REDUCTION AND DISSOCIATION OF MOLYBDENUM COMPOUNDS IN A TRANSFERRED PLASMA ARC

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ABSTRACT

Molybdenum sulfides were thermally dissociated or reduced in a transferred plasma arc using the molten surface of a concast molybdenum ingot as the anode. The purity of the ingot was dependent on the starting powders and the plasma conditions. Scaling up of the ingot reduced the power consumption and increased recovery rates. Optimum values were 10.4 kw-hrs/lb. of molybdenum at 87.5% recovery.

1. INTRODUCTION

In a low intensity arc, the plasma column contains a stream of electrons flowing from the cathode to the anode and a counter-current flow of ions from the anode to the cathode. The collisions between the electrons and larger gas particles transfers the energy to the larger particles which are heated and reach ionization temperatures. The axial temperatures of a low intensity arc plasma is usually in the neighborhood of 5,000 to 6,000°K.

Higher temperature arcs were developed by I. Langmuir in 1924 by forcing molecular hydrogen into arcs thereby dissociating the molecular hydrogen into "atomic hydrogen". The dissociation absorbed large quantities of heat which were released and utilized when the atomic hydrogen cools to the molecular state.

Very high temperatures can be obtained in "plasma arcs" by using wall stabilization phenomenon to increase the plasma pressure and density by passing the arc with a column of gas or water through a water-cooled nozzle. The heating of the larger particles of ions and neutral atoms occurs by collisions, and obtaining a thermal equilibrium of these particles with the electrons requires high energy inputs by means of high collision rates. The plasma arc provides higher collision rates and higher temperatures than open arcs thereby offering the potential for reducing refractory metal compounds.

EXPERIMENTAL APPARATUS AND PLASMA ARC REACTIONS

The D.C. transferred plasma arc consisted of a water-cooled copper cathode containing a 2% thoriated tungsten tip. Powdered reactants were fed with the plasma gas. A water-cooled copper nozzle, by channeling the flow of gas and powder reactants, acts to stabilize the arc but does not act as an anode. The arc, gases, and powder pass through the nozzle and are transferred to the molten surface of the ingot which acts as an anode. A continuous casting system was incorporated into the transferred arc system, using a 1/4"-wall water-cooled molybdenum mold. The conductivity was adequate to prevent mold erosion and also provide a mold surface withstanding temperatures of 2620°C. The ingot was continuously withdrawn from the mold as the metallic product collected in the molten anode pool.

A powder feeding device was innovated for this research. The device used a brush rotating inside a cylindrical screen which forced individual powder particles through the screen and into a gas stream flowing through the feeding device and into the plasma arc. A button melting apparatus was used for remelting. The all argon plasma arc used a metallic button as the anode.

Thermal dissociation and reduction were considered as the two means of producing metallics from oxides and sulfides. For thermal dissociation, a pure argon gas plasma appeared to be the most feasible experimentally, while for the reduction studies, an all-hydrogen or a hydrogen-argon gas plasma appeared to be the most desirable. Hydrogen reduction of oxides is a feasible method for producing molybdenum. However, hydrogen is not a final scavenger for the residual traces of oxygen in the metal so commercially carbon is added in the subsequent vacuum arc melting. Reactive transition metals (titanium, zirconium) are then added during the melting operation in order to compound the carbon and help disperse the carbides. The refractory metal sulfides are potentially capable of being hydrogen reduced to the metallic state, as shown in free energy diagrams. In commercial operations, however, the sulfides are roasted to the oxides and then reduced to metallic powders which are then consumable arc-melted.

RESULTS

The Distribution of Energy in the Arc and Arc Temperatures

The energy distribution in a typical transferred argon arc was 34% to nozzle, another 4.0% is lost to the cathode. The energy released at the ingot-anode produces a molten pool for collecting the reaction products and for additional reaction by serving as a hot medium into which is propelled cold reactants and the ionized plasma gases. The reaction rates are known to be more rapid where an activated or ionized species is used as the reactants instead of a molecular species.

Low gas flows and the use of hydrogen produced maximum heat contents in the arc gases. Mean plasma temperatures and the degree of dissociation and ionization of the arc gases were determined from the heat content values and standard tables. Thus for a transferred arc run where MoS_2 was reduced in a hydrogen plasma to molybdenum which collected on the ingot-anode, the heat content of the hydrogen gas of 373 watt hours per cubic foot represented a mean temperature of 10,400°K with hydrogen dissociation being complete and partial ionization occurring. However, these temperatures were "mean" because the assumption was made that the heat content was evenly distributed in the plasma arc.

