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Large-Batch Reduction of Molybdenum Trioxide

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July 2015

OAK RIDGE NATIONAL LABORATORY
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Materials Science and Technology Division

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Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6283
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ABSTRACT

Unconverted, isotopically-enriched molybdenum metal must be recovered from the spent radiopharmaceutical solution used in NorthStar's Technetium-99m generator and reused. The recycle process begins by recovering the metal from the aqueous potassium molybdate (K_2MoO_4) solutions as molybdenum trioxide (MoO_3) employing a process developed at Argonne National Laboratory. The MoO_3 powder is subsequently reduced to molybdenum metal powder which can be blended with new powder and further processed into a flowable form to be used to produce target disks for irradiation. The molybdenum oxide reduction process has been examined and scaled to produce kilogram quantities of metal powder suitable for processing into a useable form employing spray drying or similar technique and ultimately used for target fabrication.

1.0 BACKGROUND

Molybdenum powder is commercially produced by thermal reduction of oxides in a hydrogen atmosphere. The most commonly used oxide source materials [1-6] are molybdenum trioxide, MoO_3, and ammonium molybdate, $(NH_4)_2MoO_4$, with the former being of most interest for this project. Hydrogen reduction of molybdenum oxides occurs in stages with the predominant reactions being:

$$MoO_3 + H_2 \rightarrow MoO_2 + H_2O \quad (1)$$

and

$$MoO_2 + 2H_2 \rightarrow Mo + 2H_2O \quad (2)$$

The reduction of trioxide to dioxide (1) is highly exothermic while the reduction of dioxide to metal (2) is endothermic. Care must be taken when using pure hydrogen during the first stage of reduction to prevent excessive heat evolution which can drive the temperature above the melting point of the trioxide (795°C).

Accordingly, commercial hydrogen reduction processes for molybdenum metal powder production are typically conducted in two stages [3-6]. In the first stage, MoO_3 is reduced to MoO_2 in a hydrogen atmosphere in the temperature range of 450° to 650°. In the second stage, MoO_2 is reduced to metal in hydrogen at a temperature between 1000° and 1100°C. Diluted hydrogen is sometimes used in the first stage of reduction to prevent overheating and in some processes hydrogen from the second stage is used as the reductant in the first stage to minimize waste. Fresh, pure hydrogen is used almost exclusively in the second stage of the reduction process.

2.0 EXPERIMENTAL APPROACH

A significant number of reduction tests were conducted in hot-walled ceramic tube furnaces with small batches of commercially-available molybdenum trioxide powder and materials recovered at Argonne National Laboratory from aqueous solutions. Batch size ranged from < 10 g to ~ 25 g and furnaces with 25 mm and 75 mm inner diameter ceramic tubes and ~300 mm-long hot zones were used. The purpose of the early experiments was to examine reduction time-temperature profiles and the use of diluted hydrogen gas mixtures, e.g. argon with 4% hydrogen ($Ar/4\%H_2$) which is below the flammability limits for hydrogen. The reduction profiles and results will not be detailed in this report for the purpose of this document is to summarize large batch processing. However, one result of note is that incomplete reduction was observed for all trials using $Ar/4\%H_2$ gas mixtures thus this mixture was not used in the large-batch study.

2.1 DEHYDRATION

Characterization of the starting trioxide powders found some to be hydrated, i.e. contaminated with water. Heat treatments were examined to remove water from the powders. Heating of the trioxide powder to a temperature between 400° and 500°C in argon or hydrogen was shown to remove excess water either as adsorbed moisture or chemically bound. In early trials, dehydration was conducted as a separate processing step in which powders were loaded into open alumina trays and heated to 400°C for ~1 h in air before reduction.

2.2 REDUCTION

2.2.1 Argon/Hydrogen Atmospheres

Small batches of dehydrated MoO_3 powder (Alfa Aeser 99.5% and 99.95% MoO_3) were reduced in an open alumina tray using the hot-walled 75 mm ID ceramic tube furnace (Figs. 1 and 2). The powders were heated in a flowing mixture of argon and hydrogen, specifically Ar/7%H_2. The heating cycle was as follows and is graphically depicted in Fig. 3:

1. 10°C/min from room temperature to 550°C
2. 1°C/min from 550°C to 750°C
3. 2°C/min from 750°C to 1100°C
4. 1 h hold at 1100°C
5. 10°C/min from 1100°C to room temperature

Total time: 10 h

Using this cycle, the MoO_3 is reduced to MoO_2 in the temperature range of 550°C to 750°C. Conversion in this temperature range prevents melting of the MoO_3, which occurs at 795°C. Above 750°C, the MoO_2 begins to be reduced to Mo metal with reduction completed by 1100°C.

Additional reductions runs were conducted in the ceramic tube furnaces using molybdenum trays instead of aluminum oxide boats. A reaction between the alumina boat and molybdenum compounds during reduction occurred thus molybdenum trays were fabricated from high-purity sheet (99.95% metal) and substituted for the ceramic boats.

Fig. 1. Hot-walled furnace with 75 mm tubular ceramic chamber.

