

White Paper:

Advanced Reactor System for the Fine Control of Properties of Molybdenum Powder

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Abstract

Extensive investigation in the two-stage hydrogen reduction process for fine molybdenum powder synthesis has been conducted. Reaction thermodynamic, kinetics, grain morphology transformation mechanism, grain morphology and grain size control have been studied in detail. Pilot scale development work has been performed. Stage one reduction is highly exothermic and it proceeds as $\text{MoO}_3 \rightarrow \text{Mo}_4\text{O}_{11} \rightarrow \text{MoO}_2$. Mo_4O_{11} exists as an intermediate product which is a stable phase and has needle shaped grain morphology. Desirable MoO_2 morphology can be obtained if exothermic reaction is properly controlled in stage one reduction. The second stage reduction, $\text{MoO}_2 + \text{H}_2 \rightarrow \text{Mo} + 2\text{H}_2\text{O}$ is an endothermic reaction. The final product Mo inherits MoO_2 's morphology. Mo product grain size and size distribution is determined by stage two reduction. In both stages, grain morphology transformation mechanism follows nucleation of product phase and product phase crystal growth via chemical vapor transport. Volatile molybdenum oxide monohydrate, $\text{MoO}_2(\text{OH})_2$, is the gas phase responsible for the chemical vapor transport of Mo. Complete reduction system was designed and engineered based on this pilot development work. Optimized process parameters developed in pilot scale have been successfully scaled up by 35 times, up to a production rate of 2.4 tons quality Mo powder product per day. The system consisted of rotary (stage one) + 18 tube pusher (stage two) system which is superior to a traditional pusher + pusher system from both product quality control and cost saving.

Introduction

In the refractory metal industry, fine-grain molybdenum (Mo) powder is usually produced by a two-stage reduction process. Both Ammonium Di-Molybdate (ADM) and Molybdenum Trioxide (MoO_3) can be the starting materials with hydrogen (H_2) as the reducing gas in either case. The first stage is to convert MoO_3 or ADM to MoO_2 (molybdenum dioxide) in a rotary reduction furnace or a pusher type kiln. The second stage reduction is to convert the MoO_2 to Mo metal in a multi-tube pusher or a single tunnel pusher kiln.

In the first stage reduction, the challenge is controlling the highly exothermic reaction ($\text{MoO}_3 + \text{H}_2 \rightarrow \text{MoO}_2 + \text{H}_2\text{O}$). Rotary reactor has several advantages compared with a pusher type tunnel furnace - low energy consumption, low capital cost (smaller equipment size due to good gas-solid contact i.e., shorter residence time for complete conversion), automatic material handling, easier control of exothermic energy, low maintenance and low labor cost, plus superior product quality. Control of the MoO_2 grain morphology and apparent density is critical to the final Mo powder quality. Mo_4O_{11} is proved to be an intermediate product with unique needle shaped grain morphology which makes MoO_2 morphology control more sophisticated. Reaction via ADM to MoO_2 route is relatively easier to control; however, the bulk density and grain morphology is not as desirable. Temperature profile, H_2 dew point, H_2 flow rate, and residence time are the key process parameters for reaction and morphology control in the first stage reduction.

The second stage reduction is an endothermic reaction. A multi-tube furnace is the standard equipment for Mo particle size control. Mo powder grain size, grain size distribution, and low oxygen content are achieved in this stage. Reaction temperature, H_2 flow rate, H_2 dew point, solid material bed depth, and residence time are the major process control parameters.

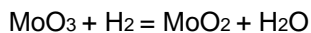
The purpose of this development work was to explore the optimized process conditions in the rotary + multi-tube pusher reactor system for desirable Mo product. The work is focused on industrial application rather than academic research. Thermodynamics, kinetics, product grain size and morphology control of the two stage reductions has been extensively investigated. Finally, issues particular to the scale-up of this process are investigated. Optimized process parameters developed in pilot scale have been used to successfully scale up this process in several installations, up to a production rate of 2.4 tons Mo product per day.

