Dissolution of Additively Manufactured Mo Disks and Structures for Accelerator Based Production of Mo-99

Chemical and Fuel Cycle Technologies Division

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1 INTRODUCTION

The press-and-sinter approach for production of Mo targets has been successfully tested and demonstrated [1-3]. The main advantage of this process is that it uses readily available technology and tools that have been tuned for production of various metal and metal oxide targets. However, certain target design specifications, such as dimensional accuracy of the diameter and thickness of the disks, are required for proper fit into a target holder and therefore place strict tolerances on sintered Mo disks intended for accelerator production. Furthermore, having a target composed of multiple disks poses certain challenges for post-irradiation processing, where there is a potential for spillage of individual disks during the manipulation for dissolution inside a processing hot cell. Additive manufacturing (AM), also referred to as 3D printing, provides capabilities to design and build a single-piece Mo target that provides the opportunity for better geometry for optimized production of Mo-99, improved cooling capability, and safer post-irradiation handling. A drawback of AM Mo structures is roughness of finished surfaces, which could reduce the effectiveness of gas cooling systems. Process development for AM Mo structures using selective laser melting is described in work by Gibson and Lowden [4].

For post-irradiation processing, it is important to look at the dissolution behavior of AM Mo structures in comparison to readily dissolved press-and-sinter Mo targets. The dissolution behavior of press-and-sinter targets has been well documented in our previous reports [5–11]. In this report, we discuss results of dissolution experiments conducted with AM Mo disks and structures (provided by Oak Ridge National Laboratory [ORNL]) in 50% hydrogen peroxide (H_2O_2).

2 EXPERIMENTAL

2.1 MATERIALS

3D-printed Mo disks and structures were manufactured and provided by ORNL. There are ~180 different process variables associated with selective laser melting of Mo. Various deposition patterns for the AM Mo disks were proposed and tested, such as i) meander; ii) stripes; iii) chessboard; and iv) total fill (not tested in dissolution studies) (Figure 1). Examples of AM Mo disks and 3D structures are shown in Figure 2. The mass of the AM Mo disks varied from ~5.5 g to 10.08 g; differences were due to variations in the diameter and thickness of produced disks. Theoretical density (TD) was in the range of 81.5–93.5% and open porosity (OP) was in the range of 6.5–18.5%.

FIGURE 1 Examples of deposition patterns used for AM Mo disks and structures.

FIGURE 2 Examples of AM Mo disk and AM Mo 3D structures: a) 29x2-mm Mo disk, 10.03 g; (b) “combined 13 disks” 3D structure, 86.04 g; (c) honeycomb 3D design, 205.1 g.

2.2 REAGENTS AND DISSOLUTION SETUP

50% H_2O_2 was obtained from Fisher Chemical (part number H341-500). AM Mo disks were dissolved in 0.6- to 1-L glass beakers by addition of 40 mL of 50% H_2O_2 . After the initial reaction, additional H_2O_2 was added in 10-mL increments until full dissolution was achieved. Foam level during the dissolution was in the range of 100–500 mL.

AM Mo structures were dissolved in a large-scale dissolution apparatus [11]. The dissolution vessel contains a glass frit on the bottom that holds the Mo structure for the dissolution. The Mo structure was inserted through a port on top of the vessel, which was closed

and sealed during actual dissolution (Figure 3a). H_2O_2 was slowly added ($\sim 110 \text{ mL/min}$) via a peristaltic pump for a sufficient period of time to achieve controlled dissolution. Shortly after H_2O_2 addition, vigorous dissolution of the Mo disks began, producing yellow-colored froth and significant bubble formation due to heat produced from the reaction. Water vapor was transferred into the condenser, which was open to the atmosphere to allow release of oxygen. The condenser was continuously drained during the dissolution.

After partial dissolution of the Mo disks, solutions of Mo-containing H_2O_2 were transferred to another vessel that was under vacuum by opening the solenoid valve at the base of the dissolution vessel (Figure 3b). Figure 4 shows a portion of the large-scale dissolution apparatus during the dissolution of AM Mo structures.

FIGURE 3 Images of parts of dissolution vessel, showing a) open insertion port that can be closed during dissolution, and b) solenoid valve on bottom of dissolution vessel for transfer of Mo solution into evaporation vessel.

FIGURE 4 Large-scale dissolution assembly used for processing AM Mo structures.

