ORNL/TM-2016/459

Gel Fabrication of Molybdenum "Beads"

R.A. Lowden
B.L. Armstrong
K.M. Cooley

November 2016

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE US DEPARTMENT OF ENERGY

DOCUMENT AVAILABILITY

Reports produced after January 1, 1996, are generally available free via US Department of Energy (DOE) SciTech Connect.

Website http://www.osti.gov/scitech/

Reports produced before January 1, 1996, may be purchased by members of the public from the following source:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone 703-605-6000 (1-800-553-6847)
TDD 703-487-4639
Fax 703-605-6900
E-mail info@ntis.gov
Website http://www.ntis.gov/help/ordermethods.aspx

Reports are available to DOE employees, DOE contractors, Energy Technology Data Exchange representatives, and International Nuclear Information System representatives from the following source:

Office of Scientific and Technical Information
PO Box 62
Oak Ridge, TN 37831
Telephone 865-576-8401
Fax 865-576-5728
E-mail reports@osti.gov
Website http://www.osti.gov/contact.html

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ORNL/TM-2016/459

Materials Science and Technology Division

Gel Fabrication of Molybdenum “Beads”

R.A. Lowden
B.L. Armstrong
K.M. Cooley

November 2016

Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, TN 37831-6283
managed by
UT-BATTELLE, LLC
for the
US DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENTS

Support provided by the Department of Energy's National Nuclear Security Administration (DOE/NNSA), Office of Material Management and Minimization's Molybdenum-99 Program.

ABSTRACT

Spherical molybdenum particles or “beads” of various diameters are of interest as feedstock materials for the additive manufacture of targets and assemblies used in the production of ^{99}Mo medical isotopes using accelerator technology. Small metallic beads or ball bearings are typically fabricated from wire; however, small molybdenum spheres cannot readily be produced in this manner. Sol-gel processes are often employed to produce small dense microspheres of metal oxides across a broad diameter range that in the case of molybdenum could be reduced and sintered to produce metallic spheres. These Sol-gel type processes were examined for forming molybdenum oxide beads; however, the molybdenum trioxide was chemically incompatible with commonly used gelation materials. As an alternative, an aqueous alginate process being assessed for the fabrication of oxide spheres for catalyst applications was employed to form molybdenum trioxide beads that were successfully reduced and sintered to produce small molybdenum spheres.

1.0 BACKGROUND

The National Nuclear Security Administration's Material Management and Minimization office is working with U.S. commercial entities and the national laboratories to accelerate the establishment of a reliable supply of ^{99}Mo produced without the use of highly enriched uranium.[1] Several approaches are being explored including linear accelerator conversion of ^{100}Mo and neutron capture using ^{98}Mo.[2] These alternate technologies require targets, fabricated from high value, limited quantity, isotopically-enriched materials; therefore minimization of waste and maximization of recovery of metal during all stages of production is crucial.

Target designs and fabrication approaches that minimize the loss of valuable materials are being developed to support the alternate methods for the production of ^{99}Mo.[3,4] Although thin disks, fabricated employing traditional powder metallurgy methods have been a primary focus for the aforementioned production processes, other target forms are being considered. For example, cylinders of packed spheres reminiscent of "sphere-pac"[5] have been discussed for neutron capture targets. The sphere-pac concept requires metal spheres of at least three different diameters (tri-modal) for efficient packing. The ability to use the smaller particles as feedstock for additive manufacture of accelerator target assemblies would be an added benefit.

Metal spheres, although simple in shape, can be challenging to fabricate especially from brittle materials. Typically metal spheres are produced from wire.[6,7] The wire is cut into short lengths which are forged or "headed" to form a rough sphere with a ring around the circumference. Another method by which metal spheres are manufactured from wire is skew rolling.[8] Skew rolling is a continuous process in which round stock is forged into spheres by specially-designed grooves in the rollers of a mill. After the initial forming stage, imperfections such as bulges or flashing are removed via grinding or similar machining process. The spheres can be further treated if needed based upon application requirements, such as surface finish, sphericity and hardness.