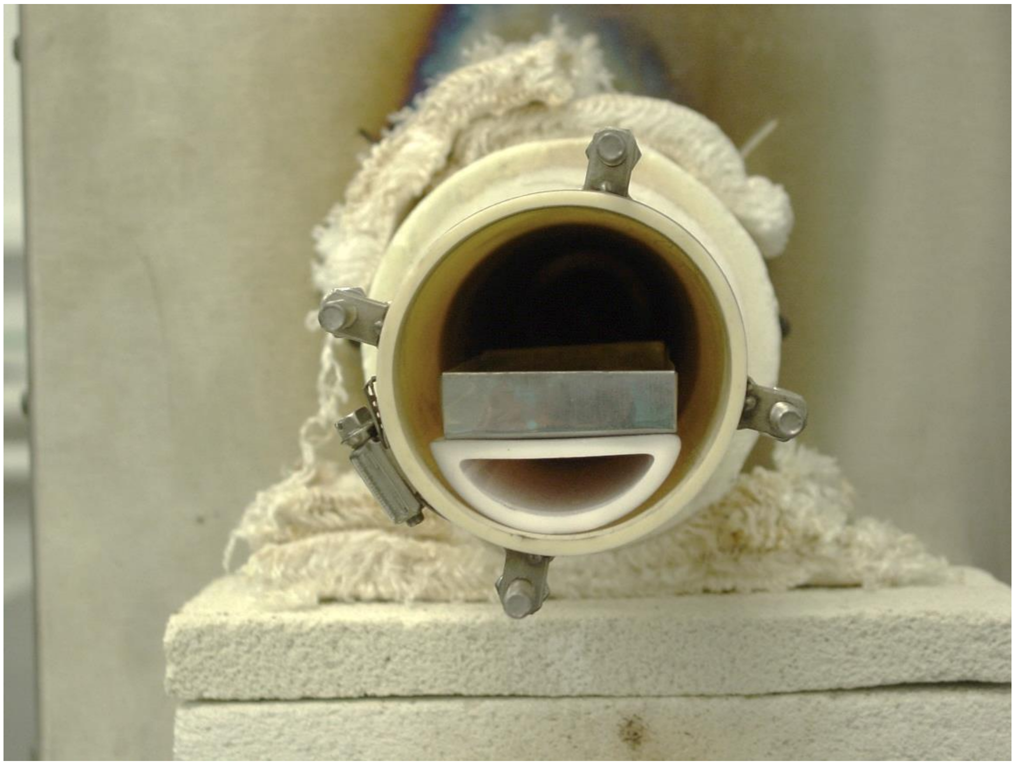

Fig. 2. Molybdenum boat being loaded into ceramic chamber of hot-walled furnace.

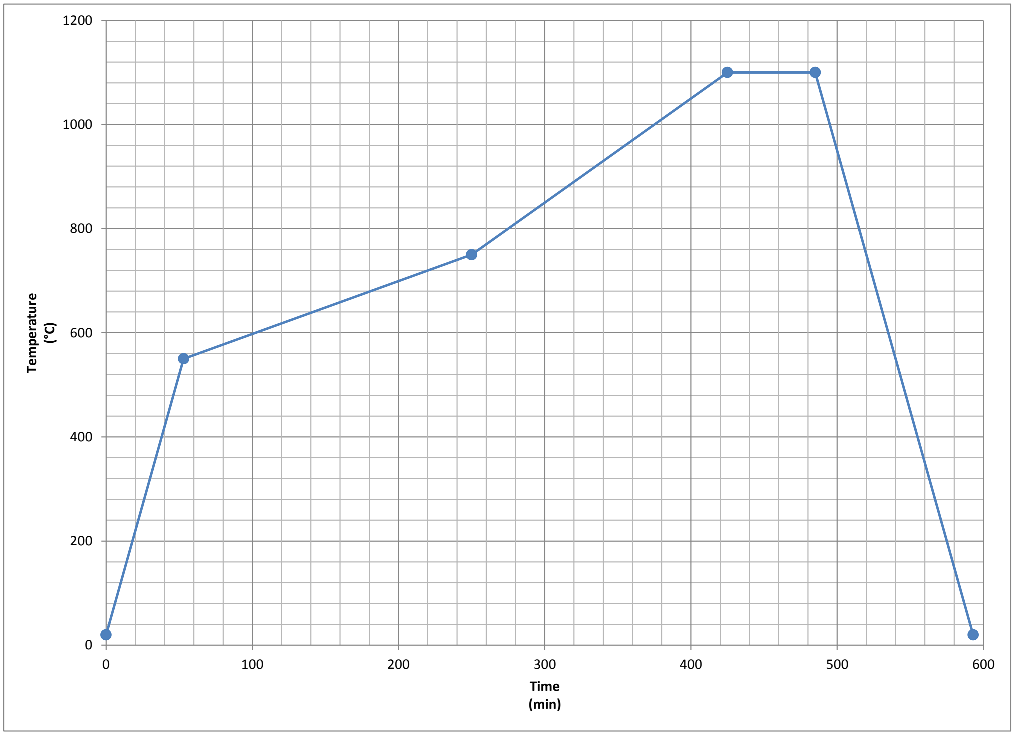

Fig. 3. Small-batch reduction time-temperature profile.

2.2.2 Pure H_2 Atmosphere in a Cold-Walled Furnace

Initial reduction trials using pure hydrogen gas were conducted in a graphite-element, cold-walled furnace (Figs. 4 and 5) with a 200 x 200 x 200 mm heated cavity. Dehydrated commercially-available MoO_3 powder (Alfa Aeser 99.5% MoO_3) was placed in open alumina trays of various depths and configurations and reduced in flowing pure H_2 gas. The heating cycle for this furnace was (also see Fig. 6):

1. 10°C/min. from room temperature to 1100°C
2. 2 h. hold at 1100°C
3. 10°C/min. from 1100°C to room temperature

Total time: 5.67 h

It was proposed that a faster heating rate was possible in this furnace because the use of pure hydrogen would result in a faster reduction rate. The furnace was designed to operate with a nominal overpressure of H_2 in the furnace chamber (~ 3 psi above ambient) which periodically releases via opening of a spring-loaded check valve. It was anticipated that the pressure pulses would enhance gas penetration into the powder bed.

Similar to the runs conducted using the ceramic tube furnace, a reaction between the alumina trays and molybdenum compounds during reduction was observed thus pure molybdenum trays were substituted for the ceramic boats. The molybdenum trays were placed inside alumina trays to prevent chemical reaction between the metal trays and graphite furnaces components.

Fig. 4. Cold-walled hydrogen furnace used in reduction studies.

