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METHOD FOR PRODUCING MOLYBDENUM FROM MOLYBDENITE (MoS_2)

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The invention herein described and claimed may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of royalties thereon or therefor.

The present invention relates to electrolytic preparation of molybdenum carbide and recovery of metallic molybdenum from the carbide.

The process of the invention is particularly adapted to recovery of molybdenum metal from molybdenite concentrates. Indigenous molybdenite (MoS_2) occurs in admixture with large percentages of other minerals such as quartz, feldspar, etc. Molybdenite concentrates containing about 90 to 95 percent molybdenite are readily obtained by conventional concentration procedures such as flotation or gravity separation. Recovery of molybdenum metal is conventionally accomplished by roasting the molybdenite concentrate to technical molybdic oxide. This oxide is either sublimed and collected as chemically pure MoO_3, or dissolved in dilute ammonia, filtered and evaporated until ammonium molybdate crystallizes. Ammonium molybdate or molybdic oxide is reduced to molybdenum powder by hydrogen reduction at 1,050° to 1,100° C. The molybdenum powder is then deoxidized, either by sintering in a hydrogen atmosphere at 2,200° to 2,300° C. or by adding carbon and arc-melting in vacuum. Process control is quite involved due to the complex chemistry of molybdenum and the high-purity feed required for metal powder production. These methods are costly and, in addition, involve excessive fume losses of molybdenum and considerable technical difficulties to produce a metal powder of uniform quality and purity.

Recovery of molybdenum metal from the oxide has also been accomplished by electrowinning from a molten bath containing dissolved molybdenum oxide. This procedure is described in Bureau of Mines Report of Investigations 5795, "Electrowinning Molybdenum: Preliminary Studies" by H. J. Heinen and J. B. Zadra and U.S. Patents 3,071,523 and 3,075,900 to Zadra et al. These prior art processes have the disadvantage that molybdic oxide, usually chemically pure, is required as feed material.

It is therefore an object of the present invention to provide a simple and efficient process for recovery of high-purity molybdenum metal from molybdenite concentrates.

It is a further object of the invention to provide a method for electrolytic preparation of molybdenum carbide from molybdenite concentrates.

It has now been found that these objectives may be accomplished by electrolytic deposition of Mo_2C from a fused salt bath comprising an alkali halide and an alkali silicate. Molybdenum metal is then recovered by decarbonization of the carbide by reaction with a metal oxide having a relatively low volatilization temperature.

The salt bath (electrolyte) that has been found to give optimum results comprises a mixture of KCl, KF and anhydrous sodium metasilicate. The KCl and KF salts form a relatively low melting bath and are excellent conductors of electricity, but they do not dissolve appreciable amounts of molybdenite. The function of sodium metasilicate is to dissolve sufficient MoS_2 and form complex ions with the dissolved molybdenum for the satisfactory

electrolytic production of Mo_2C. The carbon content of Mo_2C is derived, directly or indirectly, from the carbon anode used in the electrolysis. This carbon anode is preferably a graphite crucible that serves as both anode and container for the fused bath. Potassium halide salts are preferred over corresponding sodium halides because high-purity Mo_2C is produced under parallel electrolytic conditions.

The initial proportions of sodium metasilicate to molybdenite should be regulated between about 1.3 to 1 and about 4 to 1 by weight, respectively. If insufficient solvent salt is employed, the molybdenite is not completely solubilized and resulting electrodeposit consists of synthetic MoS_2. With increasing quantities of solvent salt in the electrolyte, the electrodeposits gradate from MoS_2 to Mo to Mo_2C to a condition where the electrodeposit dissolves as rapidly as it is formed. Electrolytic conditions for producing pure Mo_2C are, however, much easier to regulate and reproduce than those for producing pure Mo metal. The proportions of KCl-KF-Na_2SiO_3 mixture to molybdenite may vary widely but tests have established that the molybdenite content of the total mixture should be maintained between about 2 and about 20 percent by weight for optimum results.

The apparatus employed in the electrodeposition is conventional and is described in the prior art such as the above cited Bureau of Mines publication and patents to Zadra et al.

During electrolysis the temperature of the molten salts should be maintained between about 900° and about 1,100° C. The preferred current density range is from about 10 to about 100 amperes per square decimeter of cathode. Although the anode current density is not critical it is usually maintained at about one-third to one-fifth of that of the cathode.

Any suitable conductive material may be employed in the cathode; however, graphite and tungsten rods have been found most suitable. However, the anode must be made of graphite or carbon as it supplies the carbon content of the electrowon Mo_2C.

