

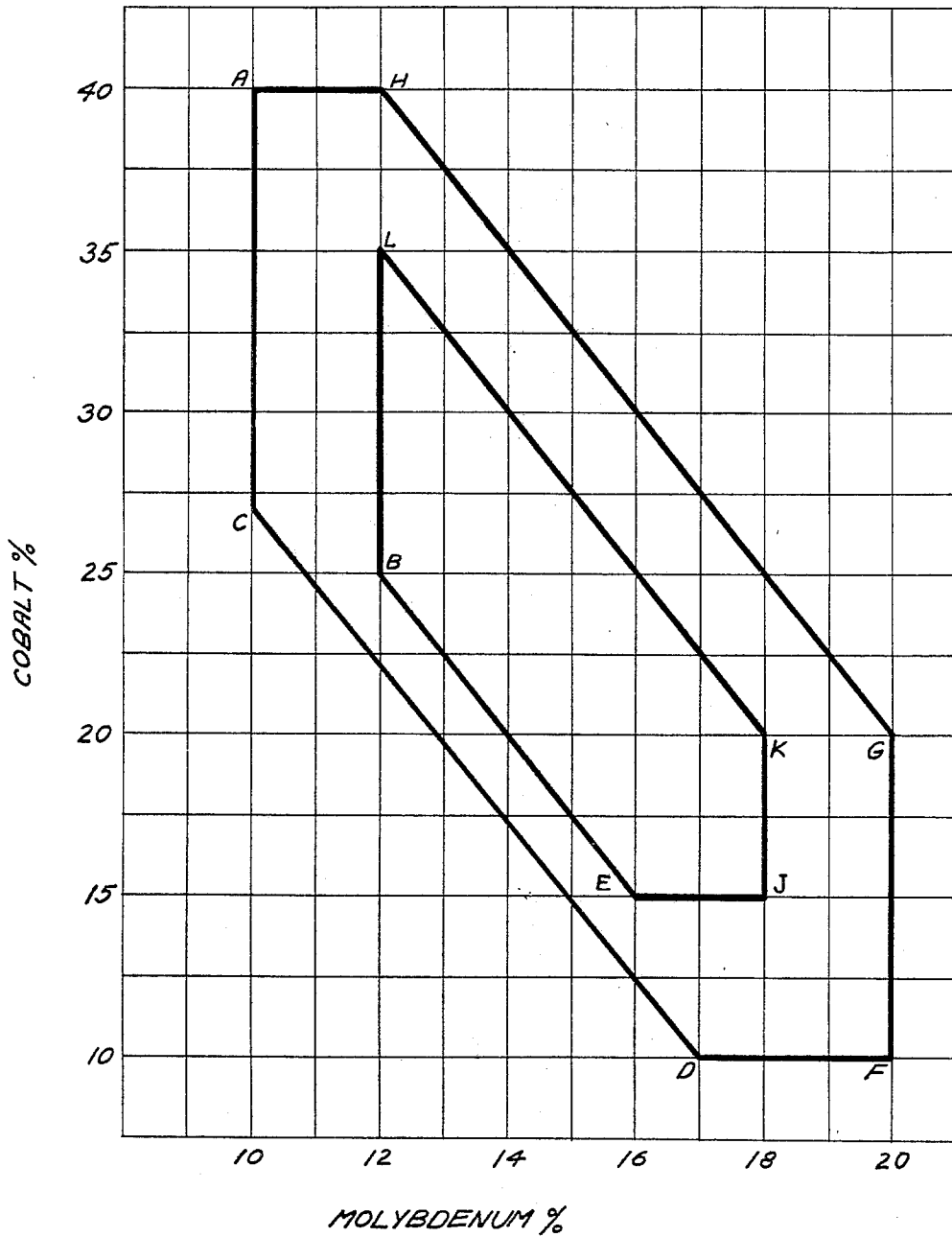
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ULTRA HARD COBALT-MOLYBDENUM-IRON ALLOYS

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**ULTRA HARD COBALT-MOLYBDENUM-
 IRON ALLOYS**

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4 Claims 10

ABSTRACT OF THE DISCLOSURE

Ferrous base alloys containing cobalt, molybdenum and nickel in correlated amounts afford exceptionally high levels of hardness, i.e., up to about Rockwell C (R_c) 70. The presence of other constituents in controlled amounts, notably titanium and/or aluminum, is beneficial.

The present invention relates to ferrous alloys and more particularly to novel, martensitic ferrous alloys capable of affording exceptionally high levels of hardness, to wit, up to about Rockwell C (R_c) 70.

