Dissolution of Sintered Mo Disks

Chemical Sciences and Engineering Division

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by

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DISSOLUTION OF SINTERED MO DISKS

1 INTRODUCTION

Argonne National Laboratory (ANL), in cooperation with Oak Ridge National Laboratory (ORNL) and NorthStar Medical Technologies, LLC (NorthStar), is working on optimization of production of sintered Mo disks. Sintered Mo disks can be used for production of Mo-99 by two paths: the Mo-100(γ , n)Mo-99 reaction or neutron capture with Mo-98 enriched or natural Mo targets using the Mo-98(n, γ) reaction. Irradiated Mo targets are then dissolved in hydrogen peroxide and converted to K₂MoO₄ in 5 M KOH to be loaded onto the RadioGenixTM generator to separate Tc-99m from Mo for medical applications. To make the production of Mo-99 cost-effective, the sintered Mo disks should have high theoretical densities and good dissolution rates. Therefore, it is important to continue the dissolution studies to optimize the disk-manufacturing process.

2 EXPERIMENTAL

Sintered Mo disks were dissolved in 30% hydrogen peroxide, which had been pre-heated to 70°C. To that end, 12×1 mm disks were dissolved in 40 mL of H₂O₂, while larger disks were dissolved in 80 mL of H₂O₂. The sintered Mo disks were provided by ORNL and were prepared from commercial natural Mo powders, Mo-100 enriched powder, and ANL-recycled MoO₃ powders after reduction to Mo metal.

3 RESULTS AND DISCUSSION

Table 1 summarizes the characterization data for Mo-100 enriched sintered disks. Disks were made from commercial as-received Mo metal powder or Mo metal from recycled MoO_3 material after the reduction to Mo metal. Disks marked as recycle blend were made of 80% commercial as-received Mo powder and 20% recycled Mo powder. Physical differences between powders can be seen in Figure 1. The particle shape for commercial as-received powders is more rounded while the recycled material exhibits sharper edges. The commercial powders sintered more easily than the recycled Mo powder. Dissolution rates varied in the range of 0.21-0.53 g/min and were mostly driven by the open porosity (Figure 2).

Table 2 compares the data for the disks made from recycled natural Mo and commercial NPA Mo powder. A significant difference in the open porosity dictates the dissolution rates. While the open porosity for the disks made from recycled Mo material and sintered at 1500-1600°C is very low (usually <1%), the open porosity of the NPA disks pressed under the same conditions (100 ksi) is >8%. There is not much difference in the dissolution rates for 0.5-mm versus 1-mm thick disks made from the recycled material.

Interesting behavior was observed for the NPA disks pressed at 100 and 200 ksi. The green densities for the disks pressed at 100 ksi were ~82.5%, and after sintering at ~1500°C, the densities increased to 89.5-91%. On the other hand, the green density of the NPA disks pressed at 200 ksi was ~92%, and the final density of the sintered disks increased by only ~1.5-1.8%. The effect of sintering temperature (1200°C to 1500°C) on the final open porosity of the NPA disks pressed at 200 ksi was significant and had a major impact on the dissolution rates, as shown by Figure 3.

Figure 4 shows significant differences in the morphology of recovered Mo powder and commercial NPA Mo powder. In the recycled material, Mo particles coalesced together and formed larger particles; a lower open porosity is obvious even before pressing the powder into disks. The morphology of recycled ANL #80 material is similar to that of the recycled Mo-100 powder (Figure 1). These two recycled MoO_3 powders were products from small-scale recovery experiments, where MoO_3 precipitate was dried in a beaker on a hot plate and then ground using a mortar and pestle. When NPA powder is pressed at 200 ksi and sintered at 1400°C to 1500°C, the open porosity is below 3%, and the dissolution rates are low (<0.35 g/min). On the other hand, when pressed at 100 ksi and sintered at 1500°C to 1550°C, the open porosity was still very high (8-9.5%), and the dissolution rates were in the range of 2.4-2.7 g/min, about ten times higher than for the disk pressed at 200 ksi and sintered at the same temperature.

Table 3 shows another set of disks made from the recycled MoO_3 powder (ANL#80) that was sintered at 1200°C -1500°C and pressed at 150-200 ksi. An increase in temperature from 1200°C to 1400°C (disks #73 and #74) reduces the open porosity from 11% to 1.6%. When higher pressure at the same sintering temperature was applied, the open porosity was also reduced, as illustrated in Figure 5.