Dissociation of MoS_2

The optimum values for MoS_2 dissociation in an argon plasma were found to be 87.6% recovery of the molybdenum with a power consumption of 20.5 kilowatt hours to produce one pound of ingot molybdenum containing 5.1% carbon and 13.7% sulfur. Because the MoS_2 feed contained 1.44% graphite, which is a natural contaminant in MoS_2, a buildup of carbides occurred on the ingot as shown by the 5.1% carbon analyses.

X-ray diffractograms of the ingot-anode showed the presence of Mo_2C while the diffractograms of the powdery residue which collected on the chamber walls of the torch system show Mo and MoS_2 patterns plus a major unidentifiable peak. Similar results were observed in the reduction studies of MoS_2.

An x-ray pattern for Mo_2S_3 has been reported but was never observed in these studies. However, x-ray diffraction of plasma products often showed patterns which were out of phase or slightly altered. These discrepancies were attributed to the tremendous thermal quenches which the plasma products undergo as they are emitted from the hot plasma.

Reduction of MoS_2

The results of MoS_2 reduction in a hydrogen plasma show a minimum power consumption of 20.2 kilowatt hours per pound of molybdenum with a recovery of 58%. Analyses of the ingot showed 0.02% carbon and 0.47% sulfur. A low-carbon MoS_2, used as the feed, was prepared by the thermal dissociation of MoS_3 in argon. The MoS_2 analyzed 0.07% carbon.

In the all-hydrogen plasma, it was observed that the excessive heat liberated by the hydrogen plasma condensing at the ingot-anode caused overheating and excessive boiling and loss of reactants and products. Because the hydrogen plasma was overheating the ingot-anode whereas the argon plasma was observed not liberating sufficient heat at the ingot surface, a mixture of argon and hydrogen was used to provide the proper heat transfer and energy at the ingot-anode.

Reductive Dissociation of MoS_2

The results of MoS_2 reductive dissociation, a term used signifying that both argon and hydrogen were used as plasma gases, are shown below. As the data evolved, changes were made in the reactants and arc conditions. The preliminary experiments also showed that if carbon were present in the MoS_2 reactants (1.44% carbon), then carbides readily formed in the ingot (0.94% carbon).

When a low-carbon MoS_2 was reductively dissociated, a low carbon-0.01% molybdenum ingot was produced. However, the sulfur content was high - 0.35%. The low carbon MoS_2 was prepared by the thermal dissociation of MoS_3 in argon at 800°C yielding MoS_2 analyzing 0.03% carbon.

A method of removing the carbon from the ingot produced from high carbon MoS_2 reactants was to add MoO_2 or MoO_3 to the powder reactants thereby allowing the formation of CO (or COS) to remove the carbon during arc reduction.

Runs were made to show the results of adding MoO_3 in oxygen: carbon ratios of 1:1, 2:1 and 4:1 to the amount of carbon present in order to form CO. These oxide additions reduced the carbon content of 1.44% to 0.10% to 0.05%. The addition of MoO_3 did not significantly increase the oxygen where no oxide was added while another run had an oxygen content of 0.01% where the oxygen:carbon ratio was 4:1.

The removal of carbon from the reactants during arc reduction was more pronounced when the less volatile MoO_2 was added as the oxidant. Also in this study, a larger 1.2" diameter ingot-anode was substituted for the 0.75" ingot-anode previously used. The larger ingot combined with the MoO_2 additive produced the highest purity ingot when arc reducing high carbon MoS_2. Using MoO_2 with an oxygen-carbon ratio of 2:1 produced from the reduction of MoS_2 containing 1.29% carbon, a high purity molybdenum ingot of the following analyses: carbon 100 ppm, sulfur 900 ppm, oxygen 100 ppm, iron $<$ 200 ppm and silicon $<$ 20 ppm. The power consumption was 20.7 KW-Hrs/lb. and the recovery was 71.6%. Without MoO_2 additions, the carbon contamination occurred (0.44%C).

By increasing the ingot-anode diameter to 1.92" and the MoS_2 feed rate to 10.7 lbs/hr, low power consumptions (10.4 KW-Hrs/lb.) and high recovery values (87.5%) were observed. The combination of the high feed rates and recovery values resulted in molybdenum being collected at a rate of 3/4 lb/hr. The average chemical analysis of the ingot showed C - 0.42%, S_2 - 0.45% and O_2 - 0.04%. A higher purity ingot should have been produced if MoO_2 were added to the MoS_2 containing 1.29% carbon, or if a low carbon MoS_2 feed were used.

The copper and iron contaminants which are present in the molybdenite concentrate were usually decreased by a factor of ten during plasma arc reduction. The more volatile contaminants like magnesium, sodium, and potassium were either reduced to only a few parts per million, or were not found in the molybdenum ingots.