As is generally known to those skilled in the art, research efforts have been somewhat intensified in recent years with the objective of developing alloys characterized by an extraordinarily high order of hardness. This has been brought about, at least in part, as a result of the fact that operating conditions, e.g., temperatures, pressures, etc., have become increasingly more severe in many areas of commercial activity. In turn, this has focused attention on the need for articles of manufacture capable of exhibiting outstanding resistance to wear and abrasion, properties which are a reflection of hardness. Among such articles might be noted dies, including cold drawing dies, bearings, axles, mandrels for drawing tubes, tools, races, etc.

In ferrous metallurgy, alloys in use for purposes contemplated herein usually contain such elements as chromium, cobalt, molybdenum, vanadium, tungsten and substantial amounts of carbon. As high carbon alloys, they are normally quenched, quenching being a prerequisite to achieving maximum hardness. But by the same token, it is this aspect which can give rise to the well known problems associated with distortion. These drawbacks are rather well documented and it will suffice to but mention that measures must be taken to obviate the same. Further, many such prior art alloys manifest an appreciable loss in hardness at moderately high temperatures, it being not uncommon to find alloys characterized by substantial hardness at room temperature but which upon exposure for relatively short periods to elevated temperature undergo a significant loss of hardness. While satisfactory for certain applications, such alloys would not be deemed suitable for relatively high temperature applications on the order of, say, about 1200° F.

It has now been discovered that hardnesses of about R_c 65 to 70 can be achieved with martensitic alloys containing special and correlated amounts of certain constituents, notably iron, cobalt, molybdenum, nickel, carbon, aluminum and titanium.

It is an object of the present invention to provide novel, martensitic ferrous alloys which are ultra hard, i.e., characterized by hardnesses of about R_c 65 and higher.

It is a further object of the invention to provide new and improved ferrous alloys characterized by a hardness upwards of about R_c 65, the hardness level being achieved by simple heat treatment and without recourse to quenching.

Another object of the invention is to provide ultra hard ferrous alloys which greatly resist softening at temperatures as high as 1200° F.

Other objects and advantages will become apparent from the following description taken in conjunction with the accompanying drawing in which there is depicted a chart in respect of cobalt and molybdenum contents pertaining to alloys within the invention as herein more fully described.

Generally speaking and in accordance with the present invention, alloys contemplated herein contain (in weight percent) from 10% to 40% cobalt; from 10% to 20% molybdenum, the cobalt and molybdenum being correlated to represent a point within the area ACDFGHA of the accompanying drawing; nickel in an amount up to 5%, e.g., 1% to 5%; up to 2%, e.g., up to 1%, carbon; up to 1.5%, e.g., up to 1%, titanium; up to 1.5%, e.g., up to 1%, aluminum, the sum of the titanium plus aluminum not exceeding about 1.5%; up to 0.5% manganese; up to 0.5% silicon; and the balance essentially iron. As will be understood by those skilled in the art, the term "balance" or "balance essentially" used in referring to the iron content of the alloys does not exclude the presence of other elements commonly present as incidental elements, e.g., deoxidizing and cleansing elements, and impurities ordinarily associated therewith in small amounts which do not adversely affect the basic characteristics of the alloys. However, elements such as sulfur, phosphorus, hydrogen, oxygen, nitrogen and the like should be maintained at low levels consistent with good commercial practice.

Supplementary elements can be present in the alloys as set forth in Table I.

TABLE I

Element:	Broad range, percent	Preferred Range, percent	Optimum Range, percent
Columbium.....	Up to 2.....	Up to 1.5.....	Up to 1.
Tantalum.....	Up to 4.....	Up to 3.....	Up to 2.
Boron.....	Up to 0.1.....	Up to 0.05.....	Up to 0.01.
Zirconium.....	Up to 0.25.....	Up to 0.15.....	Up to 0.1.
Vanadium.....	Up to 2.....	Up to 1.5.....	Up to 1.
Beryllium.....	Up to 1.....	Up to 0.5.....	Up to 0.1.
Calcium.....	Up to 0.1.....	Up to 0.075.....	Up to 0.05.
Copper.....	Up to 4.....	Up to 2.....	Up to 1.
Chromium.....	Up to 8.....	Up to 5.....	Up to 4.

The total of supplementary elements should not exceed 10%, advantageously being not more than 7%. Tungsten can be used to replace molybdenum in part on an equal atomic basis, i.e., two parts tungsten for one part molybdenum, up to 10% tungsten by weight. However, the alloys are more difficultly workable with tungsten and it is accordingly preferable that tungsten not exceed 6%.