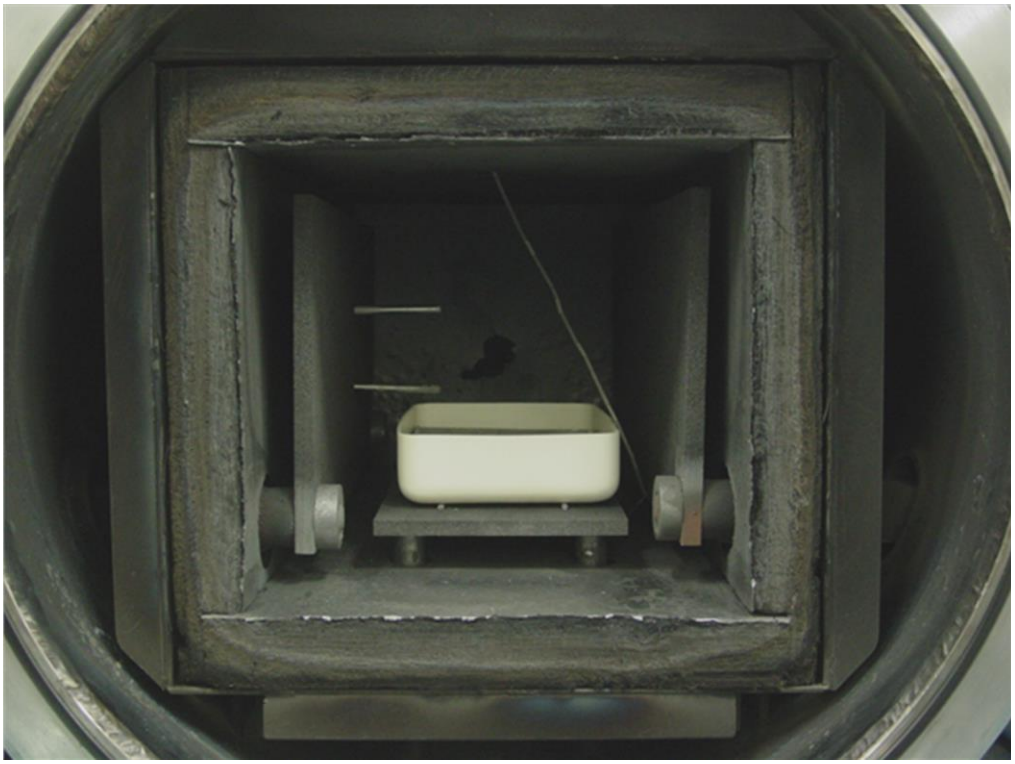

Fig. 5. Internal configuration of the cold-walled hydrogen furnace.

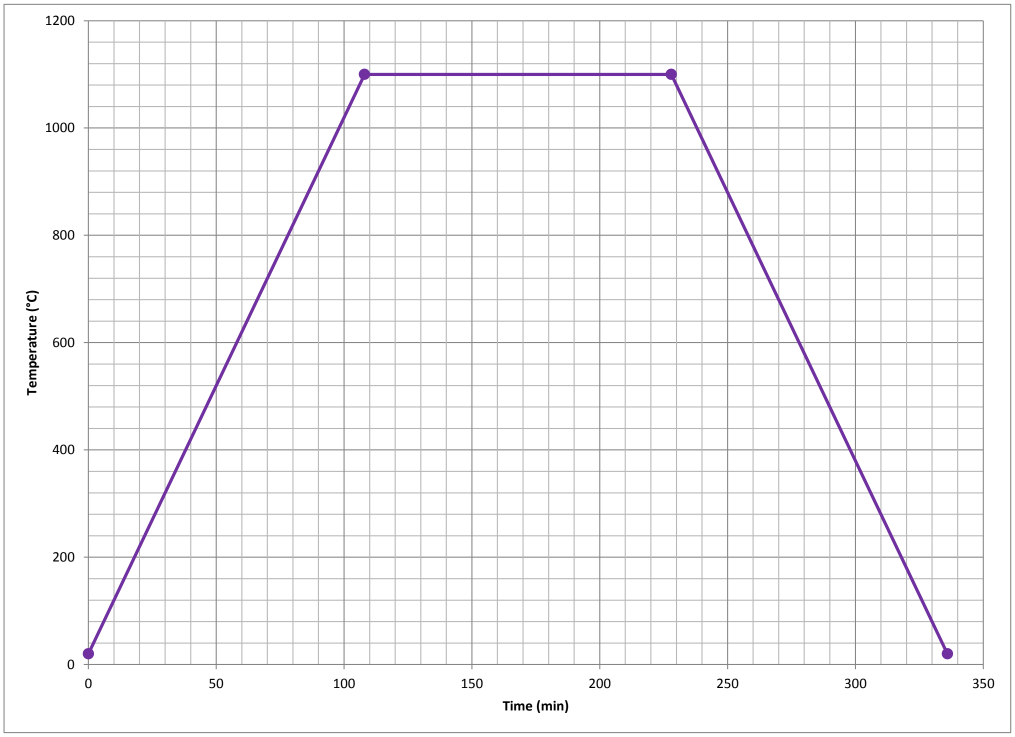

Fig. 6. Large-batch reduction, cold-walled furnace time-temperature profile.

2.2.3 Pure Hydrogen in a Hot-Walled Reduction Furnace

A furnace specifically designed for the reduction of molybdenum-containing powders that can be operated as a typical horizontal flow-through system or as a rotating kiln was procured (Figs. 7 and 8). The furnace possesses a 150 mm diameter, 450 mm long hot zone and utilizes internal baffles to control the temperature profile of the furnace. The furnace has no water cooling to prevent condensation of moisture within the reaction chamber for a dry hydrogen environment is crucial for efficient and complete reduction and low oxygen content powder. A cooled trap in the external exhaust system can be used to condense and collect the water produced during the reduction process.

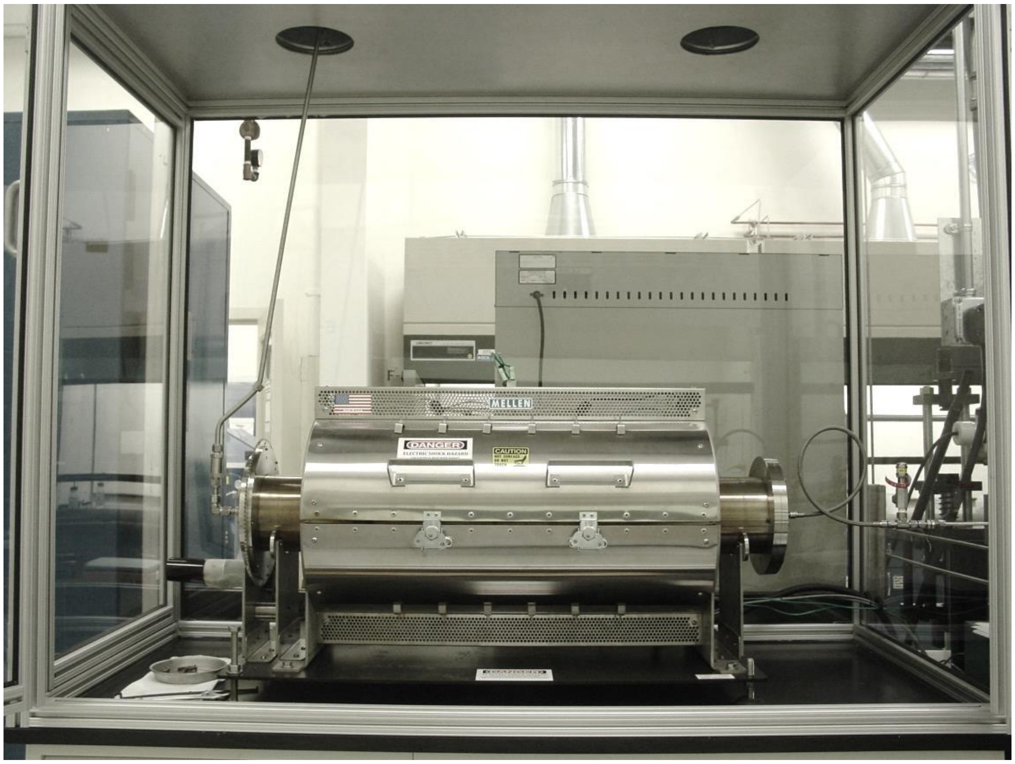

Fig. 7. Hot-walled reduction furnace with stainless steel chamber (cold trap not shown).