TABLE 1 Characteristics of Sintered Mo-100 Enriched Disks and Corresponding Dissolution Rates

#	Type	Pressure, ksi	Green Density, %	Sintering ^a		Sinter. Density, %	Open Porosity, %	Diameter, mm	Thickness, mm	Mass, g	Diss. Rate, g/min
				Temp., °C	Time, hr						
47	As-received	100	68.9	1400	1	89.7	8.2	11.56	0.99	0.98	0.43
48	As-received	100	69.2	1500	1	93.3	0.4	11.35	1.01	1.00	0.22
49	As-received	100	73.4	1400/1500	1/1	83.7/89.1	15.6/8.2	11.88	0.93	0.95	0.53
50	Recycled	100	70.8	1400/1500	1/1	88.2/94.0	7.4/0.4	10.84	1.08	0.99	0.24
51	Recycle blend	100	69.3	1400/1500	1/1	89.7/93.8	8.4/0.7	11.39	0.96	0.95	0.25
52	Recycle blend	100	73.4	1400/1500	1/1	84.9/90.1	13.7/5.6	11.76	0.95	0.97	0.43

^a Disks sintered under Ar/4% H₂ atmosphere.

FIGURE 1 SEM Images of As-Received Mo-100 Enriched Powder (Left) and Recycled Mo-100 Enriched Powder (Right). SEM images provided by Steve Nunn (ORNL).

FIGURE 2 Dissolution Rates of Mo-100 Disks Sintered at 1500°C versus Open Porosity

Another set of disks was made from a commercial PM Mo powder that had been spray dried. The particle size of spray-dried spheres was in the range of 45 to 90 μm . The spray-dried spheres were made of $\sim 5\ \mu\text{m}$ Mo powder particles that were glued together and then heated to remove the binder and partially sintered. An SEM image of the spray-dried PM Mo powder is compared to that of NPA powder in Figure 6.

Table 4 shows the characteristics of PM Mo disks together with their dissolution rates. Dissolution rates for all PM disks were very high (1.78-3.14 g/min), but several features about these disks should be discussed. Figure 7 shows the temperature profile during dissolution of the disks.

The temperature of the H_2O_2 solution for disks #83-85 increased rapidly (30°C in $\sim 20\ \text{s}$), significantly faster than that for disk #82 ($\sim 40\ \text{s}$), which is a common heating rate during dissolution of the majority of the sintered Mo disks. The dissolution reaction for disks #83-85 was vigorous, causing a large amount of splattering. A significant amount of steam was produced during this exothermic reaction, where H_2O_2 was decomposed into water vapor. Although complete dissolution occurred in about 60-70 s, a significant amount of H_2O_2 was consumed (determined by a difference in volume), with consumption rates of 35 mL H_2O_2 per minute. This is significant, and it is not the preferred dissolution behavior for processing large quantities of Mo (production-size irradiated target with ~ 300 -600 g of Mo). Good dissolution rates in the range of 1.9-2.9 g/min were observed for disks #81, #82, and #86-88 but with significantly lower consumptions of H_2O_2 (6-15 mL). This result is promising, but dissolution studies with more disks need to be performed to investigate the behavior of spray-dried Mo disks.

TABLE 2 Characteristics of Sintered Mo-100 Enriched Disks and Corresponding Dissolution Rates

#	Type	Pressure, ksi	Green Density, %	Sintering ^a		Sinter. Density, %	Open Porosity, %	Diameter, mm	Thickness , mm	Mass, g	Diss. Rate, g/min
				Temp., °C	Time, hr						
53	Recycled ANL#80	100	75.3	1300/1600	1/1	85.8/91.4	11.4/0	11.9	0.98	1.0	0.14
54	Recycled ANL#80	100	76.3	1300/1600	1/1	87.2/90.8	10.5/0	11.9	0.53	0.50	0.13
55	Recycled ANL#80	100	75.3	1400/1600	1/1	86.9/91.7	6.4/0.12	11.8	1.00	1.0	0.18
56	Recycled ANL#80	100	75.7	1400/1600	1/1	87.9/91.5	8.4/0	11.8	0.52	0.50	0.18
57	Recycled ANL#80	100	75.0	1500	1	89.1	1.5	11.9	1.00	1.01	0.34
58	Recycled ANL#80	100	76.3	1500	1	88.5	4.8	11.9	0.50	0.50	0.31
59	Recycled ANL#80	100	76.1	1500/1600	1/1	88.6/91.5	5.4/0.1	11.9	1.01	1.02	0.19
60	Recycled ANL#80	100	77.4	1500/1600	1/1	87.8/91.1	9.3/0.5	11.9	0.54	0.50	0.13
61	Recycled ANL#80	100	75.5	1600	1	92.2	0.2	11.8	0.99	1.0	0.22
62	Recycled ANL#80	100	77.0	1600	1	92.5	0.0	11.8	0.51	0.50	0.18
63	Climax NPA	100	82.6	1500	1	89.5	9.4	32.2	0.57	4.04	2.43
64	Climax NPA	100	82.2	1500	2	89.9	9.5	32.2	0.57	4.05	2.70
65	Climax NPA	100	82.5	1500/1550	1/1	88.9/90.9	10.6/8.0	32.0	0.57	4.03	2.69
66	Climax NPA	100	82.4	1550	1	90.4	9.0	32.0	0.57	4.02	2.54
67	Climax NPA	200	91.9	1200	1	93.5	4.9	32.8	0.51	3.91	1.02
68	Climax NPA	200	92.3	1300	1	93.8	4.0	32.9	0.52	3.93	0.54
69	Climax NPA	200	92.7	1400	1	94.2	2.8	32.6	0.52	3.92	0.35
70	Climax NPA	200	92.4	1500	1	94.2	0.5	32.7	0.54	3.94	0.25