3 RESULTS AND DISCUSSION

3.1 DISSOLUTION OF AM MO DISKS

First, dissolution experiments were performed to understand the effect of 3D-printing patterns (Figure 1) on the dissolution properties. For this study, ~29x1-mm AM Mo disks with various patterns were dissolved in 50% H₂O₂. A single Mo disk with a stripe pattern (Stripe-3, Table 1) was dissolved by immersion in 40 mL of 50% H₂O₂ pre-heated to 70°C. Owing to the vigorous reaction, the whole volume of H₂O₂ was consumed within ~1.5 min. Then a fresh 40-mL portion of room-temperature H₂O₂ was added, followed by additional H₂O₂ in 10-mL increments, until complete dissolution was achieved.

Since the dissolution reaction in pre-heated H₂O₂ was too strong, the remaining disks were dissolved using room-temperature H₂O₂. It was also observed that a 600-mL beaker was barely sufficient to contain the foam level created during the dissolution, so later studies were performed in a 1-L beaker. After approximately 30 s, the reaction became vigorous and the foam level reached to about the 400-mL mark. After the foam level decreased, additional H₂O₂ was added in 10-mL increments until full dissolution was observed. About halfway through the dissolution, the disks fell apart and formed small Mo pieces and wires. The results of this initial dissolution study are summarized in Table 1.

TABLE 1 Dissolution results of AM Mo disks with varying printing patterns using 50% H₂O₂

Pattern	Disk properties				Dissolution			
	d, g/cm ³	TD, %	OP, %	Mass, g	H ₂ O ₂ , mL	H ₂ O ₂ mL/g	Diss. time, min	Diss. rate, g/min
Stripe-3	9.4	92	8	5.453	80	14.7	5.5	0.991
Stripe-4	9.17	90	10	5.433	60	11.0	4.5	1.207
Stripe-5	9.46	93	7	5.477	60	11.0	4.5	1.217
Meander w/border-3	9.44	93	7	5.504	65	11.8	5	1.101
Meander w/border-4	9.47	93	7	5.497	60	10.9	4	1.374
Meander w/border-5	9.55	93.5	6.5	5.514	60	10.9	4	1.379
Meander, no border-3	9.45	93	7	5.623	60	10.7	5	1.125
Meander, no border-4	9.48	93	7	5.630	60	10.7	4	1.407
Meander, no border-5	9.43	93	7	5.624	60	10.7	4	1.406
Chessboard-1	9.44	92	8	5.477	60	11.0	5	1.095
Chessboard-2	9.42	92	8	5.510	60	10.9	4.5	1.224
Chessboard-3	9.42	92	8	5.506	60	10.9	4	1.377

D = density; TD – theoretical density; OP – open porosity

In comparison, a 4.713-g sintered Mo disk with 85% TD dissolved at a rate of 1.57 g/min but using less H₂O₂ (40 mL). Among the tested AM Mo disks, the dissolution rate of stripe- and chessboard-patterned disks was slightly slower (1.1 ± 0.1 and 1.2 ± 0.1 g/min, respectively), and AM Mo disks with meander patterns dissolved slightly faster (1.3 ± 0.1 g/min). However, the point of complete dissolution was difficult to observe because of the bubble volume. On the basis of this preliminary study, further dissolutions were performed with AM Mo disks with a meander pattern.

3.2 DISSOLUTION OF AM MO DISKS WITH VARIOUS DENSITIES

A set of AM Mo disks printed with a meander pattern were dissolved in a similar manner to the above. Disks varied in thickness from 1.393 to 1.925 mm, and TDs were in the range of 81.5–91.8%. Dissolution data are summarized in Table 2.

Overall, on the basis of the limited set of Mo disks available for this initial dissolution study, the dissolution behavior for all AM Mo disks printed with a meander pattern appears very similar, but some differences were observed. As expected, thicker Mo disks (Mo45-30-2, 3, 4, Table 2) dissolved most slowly, and additional H₂O₂ was needed for complete dissolution because of the larger Mo mass. Despite slower dissolution, total consumption of H₂O₂ was comparable to other AM Mo disks, with ~9 mL/g-Mo required. From visual observation, the dissolution behavior was very similar to that of the previous set of disks listed in Table 1. Disks started to dissolve vigorously at about 30 s and fell apart about halfway through the dissolution.