Commercially-available trioxide (Alfa Aeser 99.5% MoO_3) was used in all runs conducted using the hot-walled reduction furnace. Trays with 500 and 1000 g trioxide powder capacities were fabricated from high-purity (99.95%) molybdenum sheet. The dimensions of the trays were 250 x 100 x 50 mm and 300 x 120 x 40 mm, respectively. The depths of the trays were chosen to accommodate the aforementioned quantities of powder with a bed depth of no more than 20 mm. A molybdenum separator was added to the larger tray for latter trials to prevent fusing of the powder during the process and facilitate easier milling of the materials after each processing step (Fig. 9).

As noted in the Background section, molybdenum trioxide is typically reduced to metal using a two-step process. The two-stage reduction process permits better control of resulting powder particle size and morphology. Time-temperature profiles were selected based upon literature sources and results of small-batch experiments. A dehydration hold was included in the first stage of processing to remove water from the feedstock powder(s).

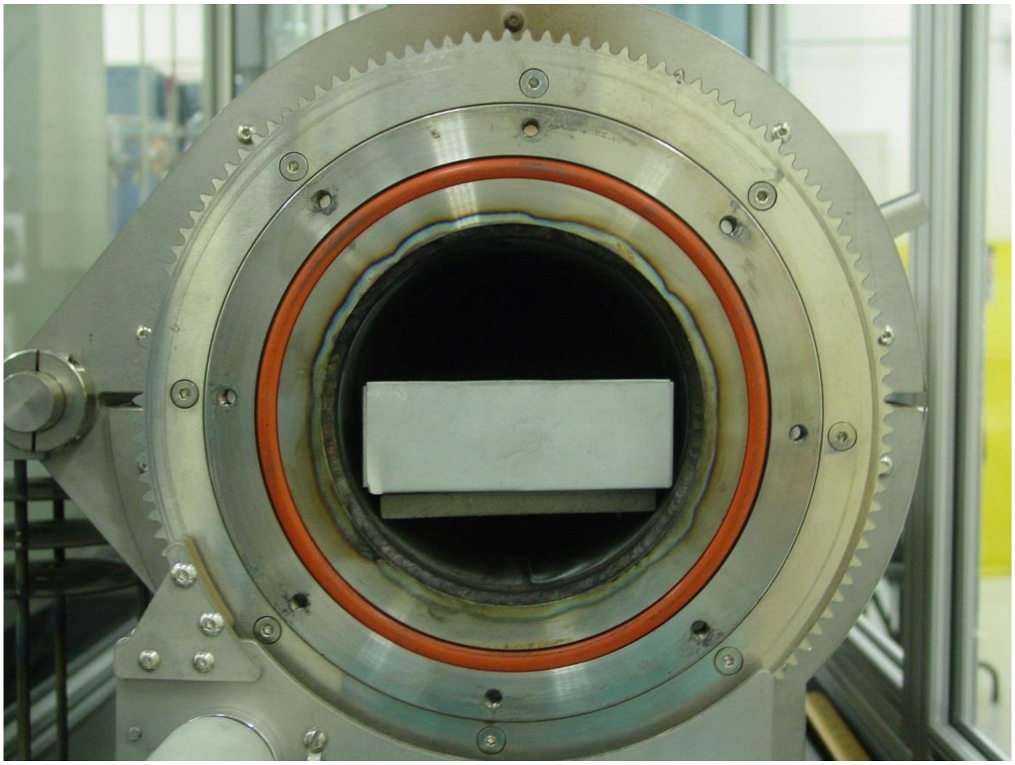

Fig. 8. End view of hot-walled reduction furnace with 1 kg MoO_3 loaded in Mo tray.

Fig. 9. Molybdenum divider used to keep bed from fusing during reduction.

The stages of the reduction process were as follows:

Stage 1: Dehydration and reduction of MoO_3 to MoO_2 (Fig. 10):

1. 10°C/min from room temperature to 400°C
2. 30 min hold at 400°C
3. 10°C/min from 400°C to 630°C
4. 2.5 h hold at 630°C
5. 10°C/min from 630°C to room temperature

Total run time: 5 h

Stage 2: Reduction of MoO_2 to Mo metal (Fig. 11):

1. 10°C/min from room temperature to 1100°C
2. 4 h hold at 1100°C
3. 10°C/min from 1100°C to room temperature

Total run time: 7 h 36 min

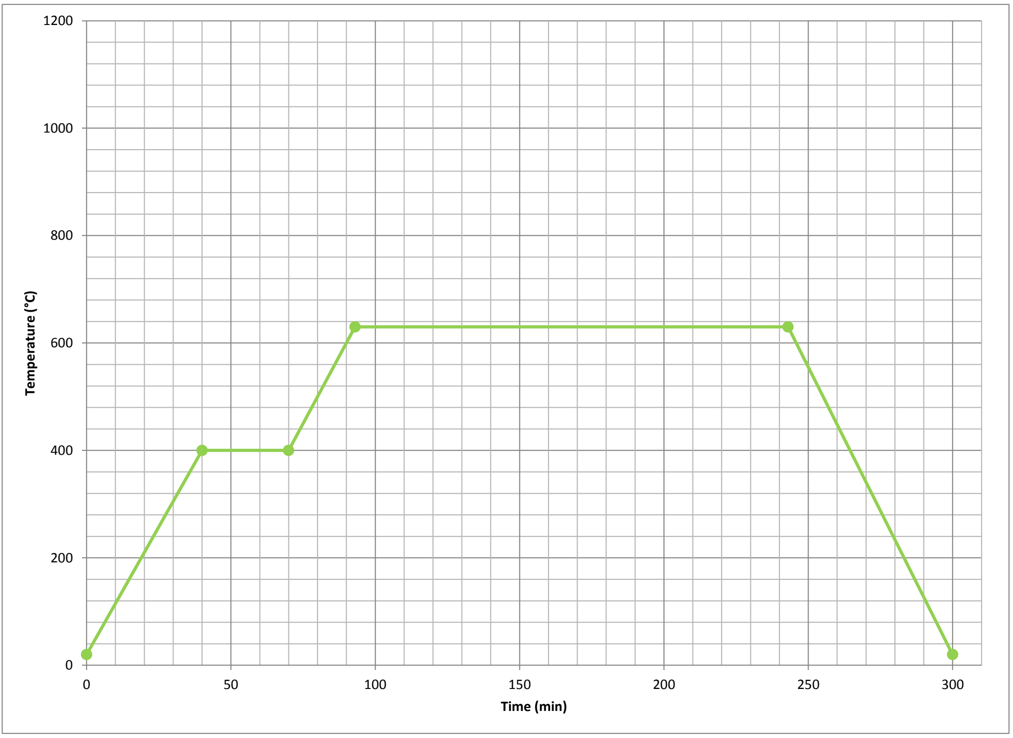

Fig. 10. Time-temperature profile for stage 1 of large-batch reduction.