Molybdenum (Mo) has many favorable properties for high-temperature structural applications including a high melting point, low thermal expansion coefficient, and high thermal conductivity.[9,10] However, in its unalloyed form, Mo is brittle at room temperature making forming by standard metallurgical techniques, difficult. Molybdenum must be heated above a certain temperature to become ductile. This brittle-to-ductile transition temperature is dependent upon a variety of factors including chemical composition and level of cold working of the metal. The hot-working or forging temperature for pure Mo is generally between 1200 °C and 1300 °C and since the metal is readily oxidized, forging operations must be either conducted in an inert atmosphere or have an oxidation allowance in the processing to final shape. The combination of these factors makes the fabrication of small molybdenum spheres employing traditional metal forming methods, impractical.

Powder metallurgy techniques can be used to fabricate small metallic spheres. Tungsten carbide ballpoint pen balls, with diameters of approximately 0.5 mm to 1 mm, are produced from powders.[11] A significant disadvantage of the powder approach is the need for unique tooling for each diameter which can be costly especially when designed for use with hard, high density materials such as molybdenum and the other refractory metals.

Sol-gel methods including internal and external gelation for the fabrication of small spherical oxide particles from aqueous solutions have been investigated for several decades for nuclear fuel applications.[12,13] Gelation processes have been employed to produce microspheres across a broad range of diameters, from 30 μm to > 1.2 mm, for use in coated particle TRISO fuels[14] and in the sphere-pac pin design.[5] These processes have been shown to be suitable for a variety of metals oxides such as uranium, thorium, aluminum, zirconium, titanium and iron.[15-17]

An alternate method for the fabrication of small Mo spheres of varying diameter and densities was proposed. It was hypothesized that molybdenum-containing microspheres could be produced via sol-gel methods using the chemical compounds being examined for the recovery of the metal from spent radiopharmaceutical solutions[2]. Molybdenum trioxide microspheres would be produced employing the gelation techniques developed to produce fuel particles. The trioxide beads would be reduced and sintered to produce metal spheres. Sintering conditions would be varied to control the density of the product and ensure desirable dissolution rates. Disappointingly, the formation of pure molybdenum trioxide beads employing the gelation processes developed to produce fuel particles was not feasible because of chemical incompatibilities.[18]

Alginate gel beads have recently received a great amount of attention.[19,20] Alginate is a natural polysaccharide found in brown algae. Alginates are widely used in the food and pharmaceutical industries and have been employed as a matrix for the entrapment of drugs, macromolecules, metals and oxides, and biological cells. Alginate “polymers” react with most polyvalent cations (except magnesium) to form cross linkages. As the concentration of polyvalent cations is increased, the algin solution, thickens, gels, and can even precipitate. The process has been used to form filaments, films and spheres. Alginates are compatible with a wide variety of materials including thickeners, synthetic resins, sugars, oils, fats, waxes, pigments and various surfactants. Microspheres with a broad range of diameters, from micrometers to many millimeters that contain a wide variety of materials can be produced using alginates.

Molybdenum carbides are being investigated as catalysts for the two-stage hydro-processing of raw bio-oil, the synthetic fuel extracted from biomass being examined as substitute for petroleum.[21] Promising activity, stability, and in situ regenerability were observed for certain molybdenum carbide catalysts which were tested in the form of small beads or spheres. The carbide catalysts were prepared by the carburization of Ca-, Co-, Ni-, or Cu-doped molybdenum trioxide (MoO_3) beads which were fabricated using an aqueous external gelation method involving alginate.[22] The approach used in this work was thus selected to produce molybdenum trioxide microspheres for evaluation.

