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BENEFICIATION AND RECOVERY OF METALS

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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 copending application Ser. No. 429,674, filed May 13, 1954, now Patent No. 2,834,671, issued May 13, 1958.

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 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.

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 connection with that more specific disclosure, the attached drawing is a flow sheet illustrative of the process.

In accordance with the present invention, metals are produced by thermochemically treating a sulfide of the metal desired, particularly metals having an atomic number of 27, 28, 42 and 74, with tin, the treatment being carried out in a non-oxidizing atmosphere, desirably hydrogen, helium or argon, or mixtures thereof at a temperature generally about 1200° C. sufficient to produce a beneficiated metal.

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 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 molydbenum may be subjected to direct reduction by tin in the presence of a non-oxidizing gas e.g. hydrogen, helium or argon, or mixtures thereof at temperatures above about 1200° C. Tin, which is a high boiling point metal, forms a volatile sulfide and thus makes it feasible for the stated purposes. Since stannous sulfide at the order of temperatures stated, has a vapor pressure that greatly exceeds the vapor pressures of molybdenite, its thermal decompositon products, and molybdenum, systems may be utilized to accelerate the desulfurization reaction and rapidly to purify the molybdenum residue, including not only direct reduction by tin in the presence of hydrogen but also the use of vacuum systems in at least later phases of the process.

In the reduction of molybdenite by tin in the absence of hydrogen, the probable major reactions are

$$2MoS_2 \rightarrow Mo_2S_3 + \tfrac{1}{2}S_2$$
$$Mo_2S_3 + 3Sn \rightarrow 2Mo + 3SnS$$
$$2Sn + S_2 \rightarrow 2SnS$$

Other reactions, probably of minor character are:

$$MoS_2(s) \rightarrow MoS_2(g)$$
$$Mo_2S_3(s) \rightarrow Mo_2S_3(g)$$
$$Sn(1) \rightarrow Sn(g)$$
$$Mo(s) \rightarrow Mo(g)$$

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 tin sulfide. These uses can best be summarized in the following series of reactions.

$$2MoS_2 + H_2 \rightarrow Mo_2S_3 + H_2S$$
$$Mo_2S_3 + 3Sn \rightarrow 2Mo + 3SnS$$
$$3SnS + 3H_2 \rightarrow 3Sn + 3H_2S$$

But actually the use of hydrogen alone is unsatisfactory because of equilibria factors. A comparison with tin, shows that in a 12 hour period with H_2, 90% of S_2 is removed while a 2 hour period with tin removes $\leq 100\%$ of S_2.

The fact that hydrogen reduces the stannous 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.

A typical materials balance for the hydrogen-tin reduction is as follows:

In	Out
100 units MoS_2	60 units Mo
116 units Sn	58 units Sn
	73 units SnS
2 units H_2	27 units H_2S
218 units	218 units

The residual SnS is readily reduced to metallic Sn in a separate furnace using one more unit of H_2 and producing 58 units of Sn plus 16 units H_2S.

In systems at the reaction temperature the low but finite vapor pressure of metallic tin facilitates the liquid-solid reaction and probably results in the more efficient gas-solid reaction with tin vapor being released at a rate comparable to its sulfurization.

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 tin, if desired, leaving the metallic molybdenum free of both sulfur and tin.

The stannous sulfide may be condensed at the cool end of the reaction chamber to a solid crystalline form readily recovered and readily reduced to metallic tin by standard industrial procedures for return to the desulfurization cycle. Hence the cost of the reducing agent for molybdenum may be largely the refining cost for high grade tin concentrate plus the cost of a small mechanical loss of new tin.

The accompanying tabulated data give the weight of molybdenum metal residue for various proportions of metallic tin reacting with standard weights of high purity molybdenite.

Stoichiometrically in tin reduction in the absence of H_2 it would require:

3.7 gms. of Sn to 1.0 gm. of S_2
1.48 gms. of Sn to 1.0 gm. of MoS_2
1.23 gms. of Sn to 1.0 gm. of Mo_2S_3
2.47 gms. of Sn to 1.0 gm. of Mo (as MoS_2)
1.85 gms. of Sn to 1.0 gm. of Mo (as Mo_2S_3)

It has been demonstrated that over half of the stoichiometric requirements for tin in the desulfurizing reaction with molybdenite can be regenerated or reduced to metallic tin during the molybdenite reduction. Hence, the vacuum can be eliminated and the tin reduction can be carried out in hydrogen with the following advantages:

