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Holtz, Jr. et al.

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[54] **HEAT RESISTANT ALLOYS OF IRON,
COBALT AND/OR NICKEL AND
ARTICLES THEREOF**

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[22] Filed: **Dec. 28, 1970**

[21] Appl. No.: **102,203**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 743,921, July
21, 1968, abandoned.

[52] U.S. Cl.**29/180**, 29/182.5, 75/0.5 BC,
75/122, 75/123 J, 75/123 K, 75/134 F,
75/170, 75/176

[51] Int. Cl.**C22c 39/10**, C22c 39/36, C22c 39/50

[58] Field of Search ..29/182.7, 180; 75/123, 0.5 BC,
75/122, 123 J, 123 K, 134 F, 170, 176

[56]

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[57]

ABSTRACT

Alloys of iron, cobalt and/or nickel containing from 0.5 to 4.0% carbon and from 5 to 60% tungsten, molybdenum or mixtures thereof characterized by the absence of "reactive" elements such as Cr, V, Cb, Ta, Ti, Si, Mn and Al. which form hard-to-reduce oxides.

7 Claims, No Drawings

HEAT RESISTANT ALLOYS OF IRON, COBALT AND/OR NICKEL AND ARTICLES THEREOF

This application is a continuation-in-part of application Serial No. 743,921, filed July 11, 1968 by the same inventors and now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to heat-resistant alloy articles and particularly to an inexpensive heat-resistant alloy which is readily workable and castable. The present invention provides alloys which are not only heat-resistant but have excellent strength and hardening ability and have particular utility in the fabrication of cutting tools, dies and wear parts, or for use as a structural alloy.

2. Description of the Prior Art

The development of alloys based on iron, cobalt, and nickel has been characterized by increasing emphasis on the ability of these materials to withstand elevated temperature environments. The structural alloys are used for such applications as turbine buckets, nozzle vanes, rotor discs, combustion liners, and other turbojet engine parts, as well as furnace parts, exhaust manifolds, high pressure steam piping, valves, and other fittings which must sustain loads at high temperatures. In addition, there are numerous tool and die applications which require both strength and wear resistance at elevated temperatures. These include tools for metal cutting and the many metalworking operations such as swaging, forging, rolling, wire drawing, shearing, and extrusion which are carried out under severe conditions of heat and sliding friction.

These thermal-resistant tool, die, and structural materials may be made by various techniques such as casting directly to shape, forging or rolling, and powder metallurgy. Their major constituent may be iron, nickel, or cobalt, and they are further strengthened by a wide range of alloying elements. However, they have one characteristic in common: all contain additions of reactive metals. A reactive metal is an element characterized by a high negative value for the free energy of formation of its oxide or oxides. Stated in another way, the oxides of reactive metals are increasingly difficult to reduce to the metallic state as the free energy of formation rises to higher negative values. For the purpose of this discussion, a value of $-40\text{K cal/gram-atom}$ of oxygen at $1,500^\circ\text{K}$. represents the dividing line between reactive and non-reactive. Thus M_2O_3 with a value of $-32\text{K cal/gram-atom}$ can be reduced by the H_2 or other reductants at comparatively low temperatures, i.e., $1,600^\circ\text{F}$., while Al_2O_3 with a free energy $=-95\text{K cal/gram-atom}$ is reducible only at extremely high temperatures.

An examination of compilations of thermal-resistant tool, die and structural alloys of the prior art shows that all conventional compositions contain chromium ($-58\text{K cal/gram-atom}$). A listing of 30 commercial nickel-base high-temperature alloys gives a range of 10 to 27 percent chromium. A similar listing giving compositions of the thermal-resistant cobalt-base tool alloys which have been marketed shows a chromium range of 18.5 to 31 percent. All 29 commercial high speed steels (AISI designation T and M series) contain 3.75 to 4.25 percent chromium, and the 18 AISI type H

hot die steels contain from 2 to 12 percent of this reactive element.

Chromium is added to these alloys primarily because of its beneficial effect upon oxidation resistance and, in the case of tool steels, its ability to give a moderate increase in the depth of hardening. Its primary drawback is the fact that its oxides are extremely difficult to remove by chemical means. Other reactive elements are also added to nearly all of the iron, cobalt and nickel thermal-resistant alloys. These elements include AL, Cb, Mn, Si, Ta, Ti, V, Zr, etc. These elements generally promote alloy strengthening or wear resistance but, as in the case of chromium, their oxides are also very difficult to reduce. Alloys containing reactive metals suffer an additional limitation in that during melting, the reactive elements present require additional protection from the atmosphere and they also react with common refractory crucible materials such as alumina, magnesia, silica, etc. This means that inert atmospheres such as argon or a vacuum and extremely inert crucible materials (beryllia, thoria, zirconia) be used or else melting must be done by arc-melting in a water-cooled copper crucible. There are obvious economic drawbacks in using these special melting methods.