2.0 TECHNICAL APPROACH

Molybdenum trioxide (MoO_3) beads were prepared using an aqueous external gelation method. A slurry was prepared by suspending MoO_3 powder in an aqueous solution of sodium alginate (50 weigh percent MoO_3, 5 weight percent alginate, balance water). Drops of the alginate-oxide slurry were metered into a 2 weight percent aqueous solution of calcium chloride ($CaCl_2$) upon which the exchange of ions between the binder and solution produced crosslinking of the alginate and the formation of rigid MoO_3 containing beads. The precipitated trioxide beads were separated from the aqueous solution, rinsed, dried, and heat-treated at 600 °C for 2 h in air to remove binder-derived hydrocarbons and produce MoO_3 beads.

The trioxide beads were reduced to metal employing the two-stage process developed for producing molybdenum metal powder.[23] Samples of the reduced beads were sintered in a molybdenum boat at 1400°C and 1600°C for one hour in a flowing argon with 4 volume percent hydrogen atmosphere. Bulk densities were calculated using diameters from image analysis and average weight per bead from batch measurements. Chemical analysis was conducted employing inductively coupled plasma optical emission spectrometry (ICP-OES).

3.0 RESULTS

The calcined molybdenum trioxide beads, formed employing the alginate process, were not spherical but possessed a range of shapes based upon the interaction of the droplet of trioxide-alginate slurry and the bath (Figure 1). This resulted in some variation in diameter as noted in the results summarized in Table 1. The trioxide beads were not fully dense but were robust enough to be handled without observable damage. The trioxide particles efficiently reduced to metal with little change in size or shape (Table 1 and Figure 1), however; the beads exhibited significant shrinkage during sintering. The beads were readily removed from the molybdenum boat and separated after both reduction and sintering. Chemical analysis of the sintered beads is presented in Table 2.

4.0 DISCUSSION

The fabrication of small molybdenum spheres across a broad range of diameters employing typical metallurgical approaches is very challenging; therefore alternate approaches involving the production of molybdenum trioxide-containing spheres that could be reduced and sintered were examined. Hollow molybdenum trioxide microspheres for use in hybrid battery cathodes have recently been prepared from ammonium heptamolybdate tetrahydrate $[(NH_4)_6Mo_7O_{24}\cdot 4H_2O]$ solutions employing hydrothermal reactions; however, these processes are only useful for the production of very small particles, typically less than 10 micrometers in diameter.[24] The gelation processes developed for nuclear fuel fabrication have been used to produce spherical oxide microspheres from tens of micrometers to millimeters in diameter using a variety of materials. Molybdenum trioxide, introduced during processing as ammonium molybdate $[(NH_4)_2MoO_4]$, has been used in the sol-gel fabrication of porous fuel kernels,[25,26] however, pure molybdenum trioxide microspheres have not been fabricated employing similar techniques. Disappointingly, the formation of pure molybdenum trioxide beads via the gelation processes used to produce fuel particles is not feasible due to chemical incompatibilities.[18]

Based upon successes in the fabrication of molybdenum-containing catalyst beads[19], molybdenum trioxide (MoO_3) beads were prepared using an aqueous external gelation method involving an alginate-MoO_3 slurry and a calcium chloride solution for crosslinking and gelation. Sodium alginate was used as the base material with calcium as the crosslinking ion for gelation. Ammonium alginate could be used to eliminate the sodium and as previously noted, alginates will react with most polyvalent cations (except magnesium) to form cross linkages.[21,22] Other elements including Sr, Ba, Al and Fe have been used as cross linking ions thus a more suitable ionic compound should be available. Alginates can also be covalently cross-linked, as an alternative to ionic cross-linking. A variety of diamines and dihydrazides