(1) The metallic tin 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, periods of time, and vacuum pressures. The temperature employed should at least be about 1200° C. and may be as high as 1500° C. or even higher, the temperature being pressure dependent since it is desired to retain tin in the liquid phase; but from 1200 to 1300° C. is preferred with 1250° or 1523° K desirable. The time may be from about 1 to 4 hours but two hours is a preferable time period. Pressures may vary. The basic tin reduction is not materially affected by the atmosphere. Helium and argon are desirably utilized at atmospheric pressures. The time may vary with temperature and rate of flow of the non-oxidizing gas. At

present, in hydrogen-tin reduction, 1.17 is a desirable tin to molybdenite ratio whereas the stoichiometric ratio is 1.48.

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 a very 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, 4.5% 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
(2) High grade, 85% MoS_2, 0.50% Cu
(3) High grade, 80% MoS_2, 1.25% Cu

A sample of high grade No. 1 shipped July 7, 1953 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 hydrofluoro+hydrochloric acids to remove oxides and allied impurities.
(3) Washing and drying.

While the oils may largely be removed by solvent leaching, as by an 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. Tin has been used for example at 200 mesh, 30 mesh, and 20 mesh; also as a molten bath. No difference has 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_2Sn reduction to produce molybdenum metal.

	MoS_2 percent	H_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.

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, lead, etc. report in distilled tin 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 tin 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 tin 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 tin. Under conditions so far employed the MoS_2 and Sn should be in contact. The molybdenite briquette is not normally wetted by molten tin at atmospheric pressures and low temperatures. However under conditions of reaction, the reduced molybdenite briquette absorbs large weights of liquid tin, is readily wetted, and has little trouble with unreacted zones. Even when partially immersed the briquette will draw molten tin throughout its pores by capillary action.

The molybdenum metal briquettes when produced are sponge like and capable of re-compression. At times excess tin is permitted to remain since it coats all the molybdenum surface and inhibits oxidation of the metal particles. Indirect evidence indicates some solubility of molybdenum in molten tin at or near the reaction temperatures. The grain size of the reduced molybdenite is very small and approximates 2–3 microns. However it will vary with source of raw materials.

Tin reduced molybdenum produced as set forth herein, were arc melted to form small buttons of metal. The sponge employed was typical of low carbon material produced by tin reduction. The sponge had been pressed at 7500 p.s.i. and sintered in a high vacuum NRC furnace at 1900° C. and 0.05 microns of mercury. But these are illustrative and not optimum conditions.

There was some oxygen pick up during melting since the arc furnace was only evacuated to 20 microns and back-filled with a 50–50 mixture of tank helium and argon. No getter was used prior to melting the button of molybdenum. Hardness tests on Rockwell machine gave values of from 74–79 points on the "B" scale which corresponds roughly to the Vicker hardness (DPH) of 135–149 or Brinell (500 kg.) 119–130. The grain boundaries are reasonably clean and the degree of grain growth during annealing cycle remarkably great.

The following observations on tin/molybdenum system may be noted. Molten tin at the temperature of direct sulfide reduction reacts rapidly (circa 1200° C.) because: (1) it wets the molybdenum readily; (2) it dissolves molybdenum; (3) it promotes grain growth by solution and reprecipitation to give uniform sized equiaxial crystals; (4) the SnS formed has a high vapor pressure at the temperature of reaction and leaves the system.

Some of the elemental additives alloy with tin and do affect the wetting phenomena by lowering contact angle and slowing up reaction. It is not necessary that the tin be added to the molybdenite in powdered form as indicated above since a pure molybdenite briquette, if partially immersed in tin will rapidly absorb the molten metal once the reaction has started due to wetting and capillary action. The resulting reduction is complete throughout briquette if the stoichiometric proportions are maintained.

The metals tin and lead occurring in the same periodic

Group IV of the atomic chart form volatile sulfides but do not form refractory compounds with molybdenum, and thereby distinguish from such reducing agents as carbon and silicon which contaminate the metal produced. Tin sulfide (SnS) is more stable than lead sulfide (PbS) at their respective boiling points and the metal tin less volatile than the metal lead, at 1500° K. Surface tension studies showed in addition that molybdenum metal was readily wetted by liquid tin at 1500° K. while liquid lead gave a low contact angle against molybdenum.

Further, tin was found to be a deoxidizing agent for molybdenum at temperatures from 1500° to 2600° K. A volatile tin monoxide is formed directly comparable to the volatile silicon monoxide. Hence, tin, a low melting point, high boiling point metal which forms a volatile sulfide and a volatile monoxide is the most desirable desulfurizer for molybdenite (MoS_2).