^a Disks #53-62 were sintered under Ar/4% H₂ atmosphere, and disks #63-70 were sintered under Ar/7% H₂ atmosphere.

FIGURE 3 Dissolution Rates of NPA Mo Disks (pressed at 200 ksi, sintered at 1200-1500°C) versus Open Porosity. Numbers next to the symbol show the densities of sintered disks in percent.

FIGURE 4 SEM Images of Mo Powder Obtained after the Reduction of Recycled ANL#80 MoO_3 Powder and Commercial NPA Mo Powder. SEM images provided by Steve Nunn (ORNL).

TABLE 3 Characteristics of Mo Disks from Recycled ANL#80 MoO₃ and Corresponding Dissolution Rates

#	Type	Pressure, ksi	Green Density, %	Sintering ^a		Sinter. Density, %	Open Porosity, %	Diameter, mm	Thickness, mm	Mass, g	Diss. Rate, g/min
				Temp., °C	Time, hr						
73	Recycled ANL#80	150	83.5	1200	1	87.8	11.0	12.5	0.90	0.98	0.45
74	Recycled ANL#80	150	83.7	1400	1	90.6	1.6	12.3	0.93	1.03	0.27
75	Recycled ANL#80	150	83.8	1500	1	91.8	0.8	12.3	0.91	1.00	0.18
76	Recycled ANL#80	200	88.2	1200	1	90.1	6.9	12.6	0.80	0.91	0.44
77	Recycled ANL#80	200	88.4	1300	1	91.8	3.6	12.5	0.86	0.99	0.33
78	Recycled ANL#80	200	88.6	1400	1	92.9	0.5	12.5	0.88	1.00	0.27
79	Climax NPA	150	90.0	1200	1	91.2	8.5	32.6	0.54	3.92	2.24

^a The disks were sintered under Ar/4% H₂ atmosphere, except NPA disk that was sintered under Ar/7% H₂ atmosphere.

FIGURE 5 Effect of Sintering Temperature and Pressing on Open Porosity of Disks Made from Recycled ANL#80 MoO₃ Powder

FIGURE 6 SEM Images of Sintered Disks Fracture and Starting Powders for NPA and PM Disks. SEM images were provided by Rick Lowden (ORNL). SEM image of PM powder was obtained from the Climax Mo Powder Product Sheet.

TABLE 4 Characteristics of Sintered Mo Disks Made from Commercial PMA Spray-Dried Mo Spheres and Corresponding Dissolution Rates^a

#	Type	Pressure, ksi	Green Density, %	Sinter. Density, %	Open Porosity, %	Diameter, mm	Thickness, mm	Mass, g	Diss. Rate, g/min	H ₂ O ₂ Spent, mL	Diss. Rate per mL H ₂ O ₂ , g/min/mL
80	Climax PMA	100	77.4	90.3	6.4	28.8	0.53	3.09	1.78	25	0.07
81	Climax PMA	100	77.1	90.6	6.3	28.8	0.53	3.13	1.97	6	0.33
82	Climax PMA	100	77.8	90.5	6.5	28.7	0.53	3.10	1.86	10	0.19
83	Climax PMA	100	76.3	90.1	7.8	28.9	0.52	3.11	2.66	35	0.08
84	Climax PMA	100	76.9	89.3	8.2	28.9	0.52	3.12	2.88	38	0.08
85	Climax PMA	100	77.0	89.1	8.4	28.9	0.53	3.14	3.14	30	0.10
86	Climax PMA	100	76.2	89.9	7.6	28.7	0.52	3.07	2.17	15	0.14
87	Climax PMA	100	76.2	89.6	8.3	28.7	0.53	3.10	2.33	13	0.18
88	Climax PMA	100	76.7	90.2	8.2	28.7	0.53	3.08	2.85	11	0.26

^a The disks were sintered under Ar/7% H₂ atmosphere at 1600°C for 4 hours.