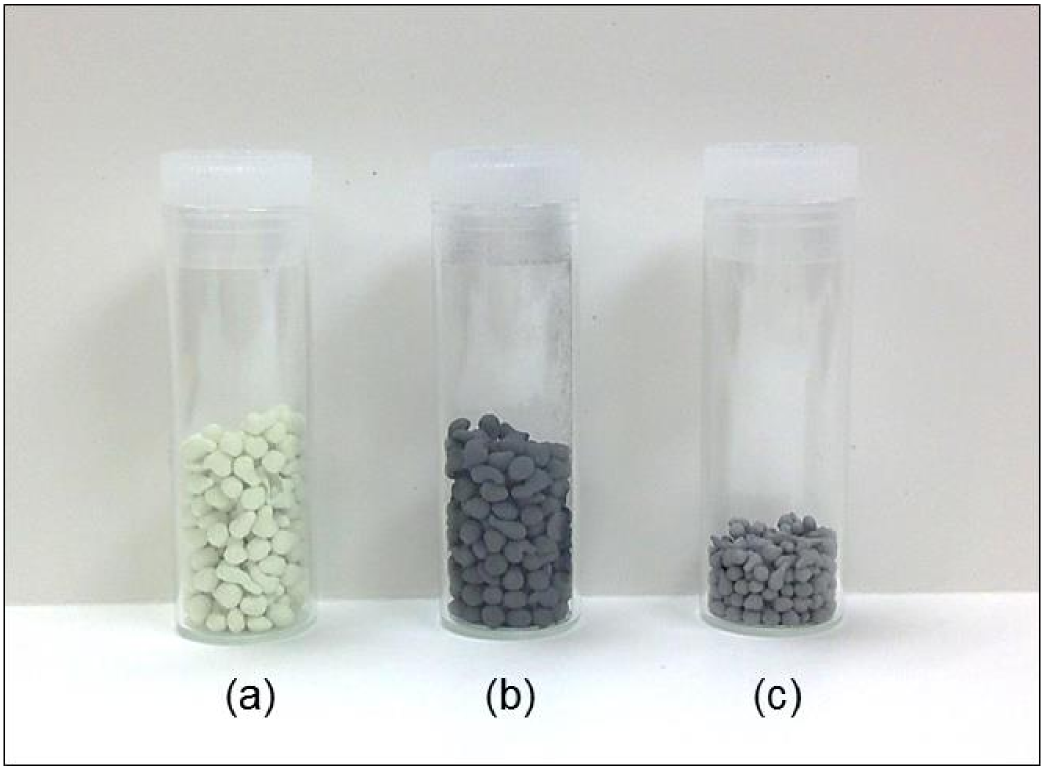

Figure 1. Calcined MoO_3 beads (a), after reduction to metal (b), and after sintering at 1400°C (c).

Table 1. Summary of the Reduction and Sintering of Mo-containing Beads

	Mass (g)	**Wt. Change (g)**	**Wt. Change (%)**	**Diameter* (mm)**	**Density* (g/cm^3)**	**% Theoretical Density**
Trioxide Beads	17.91	---	---	2.3 ± 0.3	2.60	55
Stage 1 Reduction	14.76	-3.15	-17.6	nm	nm	nm
Stage 2 Reduction	11.97	-2.79	-18.9	2.1 ± 0.2	2.17	21
Total	---	-5.94	-33.2	---	---	---
Sintered @ 1400°C	---	---	---	1.4 ± 0.2	7.71	75
Sintered @ 1600°C	---	---	---	1.2 ± 0.2	9.14	89

* Approximate since particles were assumed to be spherical.

Table 2. Chemical Analysis of Sintered Molybdenum Beads

Element	**Concentration (ppm)**	
	Sintered @ 1400°C	**Sintered @ 1600°C**
Al	< 20	< 20
B	150	140
Ca	6450	7220
Co	40	40
Cr	< 20	90
Fe	40	20
Mg	< 10	< 10
Mn	< 20	< 20
Na	50	30
Si	120	100
Sn	< 20	< 20
Ti	< 20	< 20
W	130	120
Zn	< 20	< 20

The < indicates below the limits of detectability.

have been used as alginate cross-linkers therefore it may possible to completely eliminate unwanted metallic contamination through judicious selection of alginate salt and crosslinking compound.