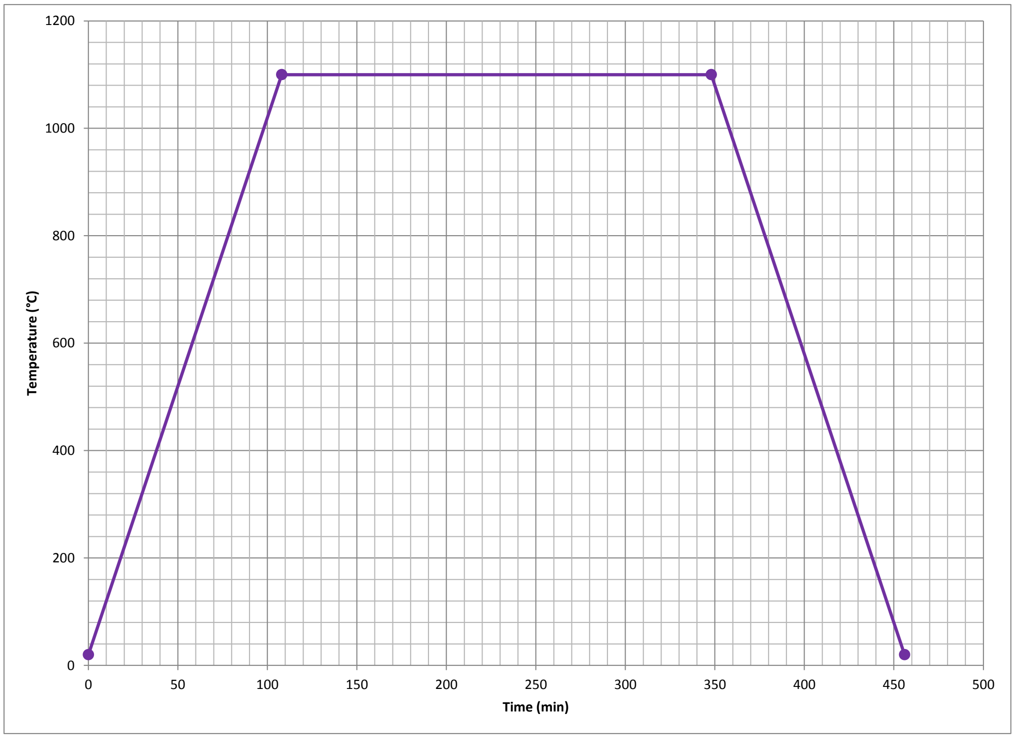

Fig. 11. Time-temperature profile for stage 2 of large-batch reduction.

The tray with converted powder was removed from the furnace after the first stage of processing to measure weight change. The dioxide powder was then removed from the tray and hand-milled using a mortar and pestle to break up any clumps prior to conducting the second reduction step. After the second reduction step, the powder and boat were again weighed, and the powder removed from the molybdenum tray. Any clumps were dispersed employing hand-milling with a mortar and pestle.

2.2.4 Powder Characterization

Particle size was measured using a Horiba La950-V2 laser diffraction particle size analyzer fitted with the mini-flow cell attachment. A circulation speed of 10 was required to keep the powder suspended for most measurements. The procedures outlined in ASTM B821-10 “Standard Guide for Liquid Dispersion of Metal Powders and Related Compounds for Particle Size Analysis” were followed using NERL high-purity water as the carrier medium with 0.01 wt.% sodium hexametaphosphate as the dispersant.

Particle size measurement of “as-reduced” powder was hindered by the presence of large agglomerates composed of smaller molybdenum metal particles (Fig. 12). Ball milling of the powder was required prior to particle size analysis. This was accomplished using high-purity molybdenum media fabricated “in-house” from 6-mm Mo rod, a media-to-powder ratio of 20:1 and hexane as the liquid.

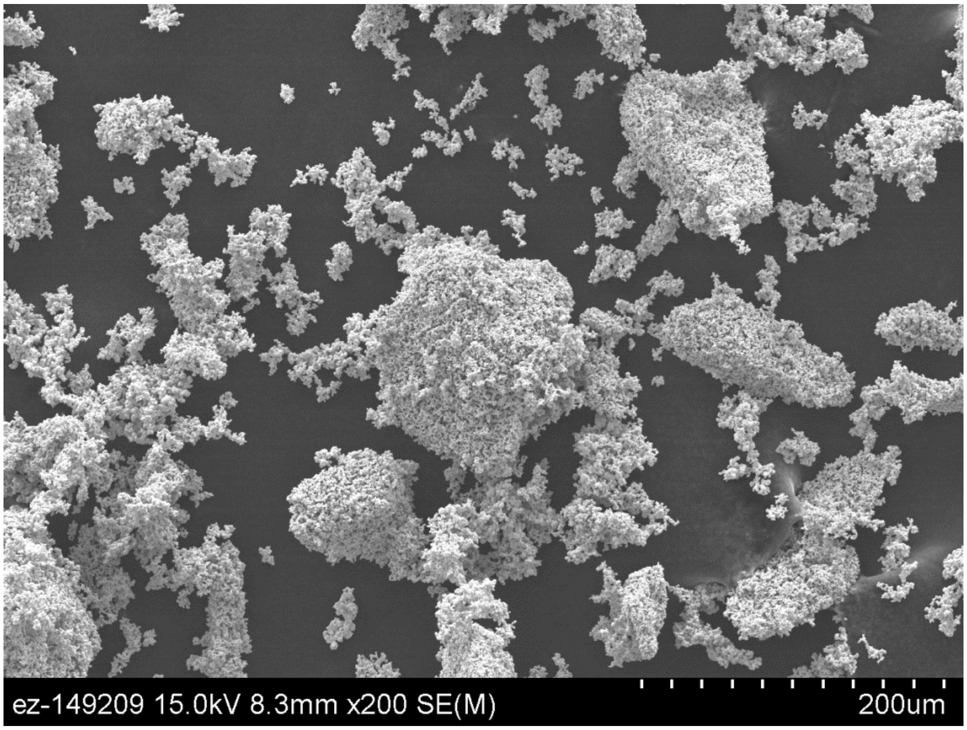

Fig. 12. Molybdenum powder produced by the reduction of trioxide in pure hydrogen using hot-walled furnace before ball milling. Note the large agglomerates of smaller particles.