SUMMARY OF THE INVENTION

The present invention provides a thermal-resistant alloy free of "reactive" elements such as chromium and vanadium, consisting essentially of about 0.5 percent to 4.0 percent carbon, about 5 percent to 60 percent of a carbide-former selected from the group consisting of "nonreactive" elements, such as tungsten, molybdenum and mixtures thereof, and the balance being M with usual impurities in ordinary amounts, wherein M is base metal selected from the group consisting of iron, cobalt, nickel and mixtures of two or more of these elements. Such alloys exhibit increased cutting speed capabilities and wear resistance by providing structures free from embrittling oxides, thereby permitting higher carbide volumes and larger contents of refractory metal alloying elements such as tungsten and molybdenum which appreciably improve the elevated-temperature strength properties. These alloys are harder than any heretofore known cast or wrought tool or die alloys based on iron, nickel or cobalt, and they gave cutting performance far superior to the conventional tool steels which were tested for comparison purposes. Further, such alloys have been found to have excellent high temperature strength, very high transverse-rupture bending strength, exceptional response to heat treatments, very high fabricability, and the ability to be produced from very low cost powders.

Also provided by the present invention are structural alloys for use in applications where great strength at high temperature is required. Such alloys are prepared by reducing the carbon content of the alloy composition set forth above to lower the hardness of the alloy to Rc 55 or below and increase the toughness. The solid-solution strengthening provided by the high tungsten and molybdenum levels results in alloys which are capable of withstanding severe mechanical stress at elevated temperatures above about 700°F . for prolonged periods of time. Moreover, these new tool and structural alloys, can be produced with an ultrafine

microstructure, and are readily hot workable into wrought products.

It is a feature of this invention that the alloys produced contain only "nonreactive" alloying constituents capable of forming compounds with oxygen which have a negative free energy of formation (K cal/gram-atom of oxygen) at 1,500° K. equal to 40 or less. Accordingly, "reactive" elements are defined herein as elements capable of forming compounds with oxygen, which compounds have a free energy of formation in the range of -41 to -100 and lower. Examples are given below:

Oxides Formed by "Reactive" Elements	Free Energy of Formation (1500°K)
V ₂ O ₅	-48
Cr ₂ O ₃	-58
Cb ₂ O ₅	-62
MnO	-66
Ta ₂ O ₅	-67
SiO ₂	-72
TiO ₂	-80
Al ₂ O ₃	-95

Oxides Formed by "Nonreactive" Elements	Free Energy of Formation (1500°K)
NiO	-27
CoO	-27
MoO ₃	-32
WO ₃	-38
Fe ₃ O ₄	-38

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The broad composition of alloys within the present invention is as follows:

About 0.5 - 4.0 percent carbon

About 5 - 60 percent of a "non-reactive" element whose oxides are easily reduced at low temperatures, and the remainder being M with usual impurities in ordinary amounts, wherein M is iron, cobalt, nickel or a mixture of two or more of these elements. All of the alloys are characterized by the complete absence of "reactive" elements such as Cr, V, Cb, Ta, Ti, Si, Mn and Al.

Molybdenum and tungsten are "non-reactive" elements which are carbide formers. Each may be absent altogether or present up to a maximum of 60 percent. Accordingly, the outside limits of such use in accordance with the present invention are:

Mo	about	0 - 60%
W	about	0 - 60%
Mo + W	about	5 - 60%

The invention will be better understood by a consideration of the examples wherein the various embodiments will be brought out in detail. Several different compositions of material were melted to form an alloy according to this invention. Illustrative compositions of these materials are given in Table I.

TABLE I

Alloy Compositions, Weight Percent

alloy	Fe	Co	Ni	W	Mo	C
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A76	—	45	—	47.25	5	2.75
A81	—	62.5	—	10	25	2.5
A82	—	37.5	10	45	5	2.5
A83	—	42.5	20	10	25	2.5
A91	—	37.5	10	35	15	2.5
A106	—	57.5	—	—	40	2.5
A113	—	56.5	—	—	40	3.5
A136	58.7	20	—	20	—	1.3
A137	38.7	40	—	20	—	1.3
A138	—	53.7	—	20	25	1.3
A146	28.1	50	—	20	—	1.3
A147	38.7	40	—	10	10	1.3
A151	38.7	40	—	—	20	1.3
A152	38.9	39.9	—	19.9	—	1.3
A163	39.2	40	—	—	20	0.8
A164	38.33	40	—	20	—	1.67
A165	39.2	40	—	20	—	0.8
A169	34	34.7	—	—	30	1.3
A170	34	34.7	—	30	—	1.3
A171	34	34.7	10	20	—	1.3
A172	34	34.7	10	—	20	1.3

The alloys of the present invention can be prepared using recognized present-day melt procedures for iron-base, cobalt-base and nickel-base alloys. Alloy articles are produced by employing alloying, melting, casting, forging, sintering and other foundry techniques as known to one skilled in the art. Each of the alloys and articles made therefrom can be produced free of deleterious oxides by chemical deoxidation procedures.

