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ELECTROLYTIC PRODUCTION OF MOLYBDENUM POWDER AND COHERENT DEPOSITS

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The invention described herein may be manufactured and used by or for the Government of the United States for governmental purposes without the payment to us of any royalty thereon in accordance with the provisions of the Act of March 3, 1883, as amended (45 Stat. 467; 35 U. S. C. 45).

The present invention relates to the production of pure molybdenum powders and molybdenum plates by the electrolysis of molybdenum compounds in molten electrolytes.

At present molybdenum powder is produced commercially by the chemical reduction of the oxide. These methods, however, involve very high costs and many technical difficulties. It is also said to be possible to produce molybdenum powders by the electrolysis of molybdenum pentachloride dissolved in molten alkali halides or other materials. However, these methods suffer from the serious disadvantage that this compound is very volatile, boils at 268 degrees centigrade, and has a considerable vapor pressure at temperatures above 150 degrees centigrade. Also the compound is decomposed by atmospheric moisture at room temperature and is therefore difficult to store and handle.

The great desirability of electrolytically producing a coherent molybdenum deposit has long been recognized. Its possible use as a coating for high-temperature and corrosion-resistant applications has induced much experimentation in this field. The further possibility of electroforming objects of molybdenum would be a great improvement over present mechanical and powder metallurgy methods. However, to date no electroplates of molybdenum thicker than a few microns have been produced by any method known to the inventors.

It is the primary object of this invention to provide a method for the production of pure molybdenum by electrolysis.

Another object of the invention is to provide a method for the electrodeposition of molybdenum that will produce thick deposits of pure metal.

Another object of the invention is to provide an electrolytic method for the production of pure molybdenum powders.

Another object of the invention is to produce molybdenum with less than 0.05 percent oxygen as an impurity.

Another object is to produce molybdenum plates with a density approaching the theoretical density of the metal.

Another object of the invention is to produce a molybdenum deposit that is malleable.

Other uses and advantages of the invention will become apparent upon reference to the specification.

In accordance with the present invention an alkali-metal hexahalomolybdate (III), M_3MoX_6 (where M is an alkali metal and X is a halogen) is dissolved in an alkali halide or a mixture of alkali halides and is electrolyzed above the melting point of the mixture in an atmosphere of argon or other inert gas. In general the alkali halides constitute from 60 to 85 percent by weight of the bath and the alkali-metal hexahalomolybdate (III)

from 15 to 40 percent by weight. The temperature range of the bath is from 600 to 900 degrees centigrade, and the current densities range from 1 to 100 amperes per square decimeter. Cathode current efficiencies approaching 100 percent are obtained throughout most of this range of current densities.

To obtain molybdenum in the form of a plate in the preferred form of the invention, potassium hexachloromolybdate (III), K_3MoCl_6 is dissolved in an eutectic mixture of lithium chloride and potassium chloride and electrolyzed at temperatures in the range of 600 degrees C. to 700 degrees C. and at current densities in the range of 1 to 10 amperes per square decimeter. The best operating conditions have been found to be at 3 amperes per square decimeter and 600 degrees C. Coherent deposits of more than 0.02 inch have been obtained, and there seems to be no theoretical limitation on the thickness. The particular property of this mixture which probably makes it so useful is the fact that it is fluid at 600 degrees C. and the bath can be operated at this low temperature, which is 300 degrees below the recrystallization temperature of molybdenum. This same mixture gives very fine grained pure powders at current densities above 10 amperes per square decimeter or at temperatures above 700 degrees C.

To obtain molybdenum in the form of a powder, K_3MoCl_6 is dissolved in an alkali halide or a mixture of alkali halides and is electrolyzed at above approximately 700 degrees C. or approximately 10 amperes per square decimeter. Exceeding either limit will cause a powder to be deposited. Actually the changeover from a plate to a powder does not take place at exactly 10 amperes per square decimeter or at 700 degrees C.; the changeover is gradual. As the temperature or current density is raised the plates become more and more porous, and there is less coherence between the grains until at some indefinite point a powder is obtained.

The best powders have been obtained from the bath comprising K_3MoCl_6 dissolved in an eutectic mixture of LiCl and KCl when the bath is operated at above 700 degrees C. or above 10 amperes per square decimeter.

Another halide mixture that gives good results is one containing equal parts by weight of sodium chloride and potassium chloride. The bath is operated at temperatures of from 800 degrees C. to 900 degrees C. and at current densities of from 1 to 100 amperes per square decimeter. The lithium chloride mixture is better in that the lithium apparently assists in producing finer grain structure in the deposits at a given temperature and in addition allows lower operating temperatures. The sodium chloride-potassium chloride bath has the advantage of being less hygroscopic and thus absorbing moisture more slowly when exposed to the atmosphere.

The molybdenum produced in the powdered form has a lower oxygen content—as low as 0.025 percent—than that usually produced by the present commercial methods. The metal as produced is malleable when the oxygen content is maintained low. The low oxygen content of the molybdenum is maintained by keeping the argon and the materials used in the bath free of oxygen and keeping the system air tight. The plates obtained are thick and coherent and have densities of up to 9.6. This compares very favorably with the theoretical density of 10.2.

Molybdenum powder in the form of dendrites having extreme purity can be obtained with current densities of between 70 and 100 amperes per square decimeter when the bath contains between 15 to 22 percent of potassium hexachloromolybdate (III).