Dissolution rates were influenced not only by disk thickness but also by TD. AM Mo disks with the highest average TD (91.6% TD; Mo45-40-7, 9, 10) dissolved slightly faster compared to lower-density disks (~81.9% average TD; Mo45-38-3, 4, 5). It was observed that after disks fell apart during the dissolution, the higher-density disks formed fine powder-like particles, while lower-density disks formed wire-like structures that took longer to dissolve. Photographs provided in Figure 5 show the particles formed during the dissolution of AM Mo disks of various densities.

TABLE 2 Dissolution results of AM Mo disks (meander pattern) with varying densities and dimensions using 50% H₂O₂

AM Mo disk ID	Disk properties					Dissolution			
	Dimensions (d×h), mm	d, g/cm ³	TD, %	OP, %	Mass, g	H ₂ O ₂ , mL	H ₂ O ₂ mL/g	Diss. time, min	Diss. rate, g/min
Mo45-38-3	28.8×1.597	8.36	81.5	18.5	6.857	60	8.8	6.33	1.083
Mo45-38-4	28.8×1.595	8.39	81.8	18.2	6.847	60	8.8	4.5	1.522
Mo45-38-5	28.8×1.494	8.45	82.3	17.7	6.753	60	8.9	4.5	1.501

TABLE 2 (Cont.)

AM Mo disk ID	Disk properties					Dissolution			
	Dimensions (d×h), mm	d, g/cm ³	TD, %	OP, %	Mass, g	H ₂ O ₂ , mL	H ₂ O ₂ mL/g	Diss. time, min	Diss. rate, g/min
Mo45-36-1	28.8×1.410	8.86	86.4	13.5	6.654	60	9.0	4.5	1.479
Mo45-36-2	29.0×1.477	8.7	84.8	15	6.869	60	8.7	4	1.717
Mo45-36-3	28.8×1.433	8.7	84.8	15	6.698	60	9.0	4	1.675
Mo45-30-2	28.9×1.899	9.08	88.5	11.5	10.075	90	8.9	10	1.008
Mo45-30-3	28.9×1.902	9.1	88.7	11.3	10.029	90	9.0	10	1.003
Mo45-30-4	28.9×1.925	9.09	88.6	11.4	9.994	90	9.0	9	1.110
Mo45-40-7	29.0×1.393	9.37	91.4	8.4	6.837	60	8.8	4	1.709
Mo45-40-9	28.9×1.369	9.42	91.8	8.1	6.667	60	9.0	4	1.667
Mo45-40-10	28.9×1.393	9.4	91.6	8.4	6.615	60	9.1	4.25	1.556

d= density; TD – theoretical density; OP – open porosity

FIGURE 5 Particles formed during dissolution of AM Mo disks: a) small particles observed with higher-density AM Mo disks, and (b) wire-like particles observed with lower-density AM Mo disks.

3.3 DISSOLUTION OF AM MO 3D STRUCTURES

Dissolution of AM Mo 3D structures was performed in a large-scale dissolution setup designed for dissolving up to 600 g of Mo. The Mo structure was placed on the glass frit at the bottom of the dissolution vessel and H₂O₂ was added via peristaltic pump. At various time increments, the solution was drained from the vessel into the secondary vessel by vacuum. After each solution transfer from the dissolver, a new portion of H₂O₂ was added to continue the dissolution, and the process was repeated until complete dissolution was achieved. A summary of dissolution results for AM Mo 3D structures is given in Table 3.

TABLE 3 Dissolution results of AM Mo 3D structures using 50% H₂O₂

AM Mo 3D structure		Mo mass, g	50% H ₂ O ₂ , mL	Diss. time, min	Diss. rate, g/min	H ₂ O ₂ , mL/g-Mo	Water condensed, mL
13-disk, conjoined		86.04	1348.5	22	3.91	15.67	506.6
Honeycomb		205.02	3299.1	41	5.00	16.10	1694.1
25-disk, conjoined		175.3	3295.0	37.3	4.70	18.80	1593.0

The smallest of the 3D structures (86.04 g), comprising 13 conjoined disks, was dissolved through ~5-min additions of H₂O₂. The maximum foam level during the dissolution reached the ~6-L mark. Owing to shorter H₂O₂ addition times, the overall processing time was slightly longer compared to other 3D structures listed in Table 3, and therefore the dissolution rate appears slower. The second and third structures (205.02 g and 175.3g) were dissolved through ~8-min additions of H₂O₂. When the second (honeycomb) structure was dissolved, the foam level during the dissolution reached the ~3-L mark, which was significantly lower compared to the 13-disk structure.

