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ELECTROREFINING OF MOLYBDENUM

Frank X. McCawley, Cheverly, Md., assignor to Chicago Development Corporation, Riverdale, Md., a corporation of Delaware

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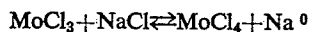
1 Claim. (Cl. 75—5)

This invention relates to the electrorefining of molybdenum. It relates particularly to molten chloride baths for refining molybdenum.

Molybdenum is known to be electrodeposited from molten alkali or alkaline earth chlorides containing a lower molybdenum chloride. A soluble anode containing molybdenum metal may be used in such baths and molybdenum transferred from anode to cathode. Such a process, however, does not refine from oxygen present in the anode or from tungsten, which is often found in molybdenum scrap to be refined. The principal impurity in commercial molybdenum is oxygen since commercial MoO_3 from which it is produced has substantially no metallic impurities.

In my present invention, I provide an electrolyte containing MoCl_3 , MoCl_4 and alkaline metal dissolved in molten alkaline chloride. By "alkaline" I mean to include sodium, potassium, calcium, strontium and barium metals.

This electrolyte is defined by an equilibrium of which the following is typical



The average effective valence in my electrolyte is 3.1–3.6 as determined by its reducing power to ferric sulphate and by total soluble molybdenum in the electrolyte. The soluble sodium (or other alkaline metal) content of the electrolyte is defined as the chemical equivalent of hydrogen evolved in acidified ferric sulphate and in my electrolyte is present from a significant amount to 0.25 cc. hydrogen evolved per gram of electrolyte.

The electrolyte of my invention is clear and reddish in color and contains from 1–5% total soluble molybdenum.

The electrolyte of my invention can be prepared in a number of ways, but I prefer to add MoCl_5 which is commercially available to a molten NaCl bath in a graphite pot which is provided with a centrally located graphite rod cathode. Comminuted pure molybdenum metal is placed on the bottom of the pot and a current passed from the pot as anode to the graphite rod cathode. The MoCl_5 is added gradually while the current is passed at 5–50 amperes per sq. ft. on the cathode. After enough MoCl_5 is added to provide the desired total soluble Mo, the current is continued until the electrolyte of my invention, as defined above, is obtained.

The molybdenum to be refined, particularly from oxygen, tungsten and any insoluble impurities is then added in comminuted form on the bottom of the graphite pot and electrolysis continued.

I obtain pure coarsely crystalline molybdenum as a deposit adherent to the cathode.

The cathode deposit is of characteristic structure and consists of a thin continuous plate on the graphite rod, a layer of salt containing fine molybdenum crystals and growing out of this layer coarse crystal intergrowths of pure molybdenum constituting at least 90% of the deposit. The molybdenum crystals are cubic in form.

Under preferred conditions, the molybdenum in the anode deposit is in highly ductile acicular crystals from 1" long and up to $\frac{1}{4}$ " in diameter. The oxygen content of these highly ductile acicular wires is less than 0.1%.

In all the following examples, the molybdenum to be refined was supported on graphite which was connected

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anodically. The electrolyte was held in a graphite pot and a centrally located graphite cathode was used.

Example I

In this example, I took a stainless steel pot 4" I.D. x 9" length and insert a cathode liner fitting snug against the pot and having a wall thickness of $\frac{3}{16}$ ". A water cooled lid fits over the steel pot and has an argon inlet and outlet. The lid is sealed tightly by means of a rubber O ring. Through the center of the lid a graphite rod is inserted through an insulated bushing. An opening with valves is also provided in the lid for the addition of salt and anode material.

In this apparatus, I placed on the bottom of the graphite 200 gms. of pure molybdenum pellets. I added two pounds of NaCl and heated to 850°C . When the salt had become molten, I added a small amount of MoCl_5 and passed a current of 1.0 amp. through the cell. I slowly added MoCl_5 until 100 grams had been added. I continued to run at 1.0 amp. until the sample of salt removed analyzed as determined by reducing power in ferric sulphate as having a valence of 3.5 and having a total soluble molybdenum content of 4.7% as determined by the Jones reductor. The salt has a sodium content as determined by hydrogen evolution in acidified ferric sulphate of 4 cubic centimeters of hydrogen per gram of electrolyte.

I then added 400 grams of tungsten-molybdenum scrap wire, pressed into pellets. The composition was 50% W, 50% Mo, .03% O_2 . I then raised the current to 10 amps. and ran for 12 hours at which time I raised the cathode rod from the salt and allowed to cool.

Upon removing the cathode from the pot, I find the cathode completely covered with acicular crystals. These crystals were up to one inch in length and had a maximum diameter of $\frac{1}{4}$ ". I removed the crystals from the cathode and observed a layer of red salt beneath these crystals. Washing both the crystals and cathode in dilute acid, the cathode showed an adherent plate on the rod. The crystals were extremely ductile and weighed 182 grams. The analysis showed them to be 99.94% Mo, .002% O_2 , .001% N_2 , .013 Fe and no trace of W.

An analysis of the electrolyte at this time showed the total molybdenum to be 4.68, valence of 3.55 and sodium 5 cc. of H_2 .

Removal of the anode material showed the pellet had dissolved in an irregular fashion. Analysis of this material showed tungsten to be 99% and a little less than 1% molybdenum.

The cathode current density of this cell during valence adjustment was 43 amps./sq. ft. and during operation 450 amps./sq. ft. The anode current density was approximately 50–100 times lower.

Example II

In this example, I used a cell as described in Example I except that the anode material was held in a graphite basket surrounding the graphite cathode.

I melt two pounds of NaCl and add slowly 130 gms. of MoCl_5 while passing a current of .5 amp. between a graphite basket of pure molybdenum and the graphite liner. The basket is used as anode and graphite as cathode. I continue to pass current until the salt analysis is 4.5% soluble Mo, a valence of 3.2 and a sodium metal content equivalent to 4.6 cc. H_2 /gms. electrolyte.

I removed the gasket of pure molybdenum and replaced it with a graphite concentric basket containing a comminuted molybdenum anode material containing .54% oxygen. I placed in the center a graphite cathode rod. I then passed current between the basket and rod so that the basket was anode and the rod cathodic. After ten hours at a current of 15 amps. or a current density of

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720 amps./ft., I raised the cathode and allowed it to cool. The cathode product was crystalline and after washing in dilute acid weighed 178 gms. It was coarse and was cubic in structure. Analysis gave the molybdenum as 99.97%, oxygen as .002%, nitrogen as .005% and iron as .012%.

The residual anode material when washed and analyzed gave molybdenum as 98.7% and oxygen as 1.1%. The analysis of the electrolyte was 4.5% soluble Mo, average valence 3.3 and 4.5 cc. H_2 /gms. electrolyte.

Example III

In this example, I proceeded as before except that I use as my salt calcium chloride. Due to the impurities usually contained in this salt, I deoxidize my bath with MoO_3 . I then proceed as in Example II. The product

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obtained is coarse crystals and upon analysis contains 99.93% Mo, .001% O_2 , .004% N_2 and .013% Fe.

What is claimed is:

As an article of manufacture discrete crystals of pure molybdenum in the form of ductile acicular crystal aggregates the individual crystals being from $\frac{1}{8}$ " to 1" long and up to $\frac{1}{64}$ " in diameter and containing not more than .002% oxygen and at least 99.94% molybdenum.

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