The use of the trivalent molybdenum compound, K_3MoCl_6, has several advantages. The compound is easily prepared and is stable in the atmosphere up to

temperatures of about 100 degrees C. Also it is thermally stable up to at least 600 degrees in the absence of water or oxygen and the compound is negligibly volatile at the temperatures of operation, 600 degrees to 900 degrees C. As a result of this stability the composition of the bath is easily maintained, as there is no loss of material due to volatility. Also no impurities are formed in the bath and additions of the salt are easily made. Further, the molybdenum in the bath may be replenished by the use of molybdenum anodes since the ions produced when the anode dissolves in the bath are of the trivalent form and the anode current efficiency of this process approaches 100 percent. For electrowinning purposes the bath may be operated with an insoluble anode, with suitable separation of anolyte and catholyte.

It will be apparent that the embodiments shown are only exemplary and that various modifications can be made within the scope of our invention as defined in the appended claims.

We claim:

1. A process for obtaining molybdenum that comprises electrolyzing a bath including 15 to 40 percent, by weight, of potassium hexachloromolybdate (III) and 85 to 60 percent, by weight, of an alkali halide electrolyte, the electrolysis taking place in an atmosphere of an inert gas.

2. A process for obtaining molybdenum that comprises electrolyzing a bath including 15 to 40 percent, by weight, of potassium hexachloromolybdate (III) and 85 to 60 percent, by weight, of an alkali halide electrolyte, the electrolysis taking place in an atmosphere of argon with said bath operated at temperatures in the range of 600 degrees C. to 900 degrees C. and at current densities in the range of 1 ampere per square decimeter to 100 amperes per square decimeter.

3. A process for obtaining molybdenum that comprises electrolyzing a bath including from 15 to 40 percent, by weight, of an alkali metal hexahalomolybdate (III) where the alkali metal is selected from the group consisting of lithium, sodium, potassium, rubidium, and cesium, and the halogen is selected from the group consisting of fluorine, chlorine, bromine and iodine, and from 85 to 60 percent, by weight, of a molten salt selected from the group consisting of alkali halides and a mixture of alkali halides, the electrolysis taking place in an atmosphere of argon at temperatures in the range of 600 degrees C. to 900 degrees C. and at current densities in the range of 1 ampere per square decimeter to 100 amperes per square decimeter.

4. A process for electroplating molybdenum that comprises electrolyzing a bath including 15 to 40 percent, by weight, of potassium hexachloromolybdate (III) and 85 to 60 percent, by weight, of an eutectic mixture of potassium chloride and lithium chloride, the electrolysis taking place in an atmosphere of argon.

5. A process for electroplating molybdenum that comprises electrolyzing a bath including 15 to 40 percent, by weight, of potassium hexachloromolybdate (III) and 85 to 60 percent, by weight, of an eutectic mixture of potassium chloride and lithium chloride, the electrolysis taking place in an atmosphere of argon with the bath operated at temperatures in the range of 600 degrees C. to 700 degrees C. and at current densities in the range of 1 ampere per square decimeter to 10 amperes per square decimeter.

6. A process for electroplating molybdenum that comprises electrolyzing a bath including 15 to 40 percent, by weight, of potassium hexachloromolybdate (III) and 85 to 60 percent, by weight, of an eutectic mixture of potassium chloride and lithium chloride, the electrolysis taking place in an atmosphere of argon with the bath operated at a temperature of 600 degrees C. and at a current density of 3 amperes per square decimeter.

7. A process for obtaining molybdenum powder that comprises electrolyzing a bath including 15 to 40 percent, by weight, of potassium hexachloromolybdate (III) and 85 to 60 percent, by weight, of an eutectic mixture of potassium chloride and lithium chloride, the electrolysis taking place in an atmosphere of argon with the bath operated at temperatures in the range of 600 degrees to 900 degrees C. and at current densities in the range of 10 amperes per square decimeter to 100 amperes per square decimeter.

8. A process for obtaining molybdenum powder that comprises electrolyzing a bath including 15 to 40 percent, by weight, of potassium hexachloromolybdate (III) and 85 to 60 percent, by weight, of an eutectic mixture of potassium chloride and lithium chloride, the electrolysis taking place in an atmosphere of argon with the bath operated at temperatures in the range of 700 degrees C. to 900 degrees C. and at current densities in the range of 1 ampere per square decimeter to 100 amperes per square decimeter.

9. A process for obtaining molybdenum powder that comprises electrolyzing a bath including 15 to 40 percent, by weight, of potassium hexachloromolybdate (III) and 85 to 60 percent, by weight, of an alkali halide electrolyte, the electrolysis taking place in an atmosphere of argon with the bath operated at from 800 degrees C. to 900 degrees C. and at current densities in the range of 1 ampere per square decimeter to 100 amperes per square decimeter.

10. A process for obtaining molybdenum powder that comprises electrolyzing a bath including 15 to 40 percent, by weight, of potassium hexachloromolybdate (III) and 85 to 60 percent, by weight, of an electrolyte made up of equal parts by weight of sodium chloride and potassium chloride, the electrolysis taking place in an atmosphere of argon with the bath operated at from 800 degrees C. to 900 degrees C. and at current densities of from 1 ampere per square decimeter to 100 amperes per square decimeter.

11. A process for obtaining molybdenum that comprises: electrolyzing a bath including 15 to 40 percent, by weight, of an alkali metal hexahalomolybdate (III) where the alkali metal is selected from the group consisting of lithium, sodium, potassium, rubidium, and cesium; and the halogen is selected from the group consisting of fluorine, chlorine, bromine, and iodine; and from 85 to 60 percent, by weight, of a molten salt selected from the group consisting of alkali halides and a mixture of alkali halides, the electrolysis taking place in an inert atmosphere.

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