In carrying the present invention into practice care must be exercised with regard to the respective amounts of the constituents in order that the alloys be of a martensitic structure (as distinct from a ferritic or austenitic) and that this structure must be attained before aging; otherwise, full hardness will not be realized. Upon solidification of a melt the alloys are austenitic but the chemistry thereof is balanced such that the alloys transform to martensite upon cooling to, say, room temperature or lower. In relation to each other, excessive amounts of one or more of the primary hardening elements molybdenum and cobalt, or the toughening (brittle resistant) constituent nickel promotes the formation of retained austenite (austenite of such stability that it does not undergo transformation) and consequent loss in hardness. On the other hand, an insufficient amount of one or more of these constituents can lead to steels of the ferritic type as contemplated herein. It is most advantageous in achieving highly satisfactory results that the alloys contain about

15% to 40% cobalt, about 12% to 18% molybdenum and about 2% to 5% nickel with the cobalt and molybdenum being correlated to represent a point falling within the area LBEJKL of the accompanying drawing.

Carbon, while it can be present in the alloys up to 2%, is not at all essential. Where ductility and toughness are especially desired, it should not exceed 0.05% and advantageously should not exceed about 0.03%. But where the presence of carbides would be necessary for a particular application, or otherwise useful, then, of course, higher carbon contents can be employed, e.g., up to 1%. For the purpose of deoxidation, malleabilization and the like, titanium and/or aluminum are beneficial and the presence of one or both of these elements in an amount of about 0.1% to 0.5% each is beneficial. Also, in amounts of about 0.5% to 1.5% these constituents can confer enhanced hardness, particularly where the amounts of cobalt and molybdenum are on the low side; however, the total amount of titanium and aluminum generally need not exceed about 1%.

In processing the alloys, air or vacuum melting practice can be utilized, preferably followed by consumable electrode melting for optimum effects. It is preferred to employ materials of high purity to thereby minimize the occurrence of inclusions, contaminants, etc. Initially formed cast ingots should be thoroughly homogenized as, for example, by soaking, at a temperature of about 2200° F. to about 2300° F. for about one hour per inch of cross section. Thereafter, the alloys can be hot worked (as by forging, pressing, rolling, etc.) and, if desired, cold worked to desired shape. A plurality of heating and hot working operations can be used and are advantageous to assure thorough homogenization of the cast structure through diffusion and to break up the cast structure. Hot working can be satisfactorily carried out over a temperature range of 2300° F. or 2200° F. down to 1400° F., e.g., 2150° F. to 1500° F., with suitable finishing temperatures being about 2000° F. down to about 1500° F. Cooling from hot working is preferably accomplished by air cooling although furnace cooling, quenching, etc., can be employed.

Subsequent to cooling from the hot working tempera-

ture to effect a transformation to the martensitic condition, the steels can be directly aged by heating at a temperature of about 850° F. to 1000° F. for about 100 hours to 0.1 hour, the longer aging periods being used in conjunction with the lower temperatures. Aging at 900° F. to 950° F. for about 1 to 8 hours is satisfactory. Where deemed advisable, a cold treatment, e.g., as by refrigeration or cold working or both, can be used prior to aging. Such a treatment is of benefit in assuring the maximum conversion of austenite to martensite. Further, where deemed necessary, the steels can be subjected to a solution annealing treatment over the range of about 1500° F. to about 2200° F. prior to aging; however, the temperature employed is dependent upon the molybdenum content such that the higher temperatures should be used with alloys containing molybdenum on the high side of the molybdenum range.

For the purpose of giving those skilled in the art a better understanding of the invention, the following description and data are given:

Several alloys, the compositions of which are given in Table II (Alloys 1 to 4 being within the invention and Alloys A through H being outside the scope thereof), were prepared either by air or vacuum melting. Upon solidification ingots were soaked at 2200° F. to 2300° F. and thereafter hot worked (except Alloys E through H which were tested as small cast specimens). The alloys were then subjected to one or more of several different aging treatments given below (in many instances an aging treatment was followed by a higher temperature treatment mainly for the purpose of obtaining relative data as to the ability of the alloys to resist softening):

I—Aged at 900° F. for 4 hours

II—Aged at 900° F. for 8 hours

III—Aged at 925° F.-950° F. for 1 hour

IV—Aged at 1000° F. for 1 hour

V—Aged at 1150° F. for 1 hour

VI—Aged or heated at 1200° F. for 4 hours

VII—Aged or heated at 1200° F. for 8 hours

VIII—Aged or heated at 1300° F. for 1 hour

IX—Aged or heated at 1300° F. for 4 hours.