The molybdenum trioxide beads formed employing the process were not spherical. Noting this was a proof of concept, no effort was expended to optimize the shape or size of the particles. There is some reason to expect that with optimization studies, spherical outcomes are possible based on the success of other techniques. Droplet formation for gelation processing of spherical particles is well-understood and performed routinely for most sizes of interest.[27] For larger sizes, a pulsed laminar-flow nozzle has been used with excellent shape and diameter control and good throughput. For smaller sizes or “fines”, a turbulent two-fluid nozzle has been used, again with good control of product quality. Alternate techniques such as jet cutting have been used to produce beads from gelatinous mixtures ranging in diameter from 120 μm to 4 mm with narrow size distributions.[28]

5.0 SUMMARY

Spherical molybdenum particles or "beads" of various diameters are of interest for targets and as feedstock materials for the additive manufacture of targets and assemblies for the production of ^{99}Mo medical isotope without the use of highly-enriched uranium. Small molybdenum spheres cannot readily be fabricated employing typical metallurgical forming techniques thus other processes to produce metal microspheres across a broad diameter range were examined. A number of techniques have been employed to produce metal oxide microspheres for a wide variety of applications. It was hypothesized that these methods could be used to produce molybdenum trioxide microspheres that could subsequently be reduced and sintered to produce metal spheres not only across a broad range of diameters but also with controlled density for optimizing dissolution behavior.

The gelation processes developed for fabricating nuclear fuel particles were examined for forming oxide beads; however, molybdenum trioxide exhibits certain chemical incompatibilities with the most commonly used gelation processes hindering the production of pure trioxide particles. As an alternative, an aqueous alginate process being assessed for the fabrication of molybdenum-containing spheres for catalyst applications was employed to form trioxide beads that were successfully reduced and sintered to produce small molybdenum particles. The density of the molybdenum beads was influenced by sintering conditions which permits optimization of dissolution behavior. Although the beads were not spherical it is evident technologies are available to produce spherical particles from gelatinous mixtures across a broad range of diameters. Alginates can be crosslinked using many different chemical compounds and are compatible with a wide variety of materials thus the chemistry of the gelatin mixture can be tailored to the application through careful selection of feedstock materials.

6.0 REFERENCES

1. P. Tkac and G. F. Vandegrift, "Recycle of enriched Mo targets for economic production of ^{99}Mo/^{99m}Tc medical isotope without use of enriched uranium", *J Radioanal. Nucl. Chem.* 308:205–212 (2016).

2. J. Harvey, *NorthStar Progress Towards DomesticMo99 Production*, presented at the 2015 Topical Meeting on Molybdenum-99 Technological Development, Boston, MA, August 31 - September 3, 2015.

3. G. Dale, et al, *Global threat reduction initiative (GTRI) accelerator production of ^{99}Mo, FY10 Report*, Los Alamos National Laboratory, LA-UR-11-2010, September 30, 2010.

4. R. A. Lowden, S. D. Nunn, J. O. Kiggans, Jr., R. J. Parten, and C. D. Bryan, *Powder Metallurgy Fabrication of Molybdenum Accelerator Target Disks*, ORNL/TM-2014/238, July 2015.

5. G. D. Del Cul, C. H. Mattus, A. S. Icenhour, L. K. Felker, and D. F. Williams, *Fuel Fabrication Development for the Surrogate Sphere-Pac Rodlet*, ORNL/TM-2005/108, July 2005.

6. http://www.emersonbearing.com/pdf/Ball_Bearing_made.pdf

7. http://www.bearingsindustry.com/manufacturing.pdf

8. Z. Pater, A. Tofil, and J. Tomczak, “Steel Balls Formed by Cross Rolling With Upsetting”, *Metalurgija* 52[1], 103-106 (2013).