Photomicrographs taken of metallic molybdenum produced by the present invention show increased grain growth of the molybdenum crystals either due to the decontamination of grain boundaries and surfaces or in combination with a separate effect. This separate effect may result from the solution of small sized molybdenum grains in the molten tin at the reaction temperatures and its reprecipitation on other grains during the reaction time or subsequent cooling cycle.

But regardless of any explanation, increased grain growth of molybdenum has been observed and has been found to be a function of the quantity of tin introduced prior to treatment.

The methods set forth above for the desulfurizing, and decontamination of molybdenum may be applied to other metals and their sulfides specifically to tungsten, cobalt and nickel, and their sulfides. In addition, these methods may be utilized in the production of intimately mixed metal powders and/or alloys, by inclusion of adjuvants as more particularly pointed out hereinafter.

The products made by this instant process have been tested by X-ray diffraction, X-ray spectroscopy, optical spectrography, and chemical methods. The indicated carbon levels are 5–50 parts per million (p.p.m.), tin 0.05 to 0.50%, sulfur .005 to 0.02%, silicon and aluminum .001 to 0.02%, iron 0.02 to 0.20%. Physical testing have shown over 80% reduction by cold rolling of vacuum sintered molybdenum briquettes. Micrometer readings of cold pressed molybdenum powder under standard cross section dies and pressures give relative purity levels. Rockwell hardness of arc melted buttons gave B scale readings of from 74–99. Metallographic examination showed clean grain boundaries.

The molybdenum powders produced by the tin reduction process are tested by standard analytical procedures employing X-rays, optical spectrography and chemical methods.

The molybdenum powder final product should be pressed into a semi-solid compact and sintered or arc melted.

The high purity powders appear to give a higher apparent density than those containing carbides, oxides, or extraneous impurity such as Al_2O_3 or SiO_2. These impurities affect the ductility and/or the cold compressability of the metal. The presence of excess tin under the same conditions reduces the percentage of voids and does not decrease the net compressability of molybdenum metal.

The introduction of tin into molybdenum metallurgy gives new products of value. Molybdenum containing 1–10% tin shows unaltered patterns of each element by X-ray diffraction methods at room temperatures. Molten tin does wet and dissolve molybdenum at 1500° K. The melting point of tin appears to rise sharply in the presence of pure molybdenum powder. Briquettes containing 75% tin, 25% molybdenum retain their sharp form up to temperatures of 1400° K or higher, yet at room temperatures they retain the ductility of tin. However,

the molybdenum-tin products behave more like amalgams than alloys.

After the metal has been produced by the process of tin hydrogen reduction, the molybdenum powder produced may be treated in various ways. Thus there may be added to it, any oxide bearing compounds or other compounds mentioned for incorporation into the molybdenum powder in application Serial No. 429,674, filed May 13, 1954 in order to improve physical properties and resistance to oxidation. They may be added during sintering, hot pressing, arc melting and extrusion.

Molybdenum, molybdenum sulfide and metallic tin have very low vapor pressures and can be assumed to have a thermodynamic activity of one. Liquid tin at 1500° K does attack molybdenum, therefore some solubility is indicated. However, X-ray diffraction studies have shown neither intermetallic compounds nor appreciable solution of molybdenum in tin at room temperatures.

Vacuum sintering removes the tin content by volatilization since tin has 100 microns pressure at 1500° K. This means that metals that dissolve in molten tin such as Ti, Zr, Co, Ni, etc., may be added to molybdenum powders in a novel form.

Hot pressing of molybdenum powders containing tin permits high density compacts with only moderate retention of tin. Tin appears to inhibit the oxidation rate for molybdenum metal. With the low oxygen content of molybdenum the possibility of introducing stable metalloids and oxides in the grain boundaries enables wide variation metal properties.

It is possible to cold roll molybdenum-tin briquettes followed by vacuum sintering to remove the tin phase. This permits ease in fabrication of certain shapes and forms.

During arc melting, tin functions as a deoxidizing agent up through the melting point of molybdenum. Since the tin will dissolve in molten molybdenum and is at its own boiling point at the melting point of molybdenum, deoxidation should be rapid.