It is a feature of this invention that metal and metal powders of the defined composition characterized by the absence of the "reactive" elements chromium, vanadium, columbium, tantalum, titanium, silicon, manganese and aluminum, are easily reduced chemically and oxides removed, e.g., by using carbon present in the alloy composition as a reducing agent. In this process, an alloy powder is jacketed in a thin-walled container, and the canned powder heated to a temperature in the range of about 1,700° to 2,100° F. A small vent can be provided for escaping gases of CO and CO₂. However, it is not necessary that a vent be provided or that the container be evacuated. 100 percent dense, oxide-free alloy stock is produced by extruding the "self-cleaned" powder into a bar and removing the jacketing material. Alternatively, the heated canned powder can be consolidated by hot pressing followed by forging, rolling and removal of the cladding.

It has also been found that it is not necessary to jacket the powders in order to remove oxide films from powders which have low softening temperatures. For example, in the case of the tool steel powders, cobalt and nickel structural alloy powders, and some cobalt base tool alloy powders, which can be softened by annealing in the temperature range of about 1,400° to 1,700° F., the alloy powders can be cleaned and softened in one step by heating them to such temperature in a reducing atmosphere of hydrogen, cracked ammonia, a hydrocarbon gas, such as methane, a mixture of CO and CO₂, or the like. After annealing the powder by slow cooling, it can be cold pressed at room temperature to form an easily handled billet. Subsequently, the billet of material is heated to about 2,000° F. in a protective atmosphere such as nitrogen, argon or the like, and extruded into 100 percent bar stock.

As a specific example of the process for making an oxide-free alloy in accordance with the present invention, the production of alloy A 138 of the foregoing Table I will be considered in detail. In this example the

alloy is made by powder metallurgy process, although it is to be understood that other methods of producing alloys can also be used.

An appropriate alloy charge, e.g., 5 pounds, of the desired composition (Co — 20W — 25Mo — 1.3C) was weighed out, melted in an induction furnace (or other suitable melting device), and atomized/quenched using a conventional atomizer. Suitable apparatus is disclosed in copending application Ser. No. 435,733, entitled "Alloy Composition and Process" filed Feb. 26, 1965, by the present inventor. The molten stream was broken up into fine particles which were quickly quenched by the high pressure inert gas stream and by the water utilized as a collection medium. The oxygen content of dried alloy powder produced in this manner was in the order of about 500 1,000 part per million.

The atomized alloy powder was then consolidated into solid stock by the following process. The powder was first enclosed in a sealed Inconel can without evacuation and with no provision for venting gas formed during subsequent heating. The welded can was heated to a temperature of approximately 2,050° F. prior to open-die, upset hammer forging on a 250 pound capacity mechanical forge unit. Forging was used to produce pancake ingots approximately one-half inch thick. After forging, the canned billets were hot rolled to approximately 0.22 to 0.24 inches using a 10 percent reduction per pass, this representing a total reduction in thickness of 90 to 92 percent of the original billet thickness. The cladding material was then removed and the rolled plate stock sectioned for metallurgical examination and mechanical property evaluations. Visual examination of photo-micrographs of the consolidated powder showed that the alloy stock was free of oxides and exhibited an ultrafine microstructure. Additional properties demonstrating that adequate hardness and thermal stability had been achieved were apparent from the following measurements:

Hardness, as-rolled	Rc 60.6
Hardness, aged at 1300°F.	Rc 66.6
Coarsening temperature	2350°F.

By lowering the carbon content of alloy A 138 (e.g., to 0.5 percent carbon) the hardness falls to a level below Rc 56 permitting use as a structural alloy. The alloy is readily hot-workable and has the ability to withstand severe mechanical stress at elevated temperatures above 700° F. for prolonged periods of time due to the solid-solution strengthening provided by the high tungsten and molybdenum levels.

The alloys of the present invention were tested for hardness and bend tests were conducted at room temperature to ascertain transverse rupture strengths. Data illustrating the test results are given for exemplary alloys in Table II.

