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METHOD OF PRODUCING MOLYBDENUM

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This invention relates to methods of producing metals including methods of reduction of their compounds, methods of decontamination including deoxidation, methods of promoting grain growth, and products resulting from such methods.

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 molybdenum by thermo-chemical treatment of its sulfide 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 of improved grain structure.

Still further objects include metals resulting from such methods.

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, molybdenum metal is produced by thermochemically treating molybdenum sulfide with tin and its alloys of comparable vapor pressure, the treatment being carried out in a non-oxidizing atmosphere, preferably under vacuum, at a temperature generally above 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 at 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 molybdenum may be subjected to direct reduction by tin 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 decomposition products, and molybdenum, vacuum systems may be utilized to accelerate the desulfurization reaction and rapidly to purify the molybdenum residue.

Furthermore in vacuum 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, the 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 (Alpha Corp. "Molykote").

Stoichiometrically 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 found that the reduction of molybdenite for example requires less than the stoichiometric amounts of metallic tin. These 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. The time may be from about 1 to 4 hours, but two hours is a preferable time period. Pressures may vary, but vacuum, particularly 0.1 to 1.0 mm. Hg is preferred. Vacuum is not necessary to the reaction since it has been carried out at atmospheric pressures in static or circulating inert atmospheres.

In the reduction of molybdenite by tin, 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:

$$MoS_3(s) \rightarrow MoS_2(g.)$$
$$Mo_2S_3(s) \rightarrow Mo_2S_3(g.)$$
$$Sn(1) \rightarrow Sn(g.)$$
$$Mo(s) \rightarrow Mo(g.)$$

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, both ½ inch and 1 inch round dies have been employed with pressures of 8000–25,000 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.

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.

Likewise tin etc. may be introduced with the compacted molybdenum for vacuum arc melting to form ingots. The present practice employs carbon which when added to excess results in carbide formation. When tin etc. is employed for this deoxidation no injurious effects result from excess quantities since the deoxidant may be volatilized after the oxygen removal.

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 following tabulated examples illustrate the invention. All weights are given in the same units. In Table I the temperature was between 1200 and 1300° C., the vacuum was from 0.1 to 0.5 mm. Hg, and the time was two hours in each example.

TABLE I

Example Nos.	Wt. MoS_2	Wt. Sn	Residue	Condensed SnS	Sn/MoS_2 Ratio	MoS_2 Stoichiometric Ratio	Mo_2S_3 Stoichiometric Ratio
1	6.0	0.0	5.260	0	0	1.48	1.23
2	6.0	1.2	4.950	0	0.2	1.48	1.23
3	6.0	2.4	4.490	1.705	0.4	1.48	1.23
4	6.0	3.6	4.260	3.510	0.6	1.48	1.23
5	6.0	4.8	3.945	5.430	0.8	1.48	1.23
6	6.0	6.0	3.820	5.600	1.0	1.48	1.23
7	6.0	6.6	3.615	7.230	1.1	1.48	1.23
8	6.0	7.2	3.580	8.740	1.2	1.48	1.23
9	6.0	7.8	3.585	9.500	1.3	1.48	1.23
10	6.0	8.4	3.568	12.670	1.4	1.48	1.23
11	6.0	8.5	3.575	12.395	1.42	1.48	1.23
12	6.0	8.6	3.545	13.595	1.43	1.48	1.23
13	6.0	8.7	3.560	8.580	1.45	1.48	1.23
14	6.0	8.8	3.570	11.195	1.47	1.48	1.23
15	6.0	8.9	3.575	14.325	1.49	1.48	1.23
16	6.0	9.0	3.570	12.895	1.50	1.48	1.23
17	6.0	9.6	3.591	10.770	1.60	1.48	1.23
18	6.0	10.2	3.563	12.548	1.70	1.48	1.23
19*	12.0	27.8	7.200	22.600	2.317	1.48	1.23

NOTE.—MoS_2=60% Mo, 40% S. Net wt. 3.60 gm. Mo. SnS=78.7% Sn, 21.3% S. Net wt. 11.28 gm Sn.
*MoS_2 briquetted separately from Sn, one side immersed in molten Sn.

Table I shows the weighed proportions of tin required to reduce 6.0 gms. of MoS_2 to 3.58 gms. Mo. This required weight approaches the stoichiometric amount for reducing Mo_2S_3 rather than MoS.

TABLE II

Reactions of Sn *with artificial* Mo_2S_3

Example Nos.	Weight Mo_2S_3	Weight Sn	Temp., ° C.	Vacuum, mm. Hg	Time, Hrs.	Residue	Sn/Mo_2S_3 Ratio	Mo_2S_3 Ratio
22	6.0	9.0	12–1,300	0.4	2	3.815	1.50	1.23
23	6.0	9.0	12–1,300	0.4	2	3.825	1.50	1.23

NOTE.—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%).

Table II shows completeness of re-action and stoichiometric relations when tin is used to reduce pure artificial Mo_2S_3.

The decontamination of molybdenum powder is exemplified in Table III, where all weights were in the same units, the temperature was from 1200 to 1300° C., and the vacuum from 0.1 to 0.4 mm. Hg, in each example.

TABLE III

H_2 *reduced* Mo *powder plus granular* Sn

Wt. Mo	Wt. Sn	Residue	Observation Grain Size
20.0	0.0	19.930	No growth.
20.0	0.1	19.920	Do.
20.0	0.2	19.920	Do.
20.0	0.4	19.915	Do.
20.0	1.0	19.915	Do.
20.0	2.0	19.890	Some growth.
20.0	4.0	19.965	Mod. growth.
20.0	10.0	20.020	Consid. growth.

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

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.

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 or 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.
(4) To stabilize the arc during vacuum arc melting procedures.

Having thus set forth our invention, we claim:

1. The method of producing metallic molybdenum from its sulfide by heating molybdenum sulfide with tin under non-oxidizing conditions at a temperature of about 1200° C. and to about 1300° C. to reduce molybdenum sulfide in the solid phase with tin in the liquid phase to obtain a purified molybdenum.

2. The method of claim 1 in which the molybdenum sulfide and the tine are briquetted prior to being heated.

3. The method of claim 1 in which the heat treatment is carried out under vacuum.

4. The method of claim 1 in which the molybdenum metal obtained is subjected to arc melting.

5. The method of claim 1 in which the molybdenum sulfide is briquetted and at least partially immersed in the tin while the latter is in molten condition.

6. The method of claim 1 in which the metal obtained is hot pressured.

7. The method of claim 1 in which volatile metal sulfides are formed and condensed, reduced to metal and the metal returned for reaction with further quantities of molybdenum sulfide.

8. The method of producing metallic molybdenum from its sulfide by heating molybdenum sulfide under non-oxidizing conditions with tin at about 1200° C. to below about 1500° C. at a temperature to reduce molybdenum sulfide in the solid phase with tin in the liquid phase.

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