Dissociation and Reduction of MoS_3

Attempts to either dissociate MoS_3 in argon or hydrogen reduction resulted in high power consumption and poor recovery values. Using both argon and hydrogen, recovery values were low (40-50%), but power consumption dropped to 27 KW-Hrs/lb. of molybdenum. Carbon and sulfur contents averaged 0.05% and 0.13% respectively. Lower carbon and sulfur contents were found in another run with a high recovery rate (83%) and high (71.2) KW-Hr/lb.

Double Decomposition of MoO_3 and MoS_2

The double decomposition reaction

$$3\ MoS_2 + 4\ MoO_3 = 7\ Mo + 6\ SO_2$$

of MoO_3 and MoS_2 was examined using stoichiometric mixtures in an argon plasma. One run had a 37% recovery of the total molybdenum available, and 60 KW-hrs/lb. of molybdenum recovered. To determine if dissociation of either MoS_2 or MoO_3 occurred rather than the double decomposition, the total percent of molybdenum available from the MoS_2 in the reactant is only 27%. Yet the overall molybdenum yield is 37%. From earlier results it was shown that argon dissociation of MoS_2 does occur but the dissociation of MoO_3 was not expected especially in an argon plasma.

Reduction of Molybdenum Oxides

When MoO_3 was fed into a hydrogen plasma, low recovery and high power consumption values were attributed to the high vapor pressure of MoO_3. Reduction of MoO_2 was readily accomplished. Ingot anode diameters of 0.75%, 1.20" and 1.92" were used. Again as in the sulfide reduction the 1.92" ingot anode resulted in the lowest power consumption 21.7 KW-Hrs/lb. The highest recovery (58%) was observed using a 1.20" anode. Carbon in the MoO_2 feed produced by the hydrogen reduction of MoO_3 at 450°C was 0.01%. The ingot analyzed 0.02% carbon, 78 ppm oxygen.

Button Remelting and Ingot Scale-Up

A further purification was achieved by button remelting the molybdenum ingots produced by the reduction of sulfides in an argon plasma arc. The purities obtained by button melting are compared to the results from button melting of commercial molybdenum. These values show that remelting increases purity and is effective in removing sulfur while partially reducing the carbon content. When the purities of the commercial molybdenum are compared to the purity of the plasma-formed molybdenum, the comparison shows that the plasma reduction (dissociation) of MoS_2 powders with a remelt operation produces molybdenum equal in purity to commercial molybdenum.

Scale-up studies were made by comparing the results of MoS_2 reduction in an argon-hydrogen plasma. Variables kept constant were gas flow, amperage, voltage and nozzle configuration. By increasing the ingot diameter from 0.75" to 1.92", the recovery can be increased by 10% (from 77 to 87%) in the higher feed (9.3 gms/min.) rates, while the lower feed rate (5.2 gms/min.) increased the recovery by about 20%. The power consumption is also improved as the ingot anode size increases. The largest ingot circumference or diameter provides the lowest power consumptions. Also, the higher feed rates results in the lowest power consumption per pound of molybdenum recovered. The optimum conditions were found with the 1.92" diameter ingot wherein the recovery was 87.5% and the power consumption was 10.4 KW-hrs/lb of molybdenum recovered, with molybdenum forming at the ingot anode.

CONCLUSIONS

MoS_2 and MoS_3 were thermally dissociated in an argon plasma as well as reduced in hydrogen-argon plasmas to metallic molybdenum in wall stabilized plasma arcs using a transferred arc mode. The molten surface of a molybdenum ingot acted as both the anode and liquid susceptor into which were impinged the plasma reaction products. As the molten molybdenum formed at the ingot anode, the molybdenum was continuously cast into 0.75", 1.20", or 1.92" diameter ingots using water-cooled molybdenum molds. Plasma arc reduction of MoS_2 containing graphite (1.29%) produced molybdenum ingots with molybdenum carbide impurities. Additions of MoO_2 and MoO_3 to the graphite containing MoS_2 resulted in the formation of low carbon (0.01%) molybdenum ingots. Plasma arc reduction of high purity MoS_2 (0.03-0.07% carbon), formed from thermal decomposition of MoS_3, also resulted in low carbon (0.01-0.02%) molybdenum ingots. Scaling up of the ingot anode from 0.75" to 1.20" to 1.92" diameter decreased the power consumption and increased both recovery and production rates. The optimum values obtained were 10.4 KW-Hrs/lb. of molybdenum recovered with a recovery value of 87.5%. The sulfur content of molybdenum formed by hydrogen reduction of MoS_2 was approximately 0.5%. By adding an oxidant such as MoO_2, sulfur levels were reduced to 0.09%. Finally, with arc button remelting, sulfur levels were reduced from 0.5 to 0.004%.