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

EXAMPLE 1

The molybdenite tin pellets are prepared by mixing dry refined molybdenite with 30 mesh granular tin in the proportion of either the stoichiometric amount for MoS_2, 160 grams of molybdenite to 237.4 grams tin; or the stoichiometric amount for Mo_2S_3, 160 grams of molybdenite to 178.1 grams tin. Various amounts both under and in excess have been employed. Inadequate tin leaves unaltered Mo_2S_3 and excess tin remains with pellet until removed by vacuum distillation.

The mixed materials are pressed in cylindrical dies, ½", and 1½" diameter dies have been employed as laboratory sizes while larger ones are usable.

The pellets are placed in a tube furnace large enough to permit gas passage. Both molybdenum boats and tube liners have been employed. The furnace is closed, flushed by purified helium or hydrogen or argon gas flow, before final evacuation by vacuum pump. They function as non-oxidizing gases.

The furnace temperature is raised as rapidly as possible to 1250° C. and held there for from 1–4 hours depending on size and number of pellets being reduced.

The SnS gas condenses in the cool end of the tube, circa 1143° K, and must be reamed out between runs. When purified hydrogen gas flow is employed in place of vacuum during reduction, the SnS is partially reduced and free tin is reclaimed for further use. When helium is employed the SnS remains as crystalline sublimate in the cool end of the tube just as in the vacuum runs.

When purified hydrogen flow is used at atmospheric pressures rather than the vacuum procedure, approximately 2 cu. ft./hour of hydrogen is needed for 52 gram pellets molybdenite plus tin (24 grams, MoS_2+48 grams Sn). Just about 6 grams of sulfur or ⅝ of the total combined sulfur in molybdenite reports as H_2S in the effluent gases. The remaining 3.6 grams reports as stannous sulfide together with some 14 grams of free tin. The rate of hydrogen feed is tied directly to the time for reduction and size of pellet. For a 52 gram pellet (24 grams molybdenum plus 28 grams of tin) and a 4 hour run it appears to require 2 cu. ft. of H_2 per hour. Thus the conditions may include:

1 cu. ft. H_2/hr	For 8 hours.
2 cu. ft. H_2/hr	For 4 hours.
4 cu. ft. H_2/hr	For 2 hours, etc.

The hydrogen feed rate reflects atmospheric pressure, hence the same quantity would be required whether the furnace operated below atmospheric pressure or above it. Operations have been carried out at 6000 ft. of altitude hence below the atmospheric pressure at sea level. The temperature and other factors have not been found to vary with pressure. However, twice atmospheric pressure may require a higher temperature. 1250° C. or 1523° K is preferred for all systems.

For any given time for reduction run, specifically 3 hours in Example 2, the hydrogen should desirably be kept at the rate of 2.1 cu. ft. per hour. If it drops to 1.5 cu. ft. and the time remains the same, sulfur will remain with molybdenum. If it rises to 2.6 cu. ft. and the time remains the same additional tin sulfide will be reduced.

The mechanism appeared to be complex because it involves:

(*a*) Gas-solid reaction within a pressed cylinder
(*b*) Liquid-solid reaction within a pressed cylinder
(*c*) Diffusion from center of pellet to surface
(*d*) Evaporation of liquid from surface
(*e*) Solution of products in reactants
(*f*) Solution of reactant in product

Physically, a pellet would go through the following stages during the heating cycle:

(1) Liquation of liquid tin from molybdenite/tin pellet
(2) Thermal decomposition of molybdenite to sesquisulfide
(3) Sulfur and tin sulfide vapor bubbling from liquid tin
(4) Re-absorption of liquid tin by partially decomposed molybdenite
(5) Evaporation of tin sulfide from surface of pellet
(6) Final evaporation of SnS+Sn from a cylindrically shaped sponge of reduced molybdenum metal

Apparently the molybdenite crystals are more resistant to thermal decomposition than to hydrogen decomposition since the hydrogen is readily absorbed in the lattice of molybdenite even at low temperatures The tin reaction occurs more readily on the sesquisulfide of molybdenum after the stable hexagonal plates of molybdenite have been destroyed because additional active centers are available for attack

In any event, it is technically more feasible to employ atmospheric pressures in the high temperature retorts necessary to the process, rather than vacuum equal to 01 mm. of Hg.

The major purpose of the tin reduction process is to avoid oxygen contamination and not to correct oxidation already present. Hence, in the hydrogen-tin process it is important to purify the gas before using, otherwise tank hydrogen will introduce oxygen into the system. The purified hydrogen will serve to inhibit dehydrogenation and cracking of petroleum oils absorbed on molybdenite. However, if fixed carbon occurs in the molybdenite, wet hydrogen would have to be employed to remove this carbon. It may be followed by purified hydrogen after the carbon removal. However some oxygen may still remain.