SEM characterization was conducted on various Mo powders employing a Hitachi S-4800 SEM. The microscopy was performed in secondary electron mode using 15KV after an initial beam alignment, followed by stigmation and focus. The images were captured at five different magnifications using a slow-speed scan, and saved in tiff format.

3.0 RESULTS AND DISCUSSION

The hydrogen reduction of molybdenum trioxide to metal occurs in stages with the predominant reactions being:

$MoO_3 + H_2 \rightarrow MoO_2 + H_2O$	Wt. Loss =	11.12%
$MoO_2 + 2H_2 \rightarrow Mo + 2H_2O$	Wt. Loss =	25.01%
$MoO_3 + 3H_2 \rightarrow Mo + 3H_2O$	Wt. Loss =	33.35%

The conversions from trioxide to dioxide and dioxide to metal result in weight losses and distinct color changes. Weight loss during stage 1 should be approximately 11%, and 25% during stage 2, with a total weight loss of about 33.4% for the reduction of trioxide to metal. Measured weight loss was compared to predicted values to assess conversion efficiency. Trioxide is typically white or slightly yellow or slightly bluish (Fig. 13). Dioxide is reddish brown (Fig. 14) and completely reduced molybdenum powder is usually light gray (Fig. 15) thus the progress of the reduction process is readily assessed via visual observation.

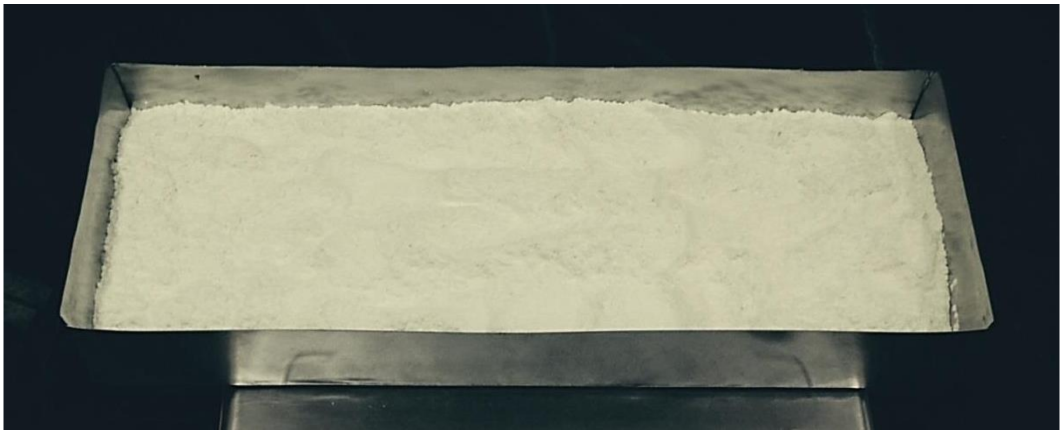

Fig. 13. One kilogram molybdenum trioxide (MoO_3) loaded into molybdenum tray.

Fig. 14. Molybdenum dioxide (MoO_2) after stage of reduction.

Fig. 15. Molybdenum powder after stage 2 of reduction.

The results of the "large-batch" reduction trials are summarized in Table 1. A 50 g sample of commercial trioxide did not reduce completely when processed in the 75 mm ceramic tube furnace using a dilute hydrogen gas mixture (Ar/7%H_2). Earlier reduction runs using the same gas mixture (Ar/7%H_2) with smaller batches (25 g or less) of trioxide proceeded to completion; however, this was not observed for a 50 g sample. As noted earlier, incomplete conversion was observed for all runs conducted using Ar/4%H_2.

The use of dilute hydrogen gas mixtures was considered for safety reasons (the lower explosive limit for hydrogen in air is 4%). Gas mixtures of argon with 4% and 7% hydrogen proved to be ineffective for reducing trioxide to metal even using the two-stage process and a small-volume furnace. Significant flow rates would be required to introduce equivalent quantities of reductant to a system using the dilute gas mixtures. Fifteen to 25 times the volume of gas would be required when using 4% to 7% hydrogen in argon as compared to pure hydrogen. This is not practical or cost effective and results in relatively high gas velocities which can hinder the reduction process.

Based upon weight loss, none of the reduction runs conducted in the graphite-element, cold-walled hydrogen furnace were 100% efficient. A concern arose immediately upon completion of the first test. The water produced by the reaction of hydrogen with the molybdenum oxide powder condensed on the cooled inner walls of the furnace. Many milliliters of water poured from the furnace when the door was opened.

Dry hydrogen is essential for the conversion of molybdenum dioxide to metal powder in the second stage of the process. The presence of moisture in the furnace chamber hinders reduction and the water could be absorbed by the powder during and after cool down. The furnace was equipped with a check valve that kept the chamber pressure above ambient to prevent backflow of air into the furnace. While it was speculated the opening and closing of this valve would enhance gas penetration into the powder bed, it impede gas flow through the exhaust and thus preventing water vapor from being removed from the chamber.

Table 1. Summary of large-batch molybdenum trioxide reduction experiments

Furnace	**Atmosphere**	**Boat (l x w x d mm) [material]**	**Bed Depth (mm)**	**Stage 1**				**Stage 2**			**Particle Size (μm)**
				MoO_3 (g)	**MoO_2 (g)**	**Change (g)**	**EFF* (%)**	**Mo (g)**	**Change (g)**	**EFF* (%)**	
Ceramic tube	Ar/7% H_2	150 x 50 x 12.5 [Mo]	< 6	50.35	---	---	---	38.23	-12.12	72	---
Cold-walled	Pure H_2	190 x 140 x 45 [Alumina]	< 6	160.24	---	---	---	112.79	-47.45	89	---
Cold-walled	Pure H_2	165 x 125 x 20 [Mo]	12.5	251.12	221.78	-29.34	105	175.28	-75.84	90	---
Cold-walled	Pure H_2	190 x 140 x 45 [Alumina]	15	518.10	---	---	---	349.50	-168.60	97	---
Hot-Walled	Pure H_2	150 x 50 x 12.5 [Mo]	6	100.07	84.71	-15.36	138	66.57	-33.50	100	4.8 ± 1.4
Hot-walled	Pure H_2	250 x 100 x 50 [Mo]	15	500.25	440.44	-59.81	108	332.72	-167.53	100	4.3 ± 1.7
Hot-walled	Pure H_2	300 x 120 x 40 [Mo]	20	1000.01	889.11	-110.90	100	665.79	-334.22	100	5.7 ± 1.8
Hot-walled	Pure H_2	300 x 120 x 40 [Mo]	20	1000.54	887.88	-112.66	101	679.50	-321.04	96[†]	5.1 ± 1.7

* EFF = Efficiency which is bulk weight loss compared to predicted weight loss.