TABLE II

Alloy:	Co, percent	Mo, percent	Ni, percent	Ti, percent	Al, percent	Heat Treatment	Hard- ness, R _c
1.....	18	18	4	0.2	0.2	I..... II..... VI..... VII.....	57 58 62 60
2.....	30	10	5	0.2	0.2	I..... IV..... V..... IX.....	55 55 53 59
3.....	40	10	5	0.2	0.2	I..... IV..... V..... IX.....	56 56 60 57
4.....	25	15	5	0.2	0.2	I..... VI.....	59 55
A.....	40	20	2	0.2	0.2	VI..... VII.....	52 62
B.....	40	20	4	0.2	0.2	I..... VI.....	35 37
C.....	40	15	0.2	0.2	Broke.....
D.....	35	10	0.2	0.2	I..... VI..... VII..... VIII..... IX.....	58 58 59 58 58
E ¹	10	10	4	0.2	I.....	53
F ¹	20	10	4	0.2	I.....	56
G ¹	25	10	5	0.2	I.....	60
H ¹	45	10	5	0.2	I.....	51

¹ Alloys E through H were solution treated at 2,100° F. for 4 hours before aging. All alloys contained less than 0.05% carbon; Alloys C and D contained 10% and 20% tungsten, respectively.

From the data in Table II, it is clear that alloys within the invention all manifested a satisfactory level of hardness. In addition, Alloys 1 through 3 reflected the capability of resisting softening at relatively high temperatures, e.g., 1200° F. In this connection, it is beneficial that the alloys contain not more than about 4% nickel. In contrast to Alloys 1 to 4, Alloys A to C and E to H all exhibited inferior hardness. Alloy D achieved a satisfactory hardness level but only upon aging at an excessively high temperature, to wit, 1200° F. Alloys which age in the region of 1200° F. to hardness levels contemplated herein have a ferritic base and are usually brittle. A further quite satisfactory alloy range in accordance herewith is as follows: about 18% to 35% cobalt, about 14% to 18% molybdenum, the cobalt and molybdenum being correlated to represent a point falling within the area ACDFGHA of the accompanying drawing, about 1% to 4% nickel, up to 4% tungsten, up to 0.05% carbon, 0.1% to 0.5% titanium, 0.1% to 0.5% aluminum, up to 0.25% manganese, up to 0.25% silicon, and the balance essentially iron.

Where ductility is not of significance, exceptionally high hardnesses can be obtained in the absence of nickel. An alloy containing nominally 40% cobalt, 20% molybdenum, 0.04% carbon, 0.2% titanium, 0.2% aluminum and less than 0.25% each of silicon and manganese with the balance being essentially iron manifested a Rockwell hardness of R_c 71 when aged at 925° F. to 950° F. for one hour. After aging at 1200° F. for 4 hours the alloy retained a remarkably high hardness of R_c 68. However, an alloy of similar composition but nominally containing 0.1% carbon rather than 0.04% carbon only possessed a hardness of R_c 51 when aged at 900° F. for 4 hours and R_c 57 when aged 1 hour at 1000° F. Thus, nickel-free alloys should contain at least 15% molybdenum and at least 25% cobalt, a suitable range being about 17% or 18% to 20% molybdenum, from 35% to about 40% cobalt, up to not more than 0.05% and advantageously not more than 0.03% or 0.04% carbon, up to 0.5% of each of titanium and aluminum, e.g., 0.1% to 0.5% of either or both, and the balance essentially iron.

In addition to dies, bearings, axles, mandrels and races, the present invention is useful in the production of tools such as high speed drills.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily

understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. An alloy consisting essentially of from 25% to 40% cobalt, from 15% to 20% molybdenum, up to 0.05% carbon, at least one metal from the group consisting of titanium in an amount of 0.1% to 0.5% and aluminum from 0.1% to 0.5%, up to 0.5% manganese, up to 0.5% silicon, up to 2% columbium, up to 4% tantalum, up to 0.1% boron, up to 0.25% zirconium, up to 2% vanadium, up to 1% beryllium, up to 0.1% calcium, up to 4% copper, up to 8% chromium, and the balance essentially iron.

2. An alloy according to claim 1 in which the sum of the columbium, tantalum, boron, zirconium, vanadium, beryllium, calcium, copper, and chromium does not exceed 7%.

3. An alloy according to claim 1 and containing 35% to about 40% cobalt, about 18% to 20% molybdenum, up to 0.04% carbon, up to 0.5% titanium, up to 0.5% aluminum, up to 0.5% manganese, up to 0.5% silicon, and the balance essentially iron.

4. An alloy according to claim 3 and containing up to 0.03% carbon, 0.1% to 0.5% titanium, 0.1% to 0.5% aluminum, up to 0.25% manganese, up to 0.25% silicon, and the balance essentially iron.

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45 HYLAND BIZOT, Primary Examiner

U.S. Cl. X.R.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,485,620 Dated December 23, 1969

Inventor(s) CLARENCE GEORGE BIEBER and JOHN RAYMOND MIHALISIN

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, Table II, Alloy A, last column "52" read --53--

SIGNED AND
SEALED
NOV 17 1970

(SEAL)

Attest

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