EXAMPLE 2

24 grams of molybdenum sulfide which had been washed with acetone and treated with HF-HCl acid mixtures to remove oxide impurities of silicon, aluminum, iron etc. was carefully mixed with 24 grams of 30 mesh analytical grade granulated metallic tin and was briquetted in a 1" diameter die under pressures of 10,000 p.s.i.

The briquette of tin and molybdenum sulfide was placed in a molybdenum metal boat and inserted in a sillimanite tube 1¼" diameter already comprising the heated zone of a silicon-carbide resistor furnace.

The tube furnace was sealed and hydrogen gas caused to flow through the furnace at rates 2.1 cubic feet per hour (approx. 1 liter/per minute). The furnace was turned on after flushing with hydrogen and the temperature allowed to rise to 1250° C. The reaction starts at 1100° C. but does not reach full vigour until 1250° C. (the boiling point of stannous sulfide). The elapsed time during temperature rise is 2 hours and 45 minutes. After reaching 1250° C. the temperature is held constant as well as the hydrogen flow rate for three hours or until the reaction is complete as indicated by the hydrogen sulfide emission dropping from 0.0365 gram per minute to 0.007 or less gram/minute. The furnace power is then turned off, hydrogen turned off and a vacuum turned on during cooling. At other times, vacuum may not be used and hydrogen continued during cooling.

After cooling to room temperature the pellet is removed from furnace weighed and analyzed for impurities. If the hydrogen flow had been less than 2 cu. ft. or had been interrupted the pellet may contain residual sulfur. If the hydrogen flow had exceeded 2.2 cu. ft., the pellet may contain excess tin. This holds only for the 3 hour run since hydrogen flow rate and time are dependent. The quantity of tin must also not vary.

	Theoretical, gms.	Actual, gms.
Charge:		
MoS_2	24	24.0
Sn	24	24.0
	48	48.0
Product:		
Mo	14.4	14.25
Sns	15.2	15.50
Sn	12.0	11.50
S (as H_2S)	6.4	+6.0
	48.0	

If no tin is used the pellet contains residual sulfur after 12 hours of treatment.

If the full stoichiometric amount of tin is used then several grams of excess tin will remain with pellet.

Typical balance

The mechanism involved is the reduction of MoS_2 and Mo_2S_3 by Sn to produce SnS as a gas phase. The SnS gas is reduced by hydrogen as it leaves the briquette surface, freeing tin which can then react with molybdenum sulfide again.

REACTIONS

1250° C. I. $2MoS_2(solid)+H_2(gas) \rightarrow Mo_2S_3(solid)+H_2S(gas)$

1250° C. II. $Mo_2S_3(solid)+3Sn(liquid) \rightarrow 2Mo(solid)+3SnS(gas)$

1250° C. III. $SnS(gas)+H_2(gas) \rightarrow Sn(liquid)+H_2S(gas)$

Thermodynamically the tin sulfide reduction reaction is less likely to occur than the molybdenum sulfide reduction, however, kinetically the gas-gas reaction is favored over the gas-solid reaction and the regeneration of liquid tin at the surface of pellet permits the molybdenite reduction to proceed with minimum amounts of tin (½ to ⅔ of stoichiometric). Additional tin sulfide is reduced beyond reaction zone and eventually all the SnS can be reduced to tin to reuse in the process.

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 stannous sulfide to be partially reduced to metallic tin for reuse in process.

(3) The presence of H_2 eliminates the need for vacuum reactors hence curtails process cost.

(4) The presence of H_2 ultimately eliminates the consumption of tin, 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