† A small quantity of dioxide was found in the corners of the tray. A smaller bed height or longer processing time would improve conversion efficiency.

Characterization of the metal powder produced by the reduction of the ~500 g batch of commercial trioxide in the graphite-element, cold-walled furnace showed the material to be agglomerates of smaller particles with a broad range of sizes and morphologies. SEM analysis found the powder to contain a significant fraction of very small particles with many below 1 μm (Fig. 16). Based on this observation and the condensation of water inside the chamber during processing, this furnace configuration was deemed impractical for the reduction of trioxide to metal powder.

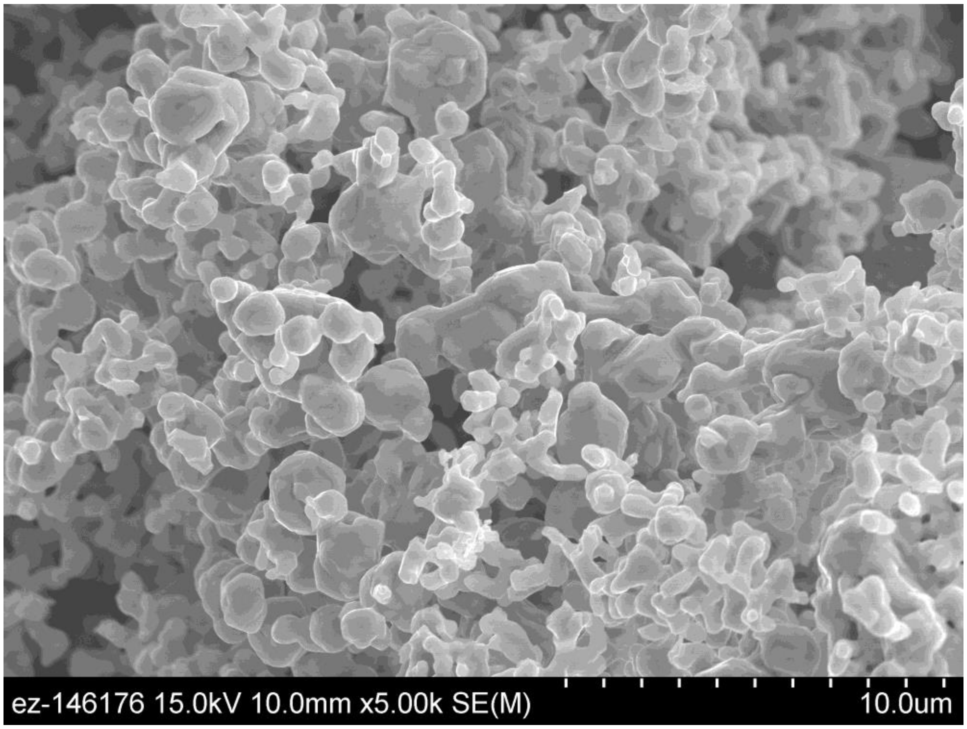

Fig. 16. Molybdenum powder from 500 g batch of trioxide processed in pure hydrogen using cold-walled furnace, particle size was not measured.

Complete reduction of molybdenum trioxide to metal powder for all batch sizes, 100 to 1000 g, was achieved in the hot-walled hydrogen furnace specifically designed for metal powder reduction. Based upon weight loss and observed color of the powder bed, some conversion to metal for the 100 and 500 g batches actually began during the first stage of reduction. Incomplete reduction was noted for the 1 kg batch of trioxide reduced in the tray with the divider. A small quantity of red-brown dioxide was found in the corners of the tray nearest to the exhaust end of the furnace. Deceasing bed depth or increasing time at temperature would likely result in full conversion.

As noted earlier, metal powders produced by the reduction of trioxide were found to be composed of relatively large agglomerates of smaller particles. Analysis determined a significant portion of the agglomerates were in the particle size range of 60 to 200 μm (Fig. 12). Although composed of smaller particles, the agglomerates appear to retain the overall shape and size of the commercial trioxide feedstock material (Fig. 17, compare to Fig. 12).

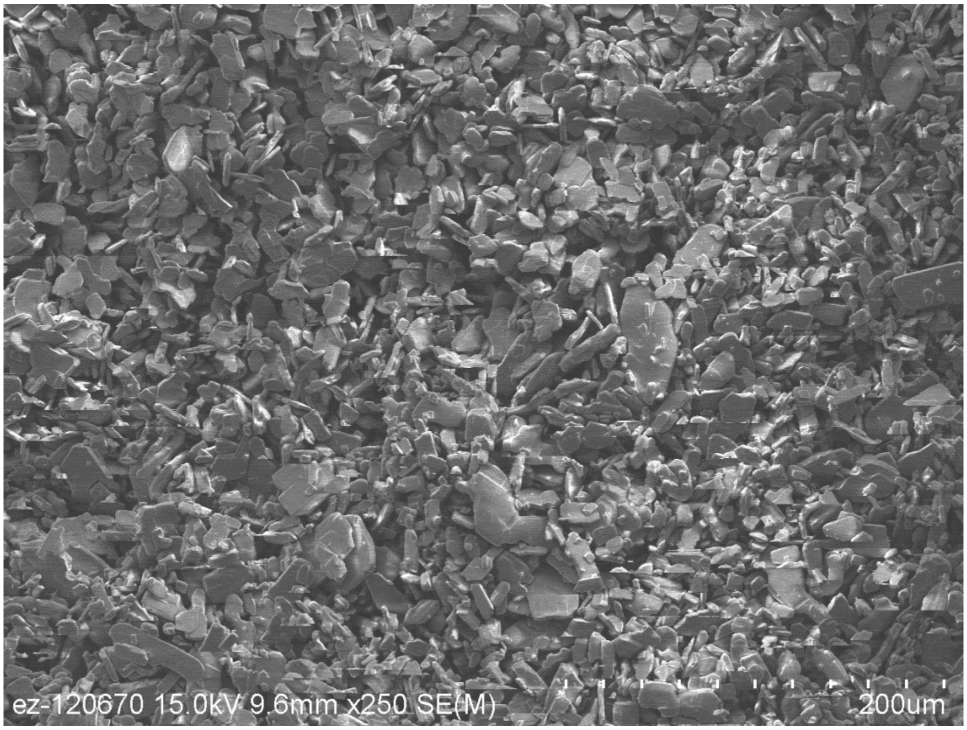

Fig. 17. Molybdenum trioxide "feedstock" materials used for the large-batch reduction study.