The second processing step of the invention is the decarbonization of Mo_2C to produce pure molybdenum metal by intense heating as exemplified by sintering or arc melting under an inert atmosphere. It has been found that a mixture of Mo_2C and MoO_3, when heated, produces Mo metal, CO, and CO_2. The over-all chemical equation may be represented as:

$$5Mo_2C+2MoO_3 \rightarrow 12Mo+4CO\uparrow+CO_2\uparrow$$

It is preferred to use chemically pure molybdic oxide rather than other volatile metal oxides to circumvent the addition of impurities to the reduced molybdenum. Any excess CoC_3 added is sublimed during heating. Optimum temperature for converting the Mo_2C-MoO_3 mixture to pure Mo has been found to be about 1500° C. However, this temperature may vary somewhat according to reaction conditions and product requirements, e.g., the reaction goes to about 99 percent completion during prolonged heating (2 hours) at 1300° C. Tests indicate the amount of MoO_3 to be mixed with Mo_2C in the arc melting process (see example) is preferably about 125 percent of theoretical as indicated in the above chemical equation. When sintering is employed, the amount of MoO_3 is preferably about 110 percent of theoretical. Sintering at a temperature of about 1500° C. for about 10 minutes under inert atmosphere has been found to produce a molybdenum powder (rather than ingot as produced in arc melting) containing less than 150 p.p.m. of carbon and 450 p.p.m. of oxygen. An arc-cast ingot made from this powder contained less than 50 p.p.m. carbon and 100 p.p.m. oxygen and had a hardness of 172 V.H.N.

The following example will serve to more specifically illustrate the invention.

Example

The electrolyte consisted of 32.5 percent KCl, 30.0 percent KF, 30.0 percent Na_2SiO_3, and contained 7.5 percent MoS_2 (as molybdenite concentrate) by weight. The mixed charge was heated externally in a graphite crucible, which served as an anode during electroylsis, to 1,000° C. to solubilize the molybdenite feed material. The cathode was a graphite rod suspended in the center of the molten bath. Electrolysis was conducted without a protective inert atmosphere at 1,000° C. and at a cathode current density of 60 amps/dm.[2]. The molybdenum content was deposited on the cathode as firmly adhering dendritic crystals of Mo_2C. The electrodeposit was withdrawn from the molten bath, air cooled, and then submerged in water to dissolve the adhering electrolyte and free the Mo_2C crystals. Average yield was 30 grams Mo_2C per 100 ampere hours of electrolysis. The carbide crystals were substantially free from impurities such as aluminum, silicon, copper, and sulfur, commonly present in molybdenite concentrates. The Mo_2C crystals were ground to minus 100-mesh to liberate any entrapped graphite or electrolyte present. The ground product was then digested in dilute hydrochloric acid, to dissolve any water insoluble contaminants that might be present, washed and dried. The Mo_2C was mixed with about 125 percent of theoretical chemically pure MoO_3 needed to decarbonize the carbide. This mixture was arc-melted in an inert atmosphere (helium)to produce molybdenum metal ingots of better than 99.8 percent purity.

Several laboratory-scale electrolytic runs were made under the operating conditions stated above and demonstrated that reproducible results can readily be obtained by the process of the invention. Typical analyses of the electrowon Mo_2C and Mo ingots obtained from molybdenite feed are shown in the following table.

Element	MoS_2 feed, percent	Electrowon Mo_2C, percent	Mo ingot,[1] percent
Mo	49.4	94.0	99.8+
S	35.1	0.04	0.002
Si	2.8	0.002	0.002
Al	0.74	0.001	0.001
Ca	0.25	0.002	0.002
Cu	0.13	0.002	0.002
Fe	0.38	0.014	0.014
C	(2)	6.0	0.07
O_2	(2)	(2)	0.008

[1] Molybdenum ingot had a hardness reading of 186 Vickers Hardness Number.
[2] Not determined.

The high degree of purity of metallic molybdenum obtained from the process of the invention is apparent from the data given in the table.

Although the above example utilizes reactants that have generally been found to give optimum results, the invention is not limited to these materials. Other molybdenum compounds such as MoO_3, $(NH_4)_2MoO_4$, Na_2MoO_4, etc., may be used as feed materials, although generally without the obvious economic advantage to be achieved in the use of molybdenite.

Alkali halides other than KCl and KF may also be used, alone or in combination. These compounds may comprise any of the alkali or alkaline earth metals, i.e., Li, Na, K, Rb, Cs, Ca, Ba or Sr, as the metallic component while the halide may be of any of the halides, i.e., fluoride, chloride, bromide or iodide.