REACTIONS OF Sn WITH MoS_2

Weight molybdenite, gms.	Weight tin, gms.	Temperature, ° C	Vacuum, mm. Hg	Time, hrs.	Residue, gms.	Condensate, SnS gms.	Actual ratio of tin to molybdenite	Stoichiometric ratio tin to MoS_2	Stoichiometric ratio tin to Mo_2S_3
6.0	0.0	12-1300	0.1-0.5	2.0	5.260	0	0	1.48	1.23
6.0	1.2	x	x	x	4.950	----------	0.2	x	x
6.0	2.4	x	x	x	4.490	1.705	0.4	x	x
6.0	3.6	x	x	x	4.260	3.510	0.6	x	x
6.0	4.8	x	x	x	3.945	5.430	0.8	x	x
6.0	6.0	x	x	x	3.820	5.600	1.0	x	x
6.0	6.6	x	x	x	3.615	7.230	1.1	x	x
6.0	7.2	x	x	x	3.580	8.740	1.2	x	x
6.0	7.8	x	x	x	3.585	9.500	1.3	x	x
6.0	8.4	x	x	x	3.568	12.670	1.4	x	x
6.0	8.5	x	x	x	3.575	12.395	1.42	x	x
6.0	8.6	x	x	x	3.545	13.595	1.43	x	x
6.0	8.7	x	x	x	3.560	8.580	1.45	x	x
6.0	8.8	x	x	x	3.570	11.195	1.47	x	x
6.0	8.9	x	x	x	3.575	14.325	1.49	x	x
6.0	9.0	x	x	x	3.570	12.895	1.50	x	x
6.0	9.6	x	x	x	3.591	10.770	1.60	x	x
6.0	10.2	x	x	x	3.563	12.548	1.70	x	x
[1] 12.0	27.8	x	x	x	7.200	22.600	2.317	1.48	1.23

[1] MoS_2 briquetted separately from Sn, one side immersed in molten Sn.

NOTE—MoS_2=60% Mo, 40% S, net weight 3.60 gm. Mo. SnS=78.7% Sn, 21.3% S, net weight 11.28 gm. SnS.

HYDROGEN REDUCED COMMERCIAL MOLYBDENUM POWDER PLUS GRANULAR TIN

Weight molybdenum, gms.	Wei ht tin, gms.	Temperature, ° C.	Vacuum, mm. Hg	Time, hrs.	Residue, gms.	Observations grain size
20.0	0.0	12-1300	0.1-0.4	3	19.930	No growth.
20.0	0.1	x	x	3	19.920	Do.
20.0	0.2	x	x	3	19.920	Do.
20.0	0.4	x	x	3	19.915	Do.
20.0	1.0	x	x	2	19.915	Do.
20.0	2.0	x	x	7	19.890	Some growth.
20.0	4.0	x	x	7	19.965	Moderate growth.
20.0	10.0	x	x	7	20.020	Considerable growth.

NOTE—1 inch dia. briquettes pressed at 25,000 p.s.i.

REACTIONS OF Sn WITH MoO_2

Weight MoO_2, gms.	Weight tin, gms.	Temperature, ° C.	Vacuum, mm. Hg	Time, hrs.	Residue, gms.	Actual ratio Sn/MoO_2	Stoichiometric ratio of tin to MoO_2
5.0	10.0	12-1300	0.4	4	3.640	2.0	1.85
5.0	8.0	x	x	2	3.685	1.6	1.85

REACTIONS OF TIN WITH SYNTHETIC OR ARTIFICIAL Mo_2S_3

Weight Mo_2S_3, gms.	Weight tin, gms.	Temperature, ° C.	Vacuum, mm. Hg	Time, hrs.	Residue, gms.	Actual ratio Sn/Mo_2S_3	Stoichiometric ratio of tin to Mo_2S_3
6.0	9.0	12-1200	0.4	2	3.815	1.50	1.23
6.0	9.0	x	x	x	3.825	1.50	1.23

NOTE.—MoO_2=75% Mo, 25% O_2, net weight=3.75 gm. Mo; probably some volatilization of MoO_2 at reaction temp. (2.2%). Mo_2S_3=66.7% Mo, 33.3% S_2, net weight=4.00 gm. Mo; probably some volatilization of Mo_2S_3 at reaction temp. (4.5%).

Various additives may be included in the methods set forth above for special effects or results. These additives may be conveniently considered in four general classes as follows:

I. Inert during sulfide reduction stage.
   (*a*) Carbides, sulfides, silicides, borides and nitrides of Ta, Zr, Ti, Hf, Cb, Th and rare earths.
   (*b*) Oxides of Ta, Zr, Ti, Hf, Cb, Th, Al, Be, and rare earths.
   (*c*) Elemental W, Co, Ni.

II. Volatile during sulfide reduction stage.
   (*a*) Oxides of Si, B, Na, K, Sn.
   (*b*) Sulfides of Sn, Si, Pb, and possibly Mn.
   (*c*) Halides of Na, K, Cu, Fe, etc.

III. Reduced to metal or react to form volatile species during sulfide reduction.
   (*a*) Sulfides of W, Co, Ni.
   (*b*) Oxides of Sn, Si, Co, Ni.
   (*c*) Elemental Sn, Si, Pb, Bi, Sb, and possibly Mn.