9. *Molybdenum: Material Properties and Applications*, https://www.plansee.com/en/materials/molybdenum.html

10. http://www.imoa.info/download_files/molybdenum/Applications_Mo_Metal.pdf

11. W.-D. Schubert, E. Lassner and W. Böhlke, “Cemented Carbides – A Success Story”, *Tungsten*, June 2010.

12. J. L. Collins, *Experimental Methodology for Determining Optimum Process Parameters for Production of Hydrous Metal Oxides by Internal Gelation*, ORNL/TM-2005/102, June 2005.

13. J. L. Collins, M. F. Lloyd, and R. L. Fellows, “The Basic Chemistry Involved in the Internal-Gelation Method of Precipitating Uranium as Determined by pH Measurements,” Radiochim. Acta 42, 121–34 (1987).

14. R. A. Lowden, *Fabrication of Baseline and Variant Particle Fuel for AGR-1*, ORNL/CF-06/02, Rev. 0, April 2006.

15. J. L. Collins, “Method of Preparing Hydrous Zirconium Oxide Gels and Spherules,” U.S. Patent No. 6,602,919 B1, Aug. 5, 2003.

16. J. L. Collins, “Method of Preparing Hydrous Titanium Oxide Gels and Spherules,” U.S. Patent No. 5,821,186, Oct. 13, 1998.

17. J. L. Collins, R. J. Lauf, and K. K. Anderson, “Method of Preparing Hydrous Iron Oxide Gels and Spherules,” U.S. Patent No. 6,599,493 B2, July 29, 2003.

18. Personal communication, J. L. Collins and R. Hunt, March 2016.

19. *Alginates*, Technical Evaluation Report Compiled by OMRI for the USDA National Organic Program, February 5, 2015

20. K. Y. Lee and D. J. Mooney, “Alginate: properties and biomedical applications”, *Prog. Polym. Sci.* **3**7[1] 106-126 (January 2012).

21. J.-S. Choi, A. Zacher, H. Wang, M. V. Olarte, B. L. Armstrong, H. Meyer III, I. I. Soykal, and V. Schwartz, “Molybdenum carbides, active and in situ re-generable catalysts in hydro-processing of fast pyrolysis bio-oil”, *Energy Fuels* **30**(6), 5016–5026 (2016).

22. J.-S. Choi, B. L. Armstrong, and V. Schwartz, U.S. Patent No. 9,012,349, April 1, 2015.

23. R. A. Lowden, J. O. Kiggans, Jr., S. D. Nunn, F. Montgomery, P. Menchhofer, and C. D. Bryan, *Large-Batch Reduction of Molybdenum Trioxide*, ORNL/TM-2014/630, July 2015.

24. P. Wanjing, L. Xiaolin, M. Xiaowei, Y. Jun Yang, W. Jiulin, N. Yanna, and H. Shin-ichi, "Molybdenum dioxide hollow microspheres for cathode material in rechargeable hybrid battery using magnesium anode", *J Solid State Electrochem* 19, 3347–3353 (2015).

25. T. A. Gens, *Preparation of Uranium and Thorium Oxide Microspheres with Controlled Porosity by a Sol-Gel Process*, ORNL-TM-1530, May 1966.

26. T. A. Gens, *Laboratory Preparation of Several Kinds of Nuclear Fuel Microspheres Using a Sol-Gel Method*, ORNL-TM-1785, March 1967.

27. R. L. Beatty, R. E. Norman and K. J. Notz, *Gel-Sphere-Pac Fuel for Thermal Reactors - Assessment of Fabrication Technology and Irradiation Performance*, ORNL-5469, November 1979.

28. U. Prusse, J. Dalluhn, J. Breford, and K. D. Vorlop, "Production of spherical beads by Jet Cutting", *Chem Eng Technol* 23, 1105-10 (2000).