Other alkaline solubilizing reagents may also be used in place of the sodium silicate to facilitate dissolution of the molybdenum compounds in the molten electrolyte, e.g., alkali metal hydroxides, oxides, peroxides, carbonates, bicarbonates and borates.

Other metal oxides that will form a metal that volatilizes at temperatures below about 2200° C. may be used in place of the MoO_3 for decarbonization of Mo_2C, e.g., MoO_2, MgO and ZnO. MoO_2 is added in the same oxide equivalent as MoO_3 as required by the carbon present and the reaction proceeds similarly. MoO_3 is, however, generally preferred as it is less expensive. Decarbonization is also applicable to mixtures of molybdenum carbides and molybdenum metal.

When alkali halides or silicates, as well as Mo compounds and decarbonizing compounds, other than those of the example are used the optimum proportions of the reactants may vary from those disclosed above. Optimum proportions may, however, be readily determined empirically by those skilled in the art.

It has been further found that the Mo_2C produced according to the process of the invention may be utilized for deoxidation of hydrogen-reduced molybdenum powder. This powder is produced in conventional metallurgical processes by reaction of MoO_3 with hydrogen at elevated temperature. The product is a molybdenum powder usually having an oxygen content of from about 0.05 to about 0.3 percent.

This hydrogen-reduced powder is conventionally deoxidized by sintering or arc-melting a charge containing 0.7 to 1.0 gram of carbon black per 100 pounds of the hydrogen reduced molybdenum powder. It has now been found that the molybdenum carbide produced by the process of the invention, when substituted for the carbon black of the conventional process in chemically equivalent amounts, is very effective for deoxidizing hydrogen-reduced molybdenum powders to yield pure molybdenum metal.

What is claimed is:

1. A process for electrolytic preparation of molybdenum carbide comprising fusing in a container a mixture of (1) a molybdenum-containing material, (2) a low melting bath from the group consisting of alkali metal halide, alkaline earth metal halide and mixtures thereof, and (3) an inorganic alkali metal compound capable of solubilizing the molybdenum compound in the bath and electrolyzing the fused mixture using a cathode and a carbon anode, to deposit molybdenum carbide at the cathode.

2. The process of claim **1** in which the container is graphite and is the anode.

3. The process of claim **1** in which the molybdenum material is a molybdenite concentrate.

4. The process of claim **3** in which the molybdenite content of the mixture is from about 2 to about 20 percent by weight.

5. The process of claim **1** in which the low melting bath is a mixture of KCl and KF.

6. The process of claim **1** in which the solubilizing alkali metal compound is sodium metasilicate.

7. The process of claim **6** in which the ratio by weight of sodum metasilicate to molybdenite is from about 1.3 to 1 to about 4 to 1.

8. The process of claim **1** in which the temperature of the fused mixture is maintained at about 900° to about 1100° C. during electrolysis.

9. The process of claim **1** in which the cathode current density during electrolysis is from about 10 to about 100 amperes per square decimeter of cathode.

10. The process of claim **1** in which the product molybdenum carbide is further reacted at high temperature in an inert atmosphere with an oxide of a metal which volatilizes at temperatures below about 2200° C. to decarbonize the Mo_2C and form high purity molybdenum metal, said high temperature being at least sufficient to cause sintering of said molybdenum metal.

11. The process of claim **10** in which the high temperature is about 1500° C.

12. The process of claim **10** in which the high temperature is supplied by an electric arc, whereby molten molybdenum is produced.

13. The process of claim **10** in which the high temperature causes sintering of the molybdenum metal.

14. The process of claim 10 in which the decarbonizing metal oxide is molybdic oxide.

15. The process of claim 10 in which the decarbonizing metal oxide is MoO_2.

16. A process for electrowinning molybdenum from molybdenite concentrates comprising fusing in a graphite container a mixture of molybdenite concentrate, KCl, KF and sodium metasilicate, electrolyzing the fused mixture, with the graphite container as anode, to deposit molybdenum carbide at the cathode, removing and purifying the deposited molybdenum carbide and subsequently reacting the molybdenum carbide, at high temperature in an inert atmosphere, with MoO_3 to decarbonize the carbide and form high purity molybdenum metal, said high temperature being at least sufficient to cause sintering of said molybdenum metal.

17. A process for producing molybdenum metal comprising reacting molybdenum carbide with molybdenum oxide at a high temperature in an inert atmosphere, said high temperature being at least sufficient to cause sintering of said molybdenum metal.

18. The process of claim 17 in which the high temperature is about 1500° C.

19. The process of claim 17 in which the high temperature causes sintering of the mixture.

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