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The Process and Complete Process System

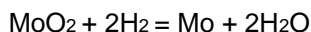
Both MoO_3 or ADM are used as feed material for Mo reduction process. ADM can be reduced directly to MoO_2 by H_2 . MoO_3 is either calcined ADM or sublimed MoO_3 . Therefore, the Mo reduction process follows either $\text{ADM} \rightarrow \text{MoO}_2 \rightarrow \text{Mo}$ route or $(\text{ADM} \rightarrow) \text{MoO}_3 \rightarrow \text{MoO}_2 \rightarrow \text{Mo}$ route. When using MoO_3 as feed for the two-stage reduction, the following reactions are considered to be of prime importance in the Mo reduction process:

The first stage reduction,



is a highly exothermic reaction. The heat of reaction at 600°C is $-155 \text{ kcal/kg-MoO}_3$. Reaction is normally carried out at above 500°C . To achieve the reduction from MoO_3 to brown colored MoO_2 is not difficult. However, to obtain MoO_2 with desired morphology, particle size, and apparent density is very challenging. At adiabatic condition, the high exothermic reaction energy will heat the material to approx. 1000°C from room temperature, which results in local hot spots and run-away reaction. Therefore, temperature and atmosphere control is critical in stage one reduction.

The second stage reduction,



is an endothermic reaction. Heat of reaction is $138.6 \text{ kcal/kg-MoO}_2$ at 1050°C . Particle size, size distribution, and oxygen content of the final Mo product are controlled in this stage.

Fig.1 is a Process Flow Diagram (PFD) of the complete reduction system Harper proposed and engineered. The major components include: a rotary for ADM calcinations to MoO_3 , a rotary reactor for stage-one reduction, a 18 tube pusher type furnace for stage-two reduction, a H_2 dryer system to recycle the H_2 gas, a dust filter for entrainment collection, a scrubber for waste gas treatment and dust collection. This complete process system features low energy consumption, low equipment cost, low raw material loss by recycling wet H_2 and dust collection, automatic material handling, low maintenance and low labor cost, gas/dust-tight and off-gas treatment for environmental protection, and superior product quality under controlled process conditions.