IV. React during sulfide reduction to form stable oxides and/or sulfides.
   (*a*) Elemental Ti, Zr, rare earth (Misch metal), Th and possibly V.

These various additives may be grouped according to particular effects which they exhibit, the class designations referring to the general classes outlined above.

A. Beneficial additives that improve the room temperature compressibility of reduced Mo briquettes.
   Class I Ta_2O_5, Cb_2O_5.
   Class II NaCl, NaF.
   Class III SnO_2, SnO, MnO_2, Sn, Si, Mn.
   Class IV None.

B. Beneficial additives that appear to clean up grain boundaries, improve crystal structure but do not apparently affect room temperature compressibility.
   Class I ZrO_2, TiO_2, ThO_2, Cr_2O_3.
   Class II SiO_2, B_2O_3, NaCl, NaF.
   Class III SnO_2, SnO.
   Class IV V.

C. Beneficial additives that appear to clean up grain boundaries, improve crystal structure but apparently decrease room temperature compressibility probably due to increased low specific gravity bulk.
   Class I FeB, AlB, TiN, Al_2O_3.
   Class II None.
   Class III CoS, Si.
   Class IV Ti, Zr, rare earths.

Among the above classified additives, low melting point oxide systems may be chosen which behave as fluxes or slag phases during the reduction to further purify the molybdenum and crystal grain boundaries. These systems may contain borosilicates, fluosilicates or other combinations which are, or have, volatile constituents the bulk of which will volatilize during the last stage of reduction leaving the contained impurities as inert segregated inclusions which do not affect the properties of purified metal.

Distinct from the low melting additives are the higher temperature stable oxides of Zr and Ti which also collect impurities by solid state diffusion and retain them in a stable, inert, segregated form not injurious to properties of refined metal. Al_2O_3 also appears to function in this manner changing color with the kind and quality of contained impurity.

The third type of purification may take place by adding a higher oxide i.e. V_2O_5 which decomposes during the early stages of desulfurization forming a stable lower oxide thus accelerating the desulfurization without affecting the final reduced metal.

Aside from the above types of purification phenomena, the stable oxide segregations very often serve to restrict the grain growth of the reduced metal. Since these oxides are thermally stable up to very high temperatures and not at all comparable to normal segregated oxides of molybdenum which volatilize or decompose rendering the grain boundaries weak, especially after coarse crystallization is present, the stable segregated oxides promote the hot strength of properly prepared metal and retain the moderately fine crystal structure of the ductile metal.

One major advantage of the present process is the production of a compacted molybdenum metal and/or alloy of molybdenum by a single mixture of raw materials, a single reduction operation and the immediate compression of the molybdenum and/or alloy sponge, for sintering, induction melting or arc melting before the metal becomes recontaminated by the outside atmosphere.

Hence when producing alloys of molybdenum the behavior of the alloying elements during the reduction stage is of extreme importance. Additives may be introduced to form (1) intermetallic alloys, (2) cermet alloys, (3) to inhibit grain growth, (4) to purify grain boundaries and (5) to act as a liquid flux or impurity solvent during reduction, comparable to slag phases in normal smelting operations.

(1) W, Ni, Co, Fe can be added prior to the reduction stage (with MoS_2) as metals, as sulfides or as oxides, and will result in a normal Mo alloy following sintering.

Ti, Zr, Th, Al, Be and the rare earth metals are added subsequent to the reduction in order to obtain normal alloys after sintering.

V, Cb, and Ta probably also fall in the latter group. This latter group must be added as metals after reduction stage.

(2) The borides, nitrides, carbides, sulfides and silicides of Ta, Zr, Ti, Hf, Cb, Th and rare earths may be added before reduction because they are stable and inert. These

materials comprise some possible cermet additives for obtaining high temperature resistance and hardness. If elemental Ti, Zr, etc. are added during reduction then stable sulfides of these metals will appear in the final Mo product.

(3) Some of the cermet additives as well as the oxides of Ti, Zr, Ta, Cb, Hf, Th and the rare earth group may be added to the MoS_2 prior to the reduction for the prime purpose of inhibiting the grain growth by introducing stable oxides into the molybdenum metal grain boundaries.

(4) Some of the stable oxide additives function as solid state purifiers in that they absorb non metallic impurities possibly by chemical action (e.g. TiO_2, ZrO_2, etc.)

