.)	932° F. (500° C.)	1472° F. (800° C.)	1832° F. (1000° C.)	2192° F. (1200° C.)	
70	28	2	2,372	1,300	cast	9.08	80.5	165.0	154.0	128.0	52.5	-----	55.0
65	25	10	2,174	1,190	21.5	7.55	77.0	78.8	79.9	68.0	22.6	-----	27.8
60	30	10	2,120	1,160	30.5	8.34	83.4	85.4	102.0	64.1	16.5	-----	29.7
55	35	10	2,200	1,205	30.5	8.40	82.0	94.7	101.0	99.0	18.3	-----	28.0
55	39	6	2,282	1,250	27.5	8.20	79	60.9	53.8	-----	36.3	-----	24.4
55	41	4	2,462	1,350	31.5	8.63	82	53	54.2	65.4	72.2	17.8	24.4
50	44	6	2,372	1,300	33.5	8.77	78	53	60.6	65	58.5	15.1	24.4
50	48	2	2,372	1,300	35.0	9.09	83	63.1	65.9	56.1	70.7	8.9	26.0

Composition (w/o)			Oxidation resistance (mg./in. <sup>2</sup> /100 hrs.)			Shock cycles from 400° F. to temperature indicated			
Co	Mo	Si	1112° F. (600° C.)	1472° F. (800° C.)	1832° F. (1000° C.)	1472° F. (800° C.)	1652° F. (900° C.)	1832° F. (1000° C.)	
70	28	2	-----	-----	-77.0	-----	-----	*50 <sub>5</sub>	*Crack on 5th cycle—no other effect.
65	25	10	0.0	0.0	-----	25	25	-----	
55	35	10	-----	+1.2	-130.0	25	25	50	*Slight crack 3rd cycle—no other effect.
55	39	6	+2.6	-3.9	-84.0	25	*25 <sub>3</sub>	50	
55	41	4	+2.6	+5.2	-77.0	25	25	50	*Crack on 17th cycle—no other effect.
50	44	6	+1.6	-7.1	-77.0	25	25	50	
50	48	2	+0.6	-2.6	-84.0	25	25	*50 <sub>17</sub>	

It will be noted from the above reported results that the RA hardness number ranges from RA 77 to RA 83.4. The room temperature transverse rupture strengths range from about 53,000 to 165,000 lbs./sq. in.; from about 56,000 to 128,000 lbs./sq. in. at 1472° F. (800° C.); as high as 72,000 lbs/sq. in. at 1832° F. (1000° C.); and as high as 17,000 lbs./sq. in. at 2192° F. (1200° C.). Impact strengths range from 24 to 55 ft. lbs./sq. in. The oxidation resistance is excellent at temperatures below 1472° F. (800° C.). At 1832° F. (1000° C.) the oxidation rate has increased to as much as 130 milligrams weight loss per sq. in. per 100 hours. This rate of oxidation is, of course, still acceptable for selected applications. It will be noted that an important characteristic of these shaped objects is their resistance to deformation at all temperatures below approximately 1800° F. All samples tested failed without yielding below 1800° F. Samples tested in transverse rupture at 2192° F. (1200° C.) failed plastically.

EXAMPLE 2

The following illustrates hot pressing as a means for converting powders of cobalt-molybdenum-silicon composition into shaped objects of the invention and further illustrates the unique properties and outstanding utility of such shaped objects. A sample of powder having the alloy composition of 55 w/o cobalt, 35 w/o molybdenum, and 10 w/o silicon was made generally in accordance with the procedure shown in Example 1 above. From a part of this sample of powder, eight test bars (¼" x ½" x 2") were hot pressed in graphite molds at 2192° F. for five minutes under approximately 3000 lbs./sq. in. The average RA hardness number for these specimens was 82. The room temperature transverse rupture strength for the specimens ranged from 83,000 to 95,000 lbs./sq. in. The average impact strength was 18 ft. lbs./sq. in. All the bars passed thermal shock cycle testing without cracking. From the balance of the sample of powder, four discs (¾" thick x 3" diameter) were hot pressed in a graphite mold at a temperature of 2192° F. for 20 minutes under 3000 lbs./sq. in. The resultant discs were determined to be flaw-free by ultrasonic testing techniques. The discs were determined to have an average bulk density of 8.10 grams/cubic centimeter and RA hardness of 82. The discs were then machined by electrospark machining to make

extrusion dies for extruding aluminum. Two of these dies were made to produce 0.850" round solid aluminum rods. This pair of dies successfully extruded twelve billets (30 lbs. each) of AA6063 aluminum alloy preheated from 800 to 850° F. at 300 ft./min. with a good finish on the aluminum. This compares to a normal production speed of 150 ft./min. under similar conditions with conventional die materials.

EXAMPLE 3

The following illustrates melting and casting as a means for converting untreated compositions of cobalt-molybdenum-silicon into shaped objects of the invention. The properties of these alloy objects are reported in Table III below.

Table III

Ultimate tensile strength (p.s.i.)	131,000
Young's modulus (×10 <sup>6</sup> p.s.i.)	35.4
Charpy V-notch impact strength (ft. lbs./sq. in.)	1.25
RA (as-cast)	75-78
RA (after heat treatment at 1600° F./15 hours)	80.5
Specific heat at room temperature (gram-cal./° C.)	.127
Specific heat at 325° F. (gram-cal./° C.)	.111
Thermal conductivity (gram-cal./sec./cm. <sup>2</sup> /° C.)	.07-.08
Coefficient of expansion (×10 <sup>-6</sup> in./in./° F.) (R.T. to 1500° F.)	10.4

The alloy objects of the invention can be machined to close tolerances with tungsten carbide tooling procedures or by grinding, electrospark machining, or ultrasonic machining. Alloy compositions containing less than 40% by weight molybdenum and less than 8% by weight silicon are readily machined with tungsten carbide tooling. The alloy compositions containing more than 40% by weight molybdenum and more than 8% by weight silicon are best machined to finished dimension by either electrospark or ultrasonic machining techniques. If desired, the alloy objects of the invention may be subjected to various metallurgical processes well known in the art; such as heat treatment, hot rolling, extrusion, or the like to develop improved properties in an anticipated manner. As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this



invention is not limited to the particular embodiments described hereinabove except as defined in the appended claims.

I claim:

1. An alloy composition consisting essentially of cobalt, molybdenum, and silicon in the proportions by weight of 50-70% cobalt, 25-48% molybdenum, and 2-10% silicon.

2. A powder metallurgy composition consisting of fine particles having a size wherein 95% of said particles pass a -240 mesh screen, and consisting essentially of cobalt, molybdenum, and silicon in the proportions by weight of 50-70% cobalt, 25-48% molybdenum, and 2-10% silicon.

3. A shaped object formed of the powder metallurgy composition of claim 2 sintered to a substantially homogeneous composite.

4. A metallurgy composition comprising a fine pre-

reacted powder having all particles pass a -240 mesh screen, and consisting essentially of cobalt, molybdenum, and silicon in the proportions by weight of 50-70% cobalt, 25-48% molybdenum, and 2-10% silicon.

#### References Cited by the Examiner

##### UNITED STATES PATENTS

1,710,445	4/29	Becket	75-170
1,949,313	2/34	Koster	75-170
2,100,218	11/37	Kelley	75-170
2,770,029	11/56	Weltz	75-176 XR

##### FOREIGN PATENTS

407,017 12/24 Germany.

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