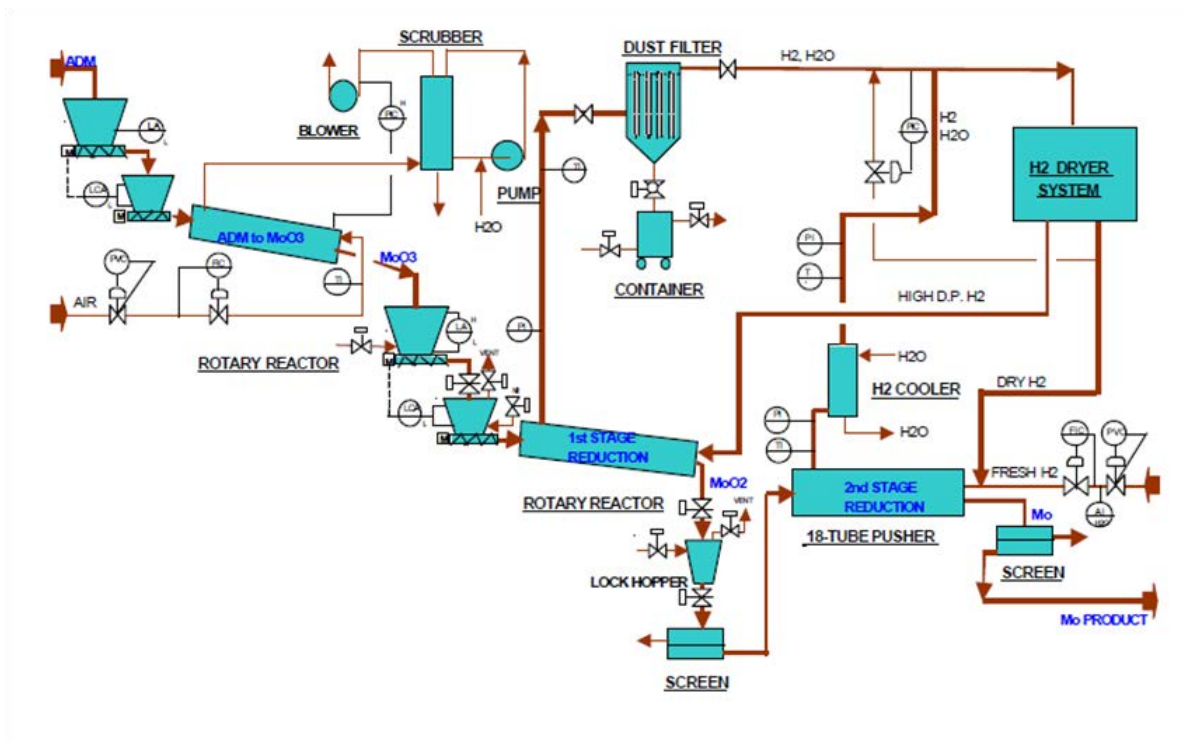


Fig. 1. Process Flow Diagram of the Complete Mo Reduction System

Pilot Reactor System

Stage-one reduction (MoO_3/ADM to MoO_2) tests were conducted in Harper R&D lab pilot rotary reactor. The furnace tube diameter is 6" and has a 60" heated length. Furnace is indirectly heated and has three heating zones for temperature control and profiling. MoO_3/ADM is fed into the furnace tube at a desired rate by a screw feeder. The tube angle and tube rotation speed is adjustable to vary the material residence time. H_2 atmosphere is the reactant gas and N_2 is used for purging. Flammable atmosphere control panel is used for gas flow control. H_2 dewpoint is adjusted via a humidifier. The off gas runs through a water bubbler and then is sent to a flare.

Stage-two reduction (MoO_2 to Mo) was conducted in a tube furnace. An alloy boat (4" wide, 2" tall, 19" long) loaded with desired MoO_2 bed depth was placed in the middle of the tube. H_2 atmosphere is the reactant gas and N_2 is used for purging. Temperature, H_2 flow rate, H_2 dewpoint, MoO_2 bed depth, residence time can be varied to simulate the multi-tube furnace operation.

Thermodynamic Analysis

Fig.2 and Fig.3 are the equilibrium gas composition vs. temperature for the two stage reductions (MoO_3 and MoO_2 reduction by H_2), which are the results from thermodynamic calculations. They are used to determine the proper H_2 dewpoint in each stage reduction.

The following conclusions can be drawn from the thermodynamic calculations:

1. Equilibrium H_2 concentration varies with reaction temperature in both stages.
2. Stage-one reduction ($\text{MoO}_3 \rightarrow \text{MoO}_2$) occurs with extremely low H_2 concentration (wet H_2).
3. Stage-two reduction ($\text{MoO}_2 \rightarrow \text{Mo}$) requires extremely high H_2 concentration (dry H_2).