TABLE II

Alloy Properties Consolidated Powder Alloy	Hardness (Rc)	Transverse Rupture Strength (psi)
A76	63.0	264,000
A82	62.2	333,000
A91	61.1	283,000
A137	72.0	279,000
A146	66.0	518,000
A151	71.4	282,000

The foregoing test results demonstrate that the tool alloys of the present invention possess excellent strength and are capable of exhibiting high hardness levels.

Cutting tests were performed using exemplary alloys of the present invention by operating the tools in comparison with what is believed to be the best prior art alloy for the service indicated. The tool life tests were obtained on Inconel 718 which is a commercial superalloy widely used in jet engines and considered among the most difficult-to-machine materials in existence. Tool alloys of the present invention were compared with the commercial high speed steel known as M43 having the following composition:

Fe — 8.7 Mo — 1.8W — 3.75 Cr — 2.0V — 8.2 Co — 1.23C.

Each of the tools, ground to the same geometry, was used to cut the test bar of Inconel 718 on a machinability lathe at 25 surface feet per minute, 0.0625 inch depth of cut, 0.005 inch/rev. feed, using a conventional coolant. A wear land of about 0.030 inch on the tool was used as the end point of the test. The results of these tests are shown in Table III.

TABLE III

Lathe Turning Test Data On Inconel 718, BHN 375

Tool Alloy	Heat Treatment	Tool Life (min.)
M43	2200°F. approx. 4 min. salt quench 1050°F. 5 min. 975°F., 2 hr + 2 hr + 2 hr	6
A138	1300°F., 25 hr	9
A136	2350°F., 3 min.* 1000°F., 2 hr + 2 hr	34
A137	2350°F., 3 min.* 1000°F., 2 hr + 2 hr	52

* oil quenched

The above results demonstrate that excellent tool life has been obtained on difficult-to-machine commercial alloys using novel alloy materials produced according to the present invention.

Alloys A 136 and A 137 are capable of being annealed so that cold pressing of their powders can be accomplished. Bar stock prepared by forging and rolling was found to be of excellent quality. Alloy A 136 was found to have a coarsening temperature of 2,325° F. and an even higher coarsening temperature was noted for alloy A 137. The ultrafine carbide particle size of this latter alloy was unchanged after 1 hour at 2,350° F. Both alloys responded to "quench and temper" hardening treatments similar to those given high speed steel. In the case of A 137, a maximum hardness of Rc 88 (Rc 72) was obtained. This value is higher than the hardness of any commercial high speed steel or cobalt base tool alloy known, and is in the range of hardness encountered in sintered carbides.

While there have been described and disclosed certain preferred embodiments of the invention in the foregoing specification, it will be understood that this invention may be otherwise embodied within the spirit and scope of the following claims.

What is claimed is:

1. A readily workable, oxide-free, thermal-resistant, alloy stock material consisting essentially be weight of about 0.5 - 4.0 percent of carbon, about 0 - 60 percent of tungsten, about 0 - 60 percent of molybdenum, wherein the total amount of tungsten plus molybdenum is in the range of about 5 - 60 percent, and the balance being base metal with usual impurities in ordinary amounts selected from the group consisting of iron, cobalt, nickel and mixtures thereof, wherein the amount in said alloy of any element capable of forming an oxide having a negative free energy of formation value higher than 40 cal/gram-atom of oxygen at 1,500° K. does not exceed the amount of such element usually present with said base metal as an ordinary impurity.

2. An alloy according to claim 1 suitable for use as a tool alloy, wherein said alloy has a hardness above Rc

56 and the ability to hold a cutting edge under high temperatures generated during metal cutting and to resist softening at temperatures of 1,000° F. and above.

3. An alloy according to claim 1 suitable for use as a structural material, wherein said alloy has a hardness below Rc 56 and the ability to withstand severe mechanical stress at elevated temperatures above 700° F. for prolonged periods of time.

4. An alloy in accordance with claim 1, in which the alloy contains about 0 - 90 percent cobalt.

5. An alloy in accordance with claim 1, in which the alloy contains about 0 - 90 percent nickel.

6. An alloy in accordance with claim 1, in which the alloy contains about 0 - 90 percent iron.

7. A fully dense, consolidated powder article of the alloy of claim 1.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,698,055 Dated October 17, 1972

Inventor(s) Frederick C. Holtz, Jr. and Hugh Morrow, III

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

Column 1, line 51, change " M_oO_3 " to " MoO_3 ";

Column 1, line 54, change "~~—~~95K" to "~~—~~95K".

Signed and sealed this 15th day of May 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

UNITED STATES PATENT OFFICE
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