The reduced powders had to be ball milled to break up the agglomerates before measuring true particle size and further evaluation or use. High-purity molybdenum media (99.95% metal), a media-to-powder ratio of 20:1 and hexane as the liquid were used in the milling process. After ball milling, the particle sizes of the powders produced in the hot-walled furnace were in the range of 4.3 to 5.7 microns. Characterization employing scanning electron microscopy showed the powders to possess characteristics similar to the commercially-available molybdenum powder used as the standard for the compaction of sintering studies (Figs. 18 and 19).

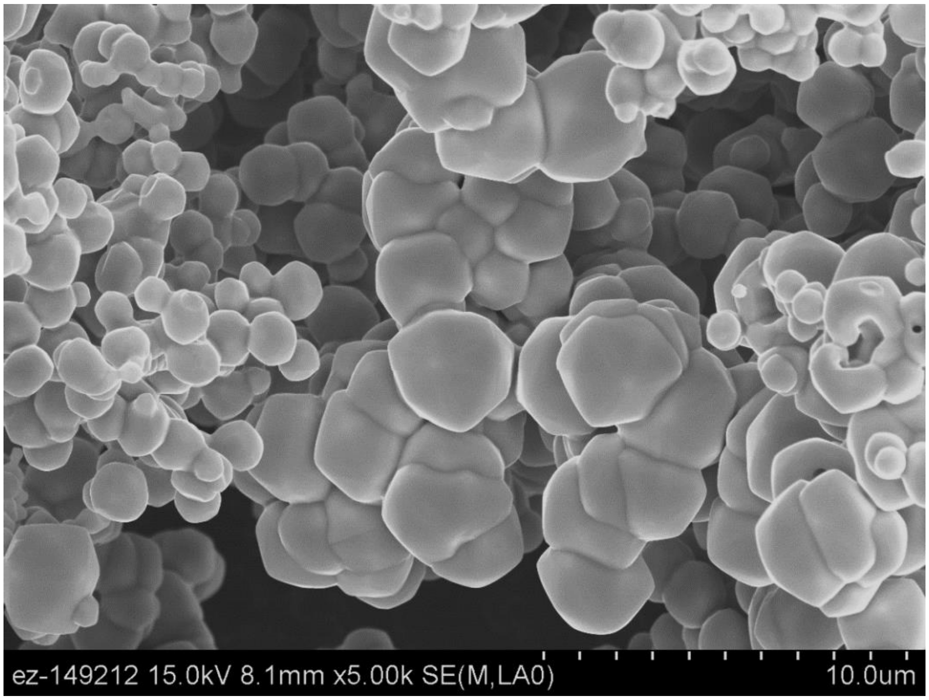

Fig. 18. Molybdenum powder from a 500 g batch of trioxide processed in pure hydrogen using hot-walled furnace, particle size = 4.3 ± 1.7 μm.

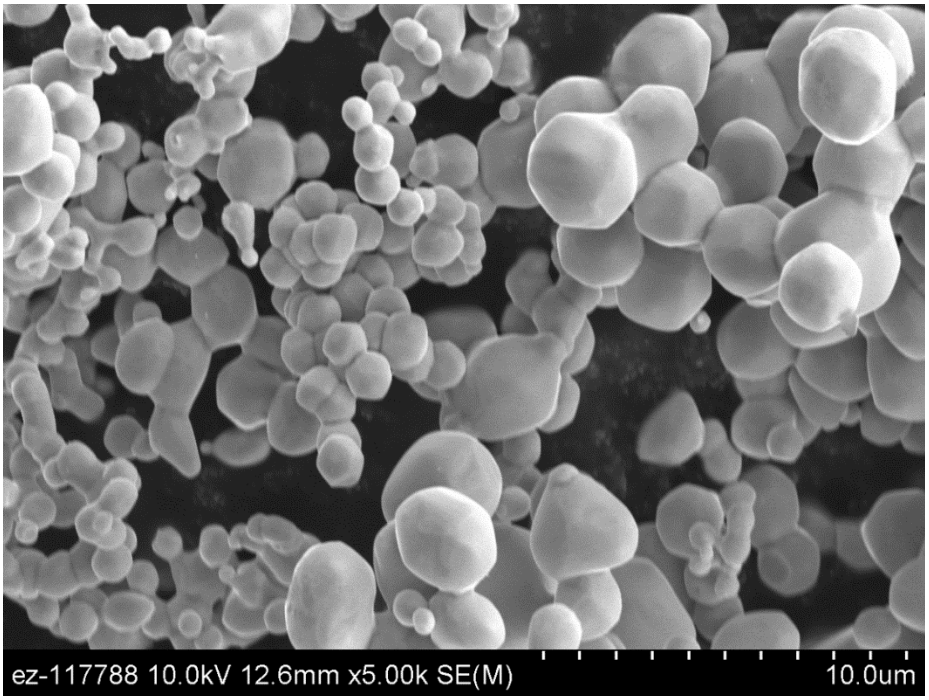

Fig. 19. Climax NPA molybdenum powder, particle size = 4.0 – 4.8 μm, which is used to produce the Climax PM spray-dried product used as the standard for target fabrication efforts.

4.0 SUMMARY AND CONCLUSIONS

Molybdenum powder was successfully produced by the thermal reduction of molybdenum trioxide using a hot-walled furnace specifically designed for the process and a pure hydrogen atmosphere. Similar to commercial production, a two-stage process was required to achieve complete reduction and control powder particle size and morphology. Batch sizes to 1 kg of trioxide were reduced to metal powder with the resulting product possessing characteristics similar to those for the commercially-available materials used in the development of the powder metallurgy approach for target fabrication. Larger batches are possible employing existing equipment with appropriately designed trays and furnace hardware.

Important lessons from the study include:

- The two stage process, with stage 1 being the reduction of trioxide to dioxide, and stage two, the conversion of dioxide to metal, proved to be most effective for controlling reduction and resulting product characteristics.

- Pure hydrogen gas is required for efficient reduction. Dilute hydrogen gas mixtures were shown to be ineffective for the reduction of trioxide in batch sizes greater than 25 g.

- The use of high-purity molybdenum trays prevents undesirable chemical reactions during reduction.

- Reduction in a cold-walled furnace is not viable. Water formed during the reduction process must be removed from the furnace chamber to achieve complete reduction and prevent contamination of the product during cooling.

- Reduction of the trioxide produces agglomerates of smaller particles that retain the shape and size of the feedstock material. The agglomerates must be milled before characterization and further powder processing and use.

- The use of a divider to keep the powder bed separated into smaller volumes prevented fusing of the powder during reduction simplifying extraction and milling.

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