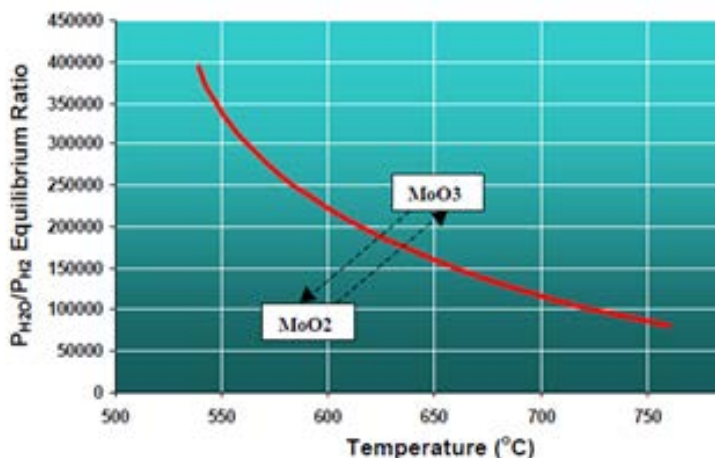


Fig.2. Chemical Equilibrium Calculations—Stage One Reduction

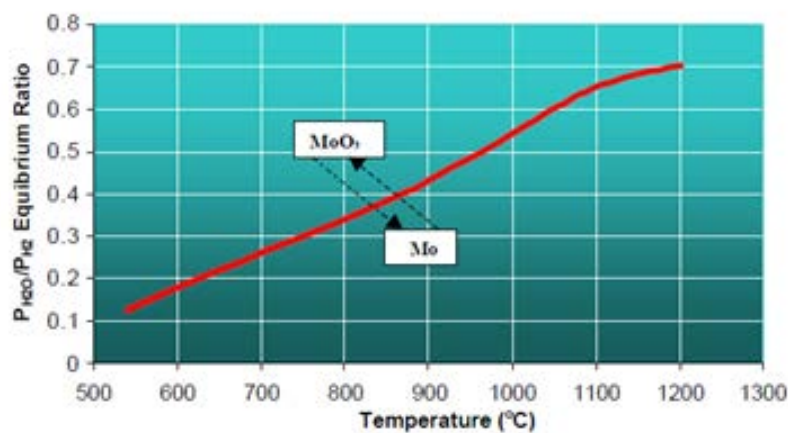


Fig.3. Chemical Equilibrium Calculations—Stage Two Reduction

Experimental Results

For the first stage reduction, experiments at different reaction conditions were performed in Harper's pilot rotary reactor. SEM photos, FSSS, Laser scattering, bulk density, O₂ content, ICP-MS etc. were analyzed to determine product morphology, particle size, size distribution, apparent density, MoO₃ conversion, impurity pick-up etc. The following process parameters for desired MoO₂ product were obtained: temperature profile, MoO₃/H₂ ratio, H₂ dew point, residence time for complete reduction. Scale-up effect, material entrainment, material flowability, tube material selection and tube internal design were investigated and tested. The desired MoO₂ product morphology, particle size, O₂% (or Mo%) content, and apparent density were achieved under those optimized process conditions.

In the second stage reduction, experiments were conducted in a tube furnace to simulate the multi-tube pusher furnace operation. The process parameters such as temperature profile, H₂ dew point, H₂ flow rate, and material bed depth were determined from the simulation tests. Product samples were also analyzed. Desirable Mo grain morphology, particle size, size distribution, O₂ content (as low as 50 ppm) were obtained under the optimized process conditions.

Reaction Kinetics and Grain Morphology Transformation

Reaction Kinetics

The shrinking core model [1,2,3] is used for the gas-solid reaction system. The rate-limiting step is either chemical reaction at the gas-solid interface, which is called "surface chemical reaction controlled", or the diffusion of reactant/product gas through a layer of the product, which is termed as "diffusion controlled".

For surface chemical reaction controlled gas-solid system, the reaction model is derived as:

$$r = k_0 e^{-E_a/RT} (P_{H_2})^m$$

$$t/t = 1 - (1 - X_{solid})^{1/3}$$

The following model is for diffusion controlled gas-solid reaction system

$$r = kgP_{H_2}$$

$$t/t = 1 - (1 - X_{solid})^{2/3}$$

Grain Morphology Transformation Mechanism

The reduction process experiences the following grain crystal structure [4] change:

MoO₃ (orthorhombic) → MoO₂ (monoclinic) → Mo (cubic)

Each of the above three solids has its unique crystal structure.