(5) When the oxide additives form a fluid phase during the reduction reaction they oft times dissolve grain boundary impurities, promote grain growth and increase the purity of the reduced metal. In this classification SiO_2, B_2O_3, MnO_2 perform the first function and then volatilize during later stages of reduction leaving segregated impurities.

NaCl and NaF also form a fluid phase which chemically converts impurities to volatile states and ultimately volatilizes leaving purified metal.

The additives themselves are given as non-limiting and non-exclusive examples only, of the ability of the new process to adapt to varying kinds of control for the production of varying classifications of molybdenum metal, molybdenum alloys and cermet type materials. The metallo-thermic reduction of molybdenite by tin is fundamentally adaptable to a wide variety of controls and that invention outlines the types of materials that may be added prior to reduction since the one stage treatment from primary mineral concentrate to metal has the greatest commercial advantage. However, it may be adapted to all types of alloys by using a two stage procedure as indicated in the data.

The molybdenum sponge metal produced by metallothermic reduction of molybdenite may be pressed (either hot or cold) to densities in excess of 70 percent of ideal. The following treatment includes sintering in an inert atmosphere, of vacuum, induction melting, arc melting for production of finished ingot, or any other standard commercial procedure for bonding metal powders. Residual tin may be left in the molybdenum sponge to advantage, namely:

(1) To coat the Mo surface and prevent oxidation prior to sintering.

(2) To serve as a volatile "getter" for removing oxygen from sintering or melting chamber.

(3) To serve as a final decontamination agent for the molybdenum metal during arc melting or sintering.

Having thus set forth our invention, we claim:

1. In the method of producing a metal selected from the group consisting of cobalt, nickel, molybdenum and tungsten by reaction from the corresponding metal sulfides the step of reacting the metal sulfide with tin as a reducing agent in a hydrogen atmosphere which is reducing as to tin sulfide as well as the metal sulfide so as to regenerate the tin upon heating the materials to an elevated temperature while the tin is in a fluid state to produce the corresponding metal in a relatively purified state.

2. The method as claimed in claim 1 in which gaseous hydrogen is introduced at a rate of 5–10 cubic feet per hour.

3. In the method of producing a metal selected from the group consisting of cobalt, nickel, molybdenum and tungsten by reaction from the corresponding metal sulfide the step of reacting the metal sulfide with tin as a reducing agent in a hydrogen atmosphere which is reducing as to tin sulfide as well as the metal sulfide so as to regenerate the tin upon heating the materials to an elevated temperature while the tin is in a liquid state to produce the corresponding metal in a relatively purified state both as to the tin and the metal for reaction with the tin in liquid form to reduce the metal sulfide to form the corresponding metal and tin sulfide.

4. The method as claimed in claim 3 in which the materials are heated to a temperature above 1200° C. for reaction.

5. The method as claimed in claim 3 in which the metal sulfide and tin are heated to a temperature within a range of 1200°–1500° C. for reaction.

6. The method as claimed in claim 3 in which the tin sulfide which is formed is reduced to tin for re-use in reduction of the metal sulfide.

7. In the method of producing molybdenum by reaction from molybdenum sulfide the step of reacting the molybdenum sulfide with tin as a reducing agent in a hydrogen atmosphere which is reducing as to tin sulfide as well as the molybdenum sulfide so as to regenerate the tin upon heating the materials to an elevated temperature while the tin is in a fluid state to produce molybdenum in a relatively purified state.

8. In the method of producing molybdenum by reaction from molybdenum sulfide the step of reacting the molybdenum sulfide with tin as a reducing agent in a hydrogen atmosphere which is reducing as to tin sulfide as well as the molybdenum sulfide so as to regenerate the tin upon heating the materials to an elevated temperature while the tin is in a liquid state to produce molybdenum in a relatively purified state.

9. The method of producing molybdenum as claimed in claim 8 in which the reactants are heated to a temperature in excess of 1200° C.

10. The method as claimed in claim 8 in which the tin sulfide that is formed is reduced to tin for re-use in the reduction in the molybdenum sulfide.

11. The method as claimed in claim 8 in which the molybdenum sulfide and tin are mixed prior to treatment.

12. The method as claimed in claim 8 in which the molybdenum sulfide and tin are briquetted prior to treatment.

13. The method as claimed in claim 12 in which the briquette is immersed in molten tin for reaction.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,020,151 February 6, 1962

John S. Nachtman et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 14, lines 1 to 3, strike out -- both as to the tin and the metal for reaction with the tin in liquid form to reduce the metal sulfide to form the corresponding metal and tin sulfide --.

Signed and sealed this 5th day of June 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents