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PREPARATION OF METALS AND ALLOYS OF MOLYBDENUM, NICKEL, COBALT, AND TUNGSTEN

John S. Nachtman, 212 Sandal Lane, Riviera Beach, Fla., and Henry Gordon Poole, 1812 W. 12th Ave., Albany, Oreg.

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This invention relates to methods of beneficiating metallic compounds and recovery of metals therefrom as well as the resulting products, and includes the production of novel types of metals having unique properties and methods for producing such products.

This application is a continuation-in-part of application Ser. No. 716,033, filed February 19, 1958, entitled "Recovery of Metals by Use of Lead," now U.S. Patent No. 3,090,686, which is a continuation-in-part of application Ser. No. 429,674, filed May 13, 1954, now Patent No. 2,834,671, and of application Ser. No. 642,377, filed February 26, 1957, now Patent No. 3,020,151.

The present commercial process for producing molybdenum by the hydrogen reduction of sublimed and recrystallized molybdenum trioxide makes it difficult to control oxygen without additions of carbon or aluminum during the arc-melting operation, resulting in detrimental effects of oxygen, nitrogen and carbon upon the physical properties of, for example, molybdenum.

One rather obvious approach would be the direct reduction of molybdenite (MoS_2) to metal in a controlled atmosphere. This might be accomplished by at least four direct methods:

I. Thermal decomposition
II. Hydrogen reduction
III. Carbon reduction
IV. Silicon reduction

Thermodynamically silicon is a most desirable reduction agent since it forms a volatile sulfide at say a temperature of 1227° C. (1500° K.). However, silicon reacts with molybdenum to form a refractory silicide. Carbon also forms a refractory carbide with molybdenum, and this method also is found wanting. Further an examination of the equilibria for either thermal decomposition or hydrogen reduction indicates a slow reaction rate at 1500° K. particularly with the former method.

For this type of metallurgical process substantially a complete reaction is needed, circa 100% reduction.

Accordingly prior art methods of producing certain metals from their ores or other compounds, such as molybdenum from molybdenite, involve needless repetitive processing, and also result in the production of contaminated metal.

Among the objects of the present invention is the production of metals—namely, molybdenum, cobalt, nickel and tungsten, by thermo-chemical treatment of their compounds utilizing reducing agents which result in metals free from contamination with impurities commonly present in such metals produced by prior art processes.

Further objects include the production of such metals free from oxygen, chlorine or other halides, sulfur, hydrogen, nitrogen, carbon, silicon, and alkali metals.

Further objects include methods of decontamination of metals produced by other processes.

Further objects include metals resulting from these processes which metals have unique compositions and exceptionally high standards of purity, and it is a principal object of the present invention to produce metal and alloy systems formed of such relatively pure molybdenum, cobalt, nickel and tungsten in combination with various

metals and metal oxides which will hereinafter be described.

Still further objects and advantages of this invention will appear from the more detailed description set forth below, it being understood that such more detailed description is given by way of illustration and explanation only, and not by way of limitation, since various changes therein may be made by those skilled in the art without departing from the scope and spirit of the present invention.

In accordance with the present invention, metals are produced by thermochemically treating a sulfide of the metal desired, particularly cobalt, nickel, tungsten and molybdenum, with lead or with tin, the treatment being carried out in a non-oxidizing atmosphere, desirably in the presence of hydrogen, helium or argon, or mixtures thereof at a temperature generally above about 1100° C. sufficient to produce a beneficiated metal. The process will be described with reference to the production of molybdenum and alloys thereof but it will be understood that these same concepts can be employed with others of the metals, cobalt, nickel and tungsten.

The process permits the production of molybdenum metal shapes by one stage reduction, compaction, pressure welding and sintering, without atmospheric contamination.

The process will be illustrated by the production of high purity molybdenum and reduced cost free from undesirable contaminants and by methods utilizing lead or tin which thus make it possible to avoid needless repetitive processing heretofore required in prior art processes. It has thus been found that sulfides of molybdenum may be subjected to direct reduction by lead or tin in a non-oxidizing atmosphere, as for example in the presence of a non-oxidizing gas, e.g., hydrogen, helium or argon, or mixtures thereof at temperatures above about 1100° C. Lead and tin, which are high boiling point metals, form a volatile sulfide and thus make them feasible for the stated purpose. Since stannous and plumbous sulfide at the order of temperatures stated have a vapor pressure that greatly exceeds the vapor pressures of molybdenum sulfide ores, its thermal decomposition products, and molybdenum vacuum systems may be utilized to accelerate the desulfurization reaction, and rapidly to purify the molybdenum residue, including direct reduction by lead or tin in the presence of, for example, hydrogen. While the description hereafter will make reference to the use of lead as the reducing agent, it will be understood that similar usage can be made of tin or lead and tin.

In the reduction of molybdenite, for example by lead, in the absence of hydrogen, the probable major reactions are:

$$2MoS_2 \rightarrow Mo_2S_3 + \tfrac{1}{2}S_2$$
$$Mo_2S_3 + 3Pb \rightarrow 2Mo + 3PbS$$
$$Pb\ (l) \rightarrow Pb\ (g)$$
$$2Pb + S_2 \rightarrow 2PbS$$

Other reactions, probably of minor character are:

$$MoS_2\ (s) \rightarrow Mo_2S_3\ (g)$$
$$Mo_2S_3\ (s) \rightarrow Mo_2S_3\ (g)$$
$$Mo\ (s) \rightarrow Mo\ (g)$$

In the presence of hydrogen, the latter enters the reactions for desulfurizing molybdenum in two ways. One is aiding the decomposition of molybdenite to the sesquisulfide and the other is in decomposing the lead sulfide. These uses can best be summarized in the following series of reactions:

$$2MoS_2 + H_2 \rightarrow Mo_2S_3 + H_2S$$
$$Mo_2S_3 + 3Pb \rightarrow 2Mo + 3PbS$$
$$3Pbs + 3H_2 \rightarrow 3Pb + 3H_2S$$

But actually the use of hydrogen alone is unsatisfactory because of equilibria factors. A comparison with lead, shows that in a 12 hour period with H_2, 90% of S_2 is removed while a 2 hour period with lead removes —100% of S_2. Further excessive quantities of hydrogen sulfide are avoided.

The fact that hydrogen reduces the plumbous sulfide during the regular run subsequent to the desulfurizing of molybdenum, despite less favorable equilibrium data, is kinetically sound since this latter reaction is a gas-gas reaction to produce a gas and a liquid rather than a gas-solid to produce gas-solid.

In an actual run at 1250° C. with lead reacted with molybdenite, MoS_2, under atmospheric pressure, using stoichiometric amounts of lead, namely 30 parts by weight of MoS_2 and 77.6 parts of lead, there were obtained 20 parts of molybdenum plus Mo_2S_3, 90 parts of lead sulfide, PbS, and 8 parts of lead, the resulting pellet having an unreacted core of Mo_2S_3. By using 20% excess of lead over the stoichiometric amount, namely, 30 parts of MoS_2 with 93 parts of lead, there was obtained 18 parts of molybdenum, 90 parts of PbS, and 15.5 parts of lead, and the resulting pellet showed no reacted core.

After completion of the reduction of molybdenite to metal, a vacuum system at the reaction temperatures permits the volatilization and removal of any excess metallic lead if desired, leaving the metallic molybdenum free of both sulfur and lead.

During reaction in an atmosphere of hydrogen, lead sulfide formed is reduced in the presence of dry hydrogen to return lead to the reaction. Also lead sulfide which is carried over may be reduced by known procedures and the recovered lead returned to the system. Accordingly the lead process can be carried out in hydrogen with the following advantages:

(1) The metallic lead is not consumed since it is readily regenerated with hydrogen.

(2) The carbon content is controlled by hydrogen without the use of oxide additions other than low partial pressures of water for fixed carbon.

(3) The cost for vacuum equipment can be eliminated for molybdenum powder production. This also simplifies retort design.

(4) The circulating hydrogen can be desulfurized by cold traps or other methods and recirculated.

(5) The reaction rates and temperature requirements are maintained at readily attainable levels.

The reactions may be carried out over a wide range of temperatures and periods of time. The temperature employed should at least be about 1100° C. and may be as high as 1450° C. or even higher, the temperature being pressure dependent since it is desired to retain lead in the liquid phase; but from 1200° to 1300° is preferred. The time may be from about 1 to 4 hours, but two hours is a preferable time period. Pressures may vary. The basic lead reduction is not materially affected by the atmosphere. Helium, hydrogen and argon are desirably utilized at atmospheric pressure. The time may vary with temperature and rate of flow of the non-oxidizing gas present. In hydrogen-lead reduction 3.0 is a desirable lead to molybdenite ratio whereas the stoichiometric ratio is 2.59. The rate of gaseous flow may vary. For example, hydrogen may be used for an 8 hour run at a rate of 1 cu. ft./hr.; for 4 hours at 2 cu. ft./hr.; or 4 cu. ft./hr. for 2 hours.

The following considerations apply to the control of purity of the molybdenite concentrate. Some of the highest grade products on the market, advertised at 99+% molybdenite actually contained 1.16+% carbon resulting from cracking of petroleum oils during their distillation from raw concentrate.

The processing of raw materials has become an important phase of this work since some of the commercially available materials seem to have been inadvertently contaminated with carbon. One concentrate obtained by prior art methods, appears to be of two qualities:

(1) Grade I—7.5% oil, .34% insolubles, .12% Fe, .01% Cu.
Grade (distilled) II—1.06% C, .37% $SiO_2+Al_2O_3$, .13% Fe, .01% Cu.
Grade (leached) III—1.16% C, .01% $SiO_2+Al_2O_3$, .16% Fe, .01% Cu.
(2) Regular grade—5.0% oil, 5.5% insolubles, 1% Fe.

Another source shows concentrates with three nominal grades and little or no hydrocarbons:

(1) High grade 85% MoS_2, 0.15% Cu
85% MoS_2 0.50% Cu
80% MoS_2, 1.25% Cu

A sample of high grade No. 1 shipped 7/7/53 analyzed as follows: 92% MoS_2, 5.00% insolubles, 0.120% Cu.

The procedure desirably used for preparing molybdenite for reduction processes desirably uses the following procedures:

(1) Solvent extraction or distillation of oils in H_2.
(2) Leaching with hydrofluoric+hydrochloric acids to remove oxides and allied impurities.
(3) Washing and drying.

While the oils may largely be removed by solvent leaching, as by organic solvent such as acetone, distillation in H_2 is more desirable. Molybdenite particle size is not critical. Sizes available in commercial products average for example 5–7 microns, 13–17 microns, etc. No differences have been experienced. Lead has been used for example at 200 mesh, 30 mesh, and 20 mesh; also as a molten bath. No differences have been detected but for operations on a laboratory scale, minus 20 mesh is preferred.

As illustrative of beneficiated molybdenite products which are obtainable by the preferred process to control purity of the molybdenite concentrate, the following is given, in tabulated form; the feed being the initial molybdenite material, the retort product being that after the heat treatment of the initial material in an atmosphere of hydrogen to give a roasted concentrate, and the final leach product being the molybdenite material ready for H_2-Pb reduction to produce molybdenum metal.

	MoS_2, percent	N_2O, percent	Oil, percent	$SiO_2+Al_2O_3$, percent	Fe, percent
Feed	70–80	10–15	5–6	4–6	0.2–1.0
Retort Product	89–94	0	0	5–7	0.3–1.2
Final Leach Product	99.5	0	0	0.05–0.1	0.05–0.07

The product is substantially free of carbon, iron and associated impurities. The small amounts of

SiO_2+Al_2O

may be beneficial.

THE ADVANTAGES

(1) The presence of H_2 during reduction permits a close control of carbon content, since molybdenite is a hydrogenation catalyst.
(2) The presence of H_2 permits the plumbous sulfide to be partially reduced to metallic lead for reuse in process.
(3) The presence of H eliminates the need for vacuum reactors, hence curtails process cost.
(4) The presence of H_2 ultimately eliminates the consumption of lead, since it itself is consumed and is contained in a final product, combined, as H_2S.

CHEMICAL ANALYSES OF PRODUCTS

Sample No.	Percent C	Percent S	Percent Acid Insol.	Percent Fe
238	.003	.003	0.10	0.09
239	.005	.003	0.08	0.12
243	.011	----------	0.05	0.04
265	.002	.003	0.05	0.09
266	.002	----------	0.05	0.07

This final leach product may be compared with prior art commercial products prior to the present invention and which show:

PRESENT COMMERCIAL PRODUCTS

98.5% MoS_2, 1.16% C, 0.05% $SiO_2+Al_2O_3$, .16% Fe

While small quantities of the alumina and iron remain, some of the silicon is removed as silicon monoxide, the remaining quantity being silica. Iron can also be controlled by special treatment. Most of the copper and tin report in distilled lead sulfides.

It would appear that most of the market available concentrates may be treated for producing metal without using the special high grade.

The wet HF leaching is satisfactory in plastic containers. There is no need for heating the mixture, prolonged washing with acid helps remove iron.

The preparation of materials for reduction in the furnace may use various techniques. Loosely mixed granular lead and molybdenite will react; however, it is preferred and recommended that the materials be briquetted. This briquetting may for example be carried out as follows:

(*a*) Mixture of MoS_2 and granular lead is briquetted. For example, in small scale operations both ½ inch and 1 inch round dies have been employed with pressures of 8,000–25,000 pounds per square inch.

(*b*) The MoS_2 may be briquetted and partially or wholly immersed in liquid lead. Under conditions so far employed the MoS_2 and lead should be in contact. The molybdenite briquette is not normally wetted by molten lead at atmospheric pressures and low temperatures.

Consideration should be given to vapor pressures. Lead boils at 1750° C. and at the boiling point of lead sulfide (1250–80° C.) has a vapor pressure of 20 to 30 mm. Hg. The lead may boil off at the reaction temperature, so that at least 20% excess lead is desirable. Furthermore the molten lead does not wet the decomposing molybdenite as did the tin, therefore it is desirable to enclose the reacting pellet partially so that the lead does not run away. This may be done by placing the pellet of 20 mesh granulated lead plus molybdenite compressed at 10,0000 to 20,000 lbs. per sq. in. in a molybdenum boat.

The molybdenum metal briquettes, when produced, are sponge-like and capable of recompression. The grain size of the reduced molybdenite is very small and approximates 2–3 microns. However, it will vary with source of raw materials.

Various additives may be employed in the practice of this invention by way of addition to the pure metals obtained or by way of combination with the metal sulfides during the reduction step. These additives and additions may be conveniently considered in two general classes as follows.

I. Additions made before or during reduction of the sulfide of the metal:

(*a*) The oxides and the oxygen bearing compounds of the metals Ni, Cr, Zr, Ti, Co, Ta, Th, W, Hf, Al, Cb, Be, Ir and the rare earths in which the oxygen bearing compounds may be in the form of zirconates, titanates, aluminates, aluminites, carbonates, etc.

II. After reduction of the sulfide of the metal to a purified metal or powder:

(*a*) The oxides and oxygen bearing compound of the

metals Ni, Cr, Zr, Ti, Co, Ta, Th, W, Hf, Al, Cb, Be, Ir and the rare earths in which the oxygen bearing compounds may be in the form of zirconates, titanates, aluminates, aluminites, carbonates, etc.

The above additions may be added to the metal powder for treatment by well known powder metallurgy techniques and then sintered and briquetted. In addition to sintering in an inert atmosphere, treatment of the mixtures to produce final products include induction melting, arc melting for the production of finished ingots, or other standard commercial procedures for bonding metal powders. The sintered material may be hot pressed, extruded, cold rolled and the like to form products of the desired shape and characteristics.

Since in the processes of the present invention, it is desired to make ductile metal, i.e., molybdenum, substantially free from oxygen, hydrogen, and nitrogen, the addition of oxides or oxygen containing compounds is for the purpose of obtaining certain desirable physical and mechanical properties over a broad temperature range and also to a controlled extent the oxidation of molybdenum at elevated temperatures. Thus certain oxides and oxygen bearing compounds are added to control grain size or to clean up grain borders.

The metal and alloy additions, as well as oxide additions, are also for the purpose of obtaining certain desirable physical and mechanical properties in the metals. The amounts of the additions may vary with the additives and the metal to which added. In general, oxides or oxygen bearing compounds may be added in amounts by weight of about 0.01 to 5% on the weight of the metal to which they are added. The amounts of metal or alloy additives may vary much more widely, such as within the range of 0.1 to 25% by weight of the metal. Nor are the various additives equivalents in their actions since, for example, oxides and oxygen bearing compounds have different effects upon the pure metal to which they are added, depending on the addition made.

In the fabrication of products with one or more of the metals nickel, cobalt, molybdenum and tungsten in combination with one of the oxides in Group II(*a*), it is preferred to make use of the combination which embodies the metal with an oxide other than that of the particular metal. For example, in the fabrication of products with the combination of molybdenum and an oxide of group II(*a*), it is preferred to make use of the combination of molybdenum with an oxide other than molybdenum.

Example 1

To the molybdenum powder, produced in accordance with the practice of this invention, addition is made of 0.1–5% by weight of zirconia. The mixture is sintered at 1800–2600° C. in a non-oxidizing atmosphere and then hot pressed to form a cermet having improved physical and mechanical properties.

Instead of zirconia any one or more of the other oxides named in II(*a*) can be susbtituted for the zirconia in the above example in the amount described.

Instead of hot pressing, the mixture can be milled, extruded, or rolled at elevated temperatures to the product or form desired.

Example 2

Tantalum in metallic form and finely divided is mixed with the molybdenum powder in an amount within the range of 1–25% by weight. The mixture is sintered at 1800–2700° C. and then the sintered product is mechanically worked to the shape desired for a cermet.

Instead of tantalum, one or more of the other metals named in I(*a*) can be substituted in the above Example 2 in the amount described.

Instead of hot pressing the sintered product, the mixture can be milled, extruded, or rolled at elevated temperature to the product or form desired.

It will be found that the modification of the metal molybdenum, nickel, cobalt, or tungsten which may be produced in accordance with the practice of this invention will be improved by the additions of one or more of the metal oxides of Group II(*a*) at least insofar as room temperature compressibility.

It will be found further that modification to include one or more of the metals in Group I(*a*) will be effective to clean up grain boundaries and improve crystal structure.

A particularly desirable combination comprises the addition of oxides of Group II(*a*) or rare earth metals to metal powders formed of a metal having a melting point above aluminum to produce desirable products by the powder metallurgy techniques.

While the invention has been particularly described with respect to reduction of molybdenum, cobalt, nickel and tungsten containing sulfide ores by use of lead or tin, in many instances it is desirable to use an alloy of lead with tin for reduction, desirably in eutectic ratios. Not only may economies be secured in this way, but by the use of such alloys, the amount of excess lead desirably used may be reduced by keeping the lead in place, and when an atmosphere of dry hydrogen is employed during reduction, a lead-tin alloy in the correct proportions gives much better control of the amount of metal required, for reduction of the sulfides.

The following example will illustrate the invention, parts being by weight unless otherwise indicated.

Example 3

Molybdenite-lead pellets were made by mixing 20 mesh granulated lead with powdered molybdenite in the ratio of 93 parts to 30 parts and compressed at 20,000 lbs./sq. in. into cylindrical pellets of ½" diameter. The pellets were placed in a molybdenum boat and subjected in a furnace to a temperature of about 1250° C. for about 4 hours. A tube furnace was used large enough to permit gas passage. 18 parts of molybdenum metal sponge were recovered after completion of the reaction. The reaction is facilitated by sweeping PbS away from the pellet by flow of a non-oxidizing gas such as argon at a rate of approximately 2 cu. ft./min. using a 1½" (inside diameter) reaction tube in a "globar" furnace.

Cobalt or nickel containing sulfides may be reduced in an analogous manner using amounts of such sulfides in ratios equivalent to the amounts of molybdenum sulfide ore.

Both cobalt and nickel sulfides form low melting eutectics with metal at 600–900° F. If the reactions are started at low temperatures and are increased to 1200–1300° C., nickel and cobalt sulfides may be retained as solid phase. If the reactions start at 1200–1300° C., natural cobalt and nickel sulfides may be liquids until the composition is less than 10% sulfur for nickel and less than 20% sulfur for cobalt. In some cases, therefore, depending on the nature of the sulfides and reacting conditions, the sulfides may be liquid during reduction and may be solids in other cases and this applies to molybdenite as well as nickel and cobalt sulfides.

The following examples further illustrate the invention:

STIOCHIOMETRIC IN HELIUM

[Temperatures 1200–1300° C.]

Briquette		Products	
MoS_2 pts	100	Mo pts	60
Sn pts	117	SnS pts	149
Pb pts	63	PbS pts	63
		Pb pts	8

NON-STOICHIOMETRIC IN HYDROGEN

[Temperatures 1200–1300° C.]

Briquette		Products	
MoS_2 pts	100	Mo pts	60
Sn pts	88	SnS pts	112
Pb pts	49	PbS pts	47
		Pb pts	8
		S_2 (as H_2S) pts	10

By increasing the hydrogen flow, over 50% of Sn and Pb will be reduced from sulfides, thus increasing H_2S production.

Briquette		Prouct s	
MoS_2 pts	100	Mo pts	60
Sn pts	88	SnS pts	56
Pb pts	49	PbS pts	23
		Sn pts	44
		Pb pts	29
		S_2 (as H_2S) pts	25

The lead reduction of MoS_2 should be carried out in a reflux type system. Hence the lead which boils off will return, thus eliminating need for 20% excess in briquette. Furthermore, carrying out this reaction in H_2 will permit even smaller proportions than stoichiometric lead to be used in the briquette. It is relatively simple to distill off excess lead from finished molybdenum metal sponge.

These examples may be carried out under the general operation as in the first example set forth above with such changes as the individual examples indicate. In general, where nickel or cobalt containing sulfides are used, equivalent amounts may be substituted for the molybdenum sulfide.

The following data is of interest in connection with the operations set forth herein.

MELTING POINTS

	° C.
PbS	1110
Ni_2S	625
Co_2S	879
SnS	880

VAPOR PRESSURES

Vapor Press., mm. Hg		1	10	40	100	200	760
PbS	° C.	852	975	1,048	1,108	1,160	1,281
Pb	° C.	976	1,164	1,312	1,424	1,524	1,750
Sn	° C.	1,600	1,825	1,990	2,115	2,215	2,450
SnS	° C.	750	860	960	1,020	1,100	1,250

Ores, particularly sulfide ores, useful for treatment in connection with this invention, include: for cobalt, cobalite $CoAsS_2$, linnaeite $(Ni, Co)_3S_4$; molybdenum, molybdenite MoS_2; for nickel, pentlandite (Fe, Ni)S, millerite NiS, linnaeite $(Ni, Co)_3S_4$, etc.

Since different metals have different effects upon the molybdenum, in many cases it is desirable to reduce molybdenite with zinc, cadmium, antimony or bismuth, and mixtures thereof, with or without lead and/or tin. The reduction will desirably take place at the temperature between 1100° C. and 1450° C. and the amounts may desirably be in stoichiometric proportions. The reduction may be carried out under non-oxidizing conditions, such as in the presence of hydrogen, helium or argon, and if desired under vacuum, a hydrogen atmosphere being preferred.

We claim:

1. In the method of producing a metal composition formed of a base metal selected from the group consisting of cobalt, nickel, molybdenum, tungsten and alloys thereof from the corresponding metal sulfide, comprising heating the metal sulfide with a metal selected from

the group consisting of tin, lead and alloys thereof in a non-oxidizing atmosphere and at a temperature above 1100° C. to produce the corresponding metal and adding to the reduction zone in a form which gives a resultant alloy upon reduction, an oxygen bearing compound of a metal selected from the group consisting of Ni, Cr, Zr, Ti, Co, Ta, Th, W, Hf, Al, Cb, Be, Ir and the rare earths in which the oxygen bearing compound is selected from the group consisting of the oxide, zirconate, titanate, aluminate, aluminite and carbonate of the metal.

2. The method as claimed in claim 1 in which the oxygen bearing compound is added in the form of a metal oxide in an amount to correspond to 1–25% by weight of the base metal.

3. In the method of producing a metal composition in which the base consists of a metal selected from the group consisting of cobalt, nickel, molybdenum, tungsten and alloys thereof, from the corresponding metal sulfide, comprising heating the metal sulfide with a metal selected from the group consisting of tin, lead and alloys thereof in a non-oxidizing atmosphere at a temperature above 1100° C. to reduce the metal sulfide and produce the corresponding purified metal, and adding an oxygen bearing compound of a metal selected from the group consisting of Ni, Cr, Zr, Ti, Co, Ta, Th, W, Hf, Al, Cb, Be, Ir and the rare earths in which the oxygen bearing compound is selected from the group consisting of the oxide, zirconate, titanate, aluminate, aluminite and carbonate of the metal.

4. The method as claimed in claim 3 in which the metal oxide is incorporated in an amount within the range of 0.01 to 5% by weight.

5. The method of improving the properties of a metal selected from the group consisting of molybdenum, cobalt, tungsten and nickel in a substantially pure state comprising combining with said metal an oxygen bearing compound of a metal selected from the group consisting of Ni, Cr, Zr, Ti, Co, Ta, Th, W, Hf, Al, Cb, Be, Ir and the rare earths in which the oxygen bearing compound is selected from the group consisting of the oxide, zirconate, titanate, aluminate, aluminite and carbonate of the metal.

6. The method as claimed in claim 5 in which the metal oxide is incorporated with the metal in an amount within the range of 0.01 to 5% by weight.

No references cited.