Two grain morphology transformation mechanisms [5] in the reduction process may occur:

- 1.) Reduction products are pseudomorphous to the Mo oxide precursors which are typically a result of slow reaction.
- 2.) The transformation of grain morphology is achieved via chemical vapor transport (CVT). The morphology of the solid product phase is different from its precursor. It is believed that a volatile molybdenum oxide monohydrate, MoO₂(OH)₂, is the gas phase responsible for the chemical vapor transport of Mo from a solid reactant phase to a solid product phase. The transformation process starts with nucleation of product phase on the surfaces of the solid reactant phase. The MoO₂(OH)₂ is generated by reaction of the reactant oxide with the water which forms during reduction. Deposition of Mo by decomposition/reduction of MoO₂(OH)₂ leads to the product nucleus growth. The MoO₂(OH)₂ partial pressure difference between the surfaces of the solid reactant phase and the solid product phase is the driving force for a chemical vapor transport. The mechanism is illustrated in Fig.4.

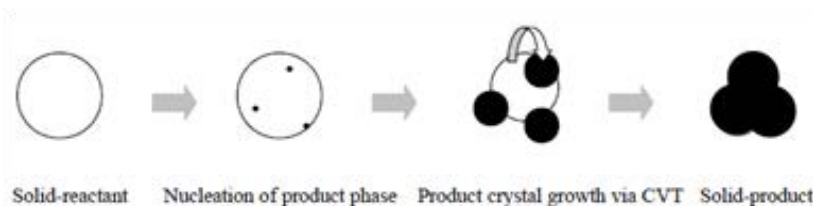


Fig.4. Illustrations of Grain Morphology Transformation Mechanism

Grain Morphology Transformation—Stage One Reduction:

It is proved by morphology study and oxygen analysis that a Mo_4O_{11} exists as a stable intermediate phase with needle shaped grain morphology during stage one reduction. Reactions follow $\text{MoO}_3 \rightarrow \text{Mo}_4\text{O}_{11} \rightarrow \text{MoO}_2$. Mechanism of the nucleation and crystal growth via CVT is illustrated in Fig. 5. The photo on the upper left corner shows the nucleation and crystal growth of the needle shaped Mo_4O_{11} grains. The photo on the upper right corner shows the nucleation and crystal growth of the regular shaped MoO_2 grains. The growth of Mo_4O_{11} or MoO_2 crystal is complete once the precursor phase is consumed via CVT.

The regular shaped dense MoO_2 grains shown in Fig. 5 can be produced at properly controlled process conditions. MoO_2 morphology determines the final Mo product morphology.

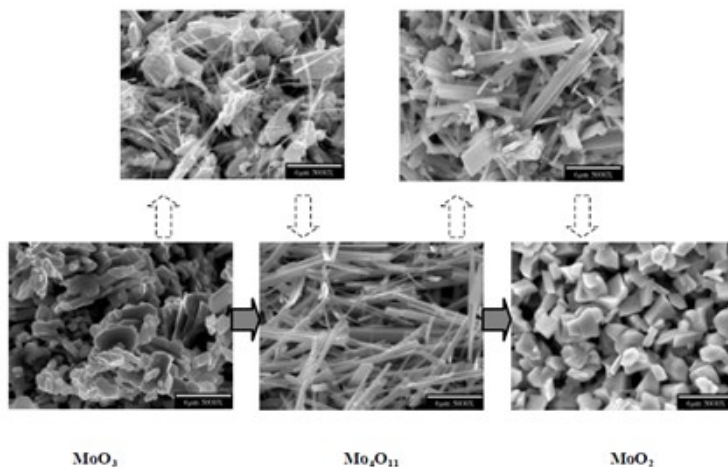


Fig. 5. Stage One Reduction—Grain Morphology Transformation Mechanism

Grain Morphology Transformation– Stage Two Reductions:

The grain morphology transformation mechanism (nucleation and crystal growth) for $\text{MoO}_2 \rightarrow \text{Mo}$ has been investigated and is illustrated in Fig.6. The photo on the top shows the nucleation and crystal growth of the spherical Mo grains. The growth of Mo crystal is complete once the precursor phase is consumed via CVT.

Experimental results show that particle size and size distribution are determined in stage two reduction. Higher reaction temperature in stage two results in larger Mo grain size. Reduction at higher H_2 dew point produces larger Mo grain size. Particle distribution can be adjusted by changing the bed depth. Low oxygen (as low as 50 ppm O_2) is achieved under the optimized process conditions.

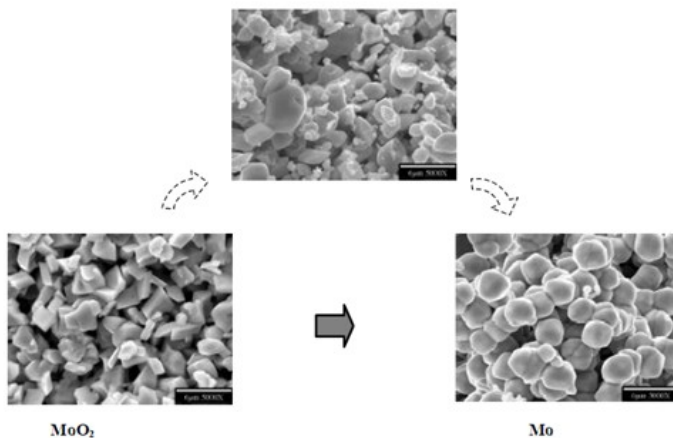


Fig. 6. Stage Two Reduction—Grain Morphology Transformation Mechanism

Product grain morphology under different process conditions:

Fig.7 shows morphologies of samples at different process conditions but using the same equipment system and the same MoO_3 feed. It is clear that desired product morphology is obtained at properly controlled process conditions (condition 1). Product morphology is inferior if process conditions are poorly controlled (condition 2).

It is also concluded from experiments that Mo inherits MoO_2 's grain morphology. This comparison in Fig. 7 is a typical example.

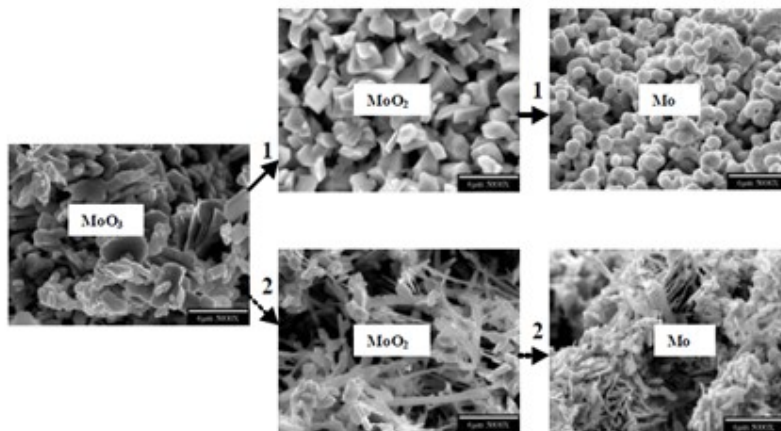


Fig. 7. Grain Morphologies of Materials Processed at Different Conditions

New Process vs. Traditional Process

Fig. 8 is a comparison of product morphologies between the new “rotary + pusher” system and the traditional “pusher + pusher” system. The morphologies of MoO_2 and Mo from the new process are superior to those from traditional process.

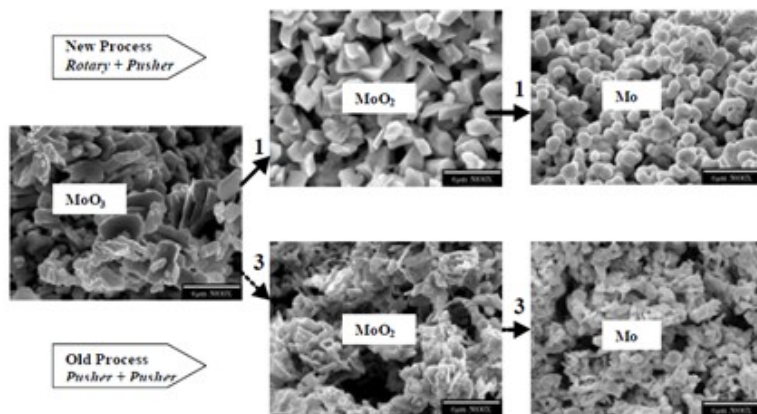


Fig. 8. Grain Morphologies of Materials Processed at Different Reactor Systems

MoO₃® MoO₂ route vs. ADM ® MoO₂ route

Fig.9 is a comparison of product morphologies from two reaction paths: MoO₃ → MoO₂ → Mo and ADM → MoO₂ → Mo. The morphologies of MoO₂ and Mo using MoO₃ as starting reactant are better than those using ADM as starting reactant.

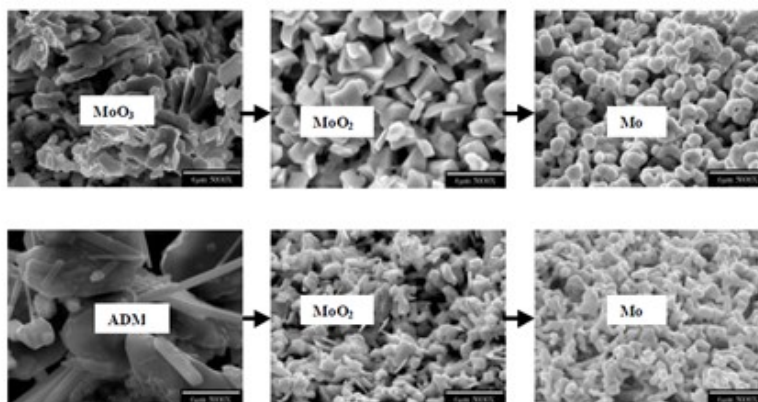


Fig. 8. Grain Morphologies of Materials Processed Using Different Feeds

Scale-Up of the Process

The data collected from the pilot scale tests were applied to the system scale-up design. The major issue for the scale-up is the exothermic reaction control in the rotary reactor for stage-one reduction. Temperature control, H₂ dew point and flow control, residence time, and entrainment collection are important in both stages. System completion was also part of the engineering design effort. The system includes H₂ recycling, dust collection, off-gas treatment, product sieving etc. The process has been scaled-up by 35 times, up to a production rate of 2.4 tons Mo product per day. The process scale-up is successful and reduction plants from the scale-up are producing quality products as designed.

General Conclusion

1. Stage one reduction proceeds as MoO₃® Mo₄O₁₁ ® MoO₂. Mo₄O₁₁ exists as an intermediate product which is a stable phase and has needle shaped grain morphology.
2. Desirable MoO₂ morphology can be obtained if exothermic reaction is properly controlled in stage one reduction.
3. Mo inherits MoO₂'s morphology, in other words, MoO₂ morphology determines final Mo product morphology.
4. Mo product grain size and size distribution is determined by stage two reduction. Temperature, H₂ flow rate and dew point, residence time, and bed depth are the key parameters.
5. MoO₃ → MoO₂ → Mo produces better Mo product than ADM → MoO₂ → Mo.
6. Grain morphology transformation mechanism follows nucleation of product phase and product phase crystal growth via chemical vapor transport. Volatile molybdenum oxide monohydrate, MoO₂(OH)₂, is the gas phase responsible for the chemical vapor transport of Mo.
7. Stage-two reduction requires very dry H₂ to achieve complete conversion. However, stage-one reduction can be achieved by using wet H₂.
8. Complete reduction system was designed and engineered based on this pilot scale development work. Optimized process parameters developed in pilot scale have been successfully scaled-up by 35 times, up to a production rate of 2.4 tons quality Mo powder product per day. This rotary (stage one) + pusher (stage two) system is superior to a traditional pusher + pusher system from both product quality control and cost saving.

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