The 25-disk structure dissolved at approximately the same rate as the honeycomb structure. The foam level reached the ~3-L mark after 6 min of H₂O₂ addition and reached 4 L at the end of the 8-min addition period. Complete dissolution of the structure was achieved after three 8-min additions of H₂O₂.

Progress during the dissolution of the second structure is shown in Figure 6, where it can be seen that dissolution (pitting) occurred at the point on the structure directly under the H_2O_2 stream from the addition line, while the rest of the structure was only slightly affected. After the third H_2O_2 addition, the majority of the structure was dissolved.

FIGURE 6 Progress during dissolution of honeycomb AM Mo 3D structure, showing a) undissolved structure, b) 1st addition of H_2O_2 , c) after 1st addition of H_2O_2 , and d) after 3rd addition of H_2O_2 .

Temperature profiles during the dissolution of AM Mo 3D structures were measured within the dissolution vessel at the bottom (frit level), middle (foam level), and top (head space) of the vessel; an example of the temperature profiles for the honeycomb structure is shown in Figure 7. As the H_2O_2 is added, the temperature at the bottom of the vessel rises very rapidly (in a few seconds) from $\sim 20^\circ\text{C}$ to $\sim 109^\circ\text{C}$. The highest temperature (129.7°C) was recorded in the middle of the vessel, where foam formation occurs. This finding is likely due to partial cooling of the bottom of the vessel by addition of fresh H_2O_2 (at room temperature), whereas the foam level remains almost unaffected by addition of fresh H_2O_2 . The temperature in the head space of the dissolution vessel reached 101.1°C . As the addition period ended, the temperature dropped below 100°C and rose again with the next addition of H_2O_2 . Temperature profiles observed during the dissolution of AM Mo 3D structures are comparable to those obtained for dissolution of up to 600 g of sintered Mo disks.

Dissolution rates observed for 3D Mo structures were in the range of $\sim 4\text{--}5$ g/min, which compares well to the large-scale dissolution studies using 600 g of sintered Mo disks, where rates were in the range of $3.4\text{--}6.7$ g/min. Overall, dissolution properties of AM Mo disks and 3D structures are comparable to dissolution properties of sintered Mo disks. The main difference is that AM Mo disks fall apart about halfway through the dissolution, forming either fine particles or wire-like structures. The type of particles formed during dissolution seems to be related to the TD. In the case of sintered Mo disks, dissolution usually progresses by continuous shrinking of the sintered target, and towards the end of the dissolution the disks fall apart to form fine Mo particles that usually dissolve very quickly.

FIGURE 7 Temperature profile in dissolution vessel obtained during the dissolution of honeycomb AM Mo structure (205 g) using 50% H_2O_2

4 CONCLUSION

This report summarizes an investigation into the H_2O_2 dissolution of additively manufactured Mo disks and 3D structures produced by selective laser melting. Various printing patterns and theoretical densities were tested. Despite very similar dissolution behavior observed for all patterns, small differences were observed in AM Mo disks printed with different patterns. Of the patterns tested, disks printed using the meander pattern (with or without a border) dissolved slightly faster than those with striped or chessboard patterns. In tests of dissolution of AM Mo disks with different densities, it was observed that after the disks fell apart, higher-density disks formed fine Mo powder-like particles, while lower-density disks formed wire-like structures that took a bit longer to dissolve. Based on limited dissolution testing of AM Mo disks, there is some indication that higher-density disks dissolve slightly faster, which is the opposite of the behavior observed for sintered Mo disks.

The dissolution behavior of AM Mo 3D structures was very similar to that observed for large-scale dissolution of sintered Mo disks. Dissolution rates for AM Mo 3D structures with masses of 86–205 g were approximately 4–5 g/min, well within the range of dissolution rates observed for up to 600 g of sintered Mo disks (3.4–6.7 g/min).

Future studies should concentrate on dissolution of AM Mo 3D structures with various densities to better understand the effect of theoretical densities on dissolution rates, which could play an important role in decision-making for the selection of sintered versus AM Mo disks for accelerator production of Mo-99.

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