FIGURE 7 Temperature Profile during the Dissolution of PM Mo Disks

Data about the last set of sintered disks received from ORNL, including the dissolution rate, are listed in Table 5. Noticeable differences in the disk diameter between recycled and commercial Mo powders are due to the increased shrinking of disks made from the recycled material. This recycled MoO_3 powder was a product of a large-scale recovery experiment, where a final MoO_3 precipitate was dried in an oven at 160°C and then ground using an electric mill. Another noticeable difference was the density after sintering. While the NPA disks had densities in the range of 90.2-91.4%, the disks made from recycled material have densities in the range of 96.7-97.5% for the same sintering conditions. This difference was due to the size of the recycled Mo powder particles. The SEM images in Figure 8 show a significant difference in the size of the starting Mo powders.

We found that the particle size of the Mo powder may depend on the mass of MoO_3 used for the reduction process. The composition of the atmosphere, especially the water content, can also affect the size of the reduced Mo particles. For the smaller batch size (~ 30 g), the gas diffusion and water removal in and out of the bed are more rapid. Increasing the batch size to 500-1000 g leads to the production of Mo powder with a larger particle size, which is more comparable to the particle size of the commercial NPA powder. As expected, the dissolution rates for NPA disks were high (1.25-1.56 g/min) but were significantly lower than those for NPA disks #63-66 (Table 2) sintered at the same temperature. This result is most likely due to the lower open porosity of the disks (#92-94). On the other hand, one would expect a low dissolution rate for the disks made from ANL recycled MoO_3 powder (#89-91) because of the very high packing densities (96.7-97.5%) and very low open porosity (0.24-0.32%). Surprisingly, the dissolution rates were extremely high (0.59-0.6 g/min) for such dense disks. This finding could be attributed to their grainy surface (Figure 9), which is due to the sintering properties of the powder composed of large agglomerates, ten to hundreds of microns (Figure 8).

TABLE 5 Characteristics of Sintered Mo Disks Made from Recycled MoO₃ Powder and Commercial NPA Powder

#	Type	Pressure, ksi	Green Density, %	Sintering ^a		Sinter. Density, %	Open Porosity, %	Diameter, mm	Thickness, mm	Mass, g	Diss. Rate, g/min
				Temp., °C	Time, hr						
89	ANL recycled MoO ₃	100	65.7	1500	1	97.5	0.32	26.7	0.58	3.14	0.59
90	ANL recycled MoO ₃	100	67.1	1500	1	97.3	0.24	26.7	0.56	3.10	0.60
91	ANL recycled MoO ₃	100	65.3	1500	1	96.7	0.32	26.7	0.57	3.10	0.59
92	Climax NPA	100	78.8	1500	1	91.2	3.80	29.0	0.51	3.11	1.56
93	Climax NPA	100	80	1500	1	90.2	4.10	28.9	0.51	3.15	1.26
94	Climax NPA	100	81.6	1500	1	91.4	3.60	28.9	0.52	3.13	1.25

^a The disks were sintered under Ar/7% H₂ atmosphere.

FIGURE 8 SEM Images of As-received Commercial NPA Powder and Reduced Small Batch (30 g) of ANL Recycled MoO_3 Powder. SEM images provided by Rick Lowden (ORNL).

FIGURE 9 Photograph of Disk #90 (Table 5) Made from ANL-Recycled MoO_3 Powder and NPA Disk #92. The NPA disks had a noticeably smoother surface than the disks made from recycled material.

For future production of sintered disks made from recycled material, kilogram quantities of reduced Mo powder will need to be milled and then spray-dried. Nevertheless, the fast dissolution of dense disks made from large-scale recycled material is promising for future production of sintered disks. Several batches with kilogram quantities of ANL recycled MoO_3 powder will be sent to ORNL next fiscal year to test the large-scale reduction process and production of sintered Mo disks from recycled material.

4 CONCLUSION

Dissolution studies with disks prepared at ORNL revealed several new features that are important for the manufacturing of sintered Mo disks from recycled material for a production facility. The size of the MoO_3 batch for the reduction can affect the particle size of Mo powder, and milling of the produced Mo powder may be required. Although the open porosities of the disks made from commercial powders were important for the dissolution kinetics, dissolution studies from large-scale recycled Mo material showed that even disks with very low open porosity ($<0.4\%$) and high packing densities ($\sim 97\%$) can dissolve quickly (0.6 g/min). Spray-dried sintered Mo disks showed very high dissolution rates ($\sim 2\text{-}3 \text{ g/min}$), but some disks dissolved so vigorously that the method would not be suitable for processing of production targets in a hot cell facility. However, spray-dried disks made from recycled Mo material should be explored further and in more detail next fiscal year.

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