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Compaction and Sintering of Molybdenum Powders

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ABSTRACT

To support the development of Mo-99 production by NorthStar Medical Technologies, LLC, Mo metal powders were evaluated for compaction and sintering characteristics as they relate to Mo-100 accelerator target disk fabrication. Powders having a natural isotope distribution and enriched Mo-100 powder were examined. Various powder characteristics are shown to have an effect on both the compaction and sintering behavior. Natural Mo powders could be cold pressed directly to >90% density. All of the powders, including the Mo-100 samples, could be sintered after cold pressing to >90% density. As an example, a compacted Mo-100 disk reached 89.7% density (9.52 g/cm³) after sintering at 1000°C for 1 hr. in flowing Ar/4%H₂. Higher sintering temperatures were required for other powder samples. The relationships between processing conditions and the resulting densities of consolidated Mo disks will be presented.

Introduction

NorthStar Medical Technologies, LLC has developed a new process for the production of Mo-99 which is utilized in the radio-pharmaceutical industry to obtain the daughter product, Tc-99m, the most commonly used radioisotope for medical diagnostics. The NorthStar process involves photon irradiation of Mo-100 targets in an electron accelerator to produce Mo-99 by the (γ, n) reaction. The Mo-100 targets are thin disks of partially consolidated metal powder. The disks are typically made by cold pressing the powder in a steel die and then sintering the pressed disks in a furnace to achieve the desired density of about 90% of theoretical. The disks must be made in a repeatable manner to meet physical property acceptance criteria which include: diameter, thickness, flatness, and density. And, because of the high cost of Mo-100 isotope powder, it is desirable to meet these criteria without machining the disks.

Molybdenum is a refractory transition metal with a relatively high melting temperature of 2610°C. The high melting temperature, combined with good strength and stiffness, make Mo useful for crucibles, glass-melting electrodes, nuclear industry components, thermocouple

sheaths, and various aerospace applications. Mo is also commonly used as an alloying element in steel and super alloys. Sintering of Mo powder has been investigated for many years. [1-9] In early studies, methods for enhancing sintering rates by the addition of activators such as Ni or Pt group metals was examined. [1,2] The activating metals were used to increase diffusion rates in the bulk material or at the grain boundaries. More recently, researchers have investigated acceleration of the sintering process through the use of specialized processing methods, such as microwave sintering and spark plasma sintering. [3-5] In addition, other investigators have looked at processing Mo powders to remove residual oxygen and also at producing powders having a fine particle size. [6,7] There have also been efforts to model the sintering behavior of Mo powders. [8,9] In examining these studies, there are apparent inconsistencies in the processing conditions that are reported to be required to achieve good sintered densities. For example, some studies indicate that good densities were reached at 1400°C, while others indicate that temperatures of 1800°C or higher are needed. [3,9] Sintering times also vary considerably, with some researchers using up to 100 hr. at peak temperature to optimize the results. [6] In most of the studies cited, one type of Mo powder was used for the experiments. Since Mo powders from different suppliers, and different grades from the same supplier, can have widely varying characteristics, this may explain some of the inconsistencies in the findings.

In the present study, a variety of Mo powders from various sources was evaluated to determine how the powder characteristics affect the processing parameters that are needed to achieve a consolidated density of 90% or greater. Samples of Mo-100 isotope powder were included in the study for preliminary determination of processing requirements.

Experimental

Molybdenum metal powders having a purity of greater than 99% (metals basis) were obtained from commercial suppliers. Samples from 5 lots of Mo-100 powder were obtained from IsoFlex USA. A list of the suppliers and the powder description provided by the supplier is given in Table 1. A sample of each of the powders was examined by scanning electron microscopy (SEM) to evaluate primary particle size, particle morphology, and the extent to which the particles were agglomerated. Particle size distribution was determined using laser light scattering (Horiba LA-950V2) with the particles suspended in high purity ethanol. BET analysis (Quantachrome Autosorb-1) was used to determine the surface area of the powders.

Table 1. Molybdenum powder supplier data.

Molybdenum Supplier	Grade	Purity, %	Oxygen, ppm	Particle Size
Alfa Aesar	10030	99.95	-	3-7 μm
Atlantic Equipment Engineers	MO-103	99.80	-	-325 mesh
Climax Molybdenum	EM2	99.97	1489	-100 mesh
Climax Molybdenum	EM-NM3	-	-	-
Climax Molybdenum	HDFM	99.97	1444	$d_{50} = 9.5 \mu\text{m}$
Climax Molybdenum	NPA	99.98	1084	-230 mesh
IsoFlex USA	Mo-100	>99	-	-

Cylindrical steel dies were used to press the powders into disks having a diameter of 9.53 mm (0.375 in.), 12.7 mm (0.5 in.), or 25.4 mm (1.0 in.). The 9.53 mm and 12.7 mm disks were compacted at 34.5, 69, 137.9, 344.8, 689.5, or 1379 MPa (5, 10, 20, 50, 100, or 200 ksi) using a hand-operated Carver pneumatic press. The 25.4 mm (1.0 in.) disks were compacted at 1379 or 1723.8 MPa (200 or 250 ksi) using an automated servo-hydraulic press (Instron Model 1335). The die walls and die plunger were coated using a solution of stearic acid in either acetone or MEK to reduce die wall friction. No binder or lubricant was added to the Mo powder. The as-pressed density (green density) of the disks was determined by weighing and measuring the dimensions or by Archimedes method using immersion in high purity ethanol.

Sintering of the pressed Mo disks was conducted in a tube furnace with an atmosphere of flowing Ar/4% H_2 gas. The furnace was first purged with flowing Ar, after which an Ar/4% H_2 flow rate of 0.2 standard liters/min. was maintained. The peak sintering temperature varied from 1000°C to 1650°C. The heating rate was 10°C/min. and the samples were held at the peak sintering temperature for 1 hr. The density of the sintered disks was measured by Archimedes method using immersion in high purity ethanol.

Results and Discussion

Powder Characteristics

Examination of powder samples by SEM revealed that most of the powder grades consisted of agglomerates of fine, equiaxed primary particles, which often showed a prismatic form. The agglomerates were typically made up of strongly bonded particles with well-established necks and diffusion bonds between the primary particles. The primary particle sizes ranged from 100 nm or less, to greater than 5 μm . SEM micrographs of the natural Mo powders are shown in Fig. 1. Fig. 2 shows a typical micrograph of powder from one of the 5 different Mo-100 lots. The primary particle size for all of the lots was similar, about 0.4 to 1.0 μm . Some variability was observed in the size of the agglomerates in different lots. The primary particle size range for all of the powders as determined from the SEM micrographs is listed in Table 2.

The median particle size of the powders, as determined by laser light scattering, was typically larger than the primary particle size observed in the SEM. This difference can be attributed to the agglomerates in the powders being counted as single particles by the light scattering technique. The median particle size values are shown in Table 2. Also listed are the BET surface area measurement results and the calculated spherical equivalent diameters based on the surface area values.

Die Pressing

The relationship between die pressing pressure and the resulting as-pressed density is shown by the graph in Fig. 3. It can be seen that there is a non-linear increase in the density of the compacted disks as the pressure increases. It can also be seen that there is some variability in the as-pressed density at a given pressure for the different powders. This difference appears to be most closely correlated with the surface area of the powders. The Mo-100 and the EM-NM3 powders have the highest surface areas and the lowest densities for a given applied pressure.

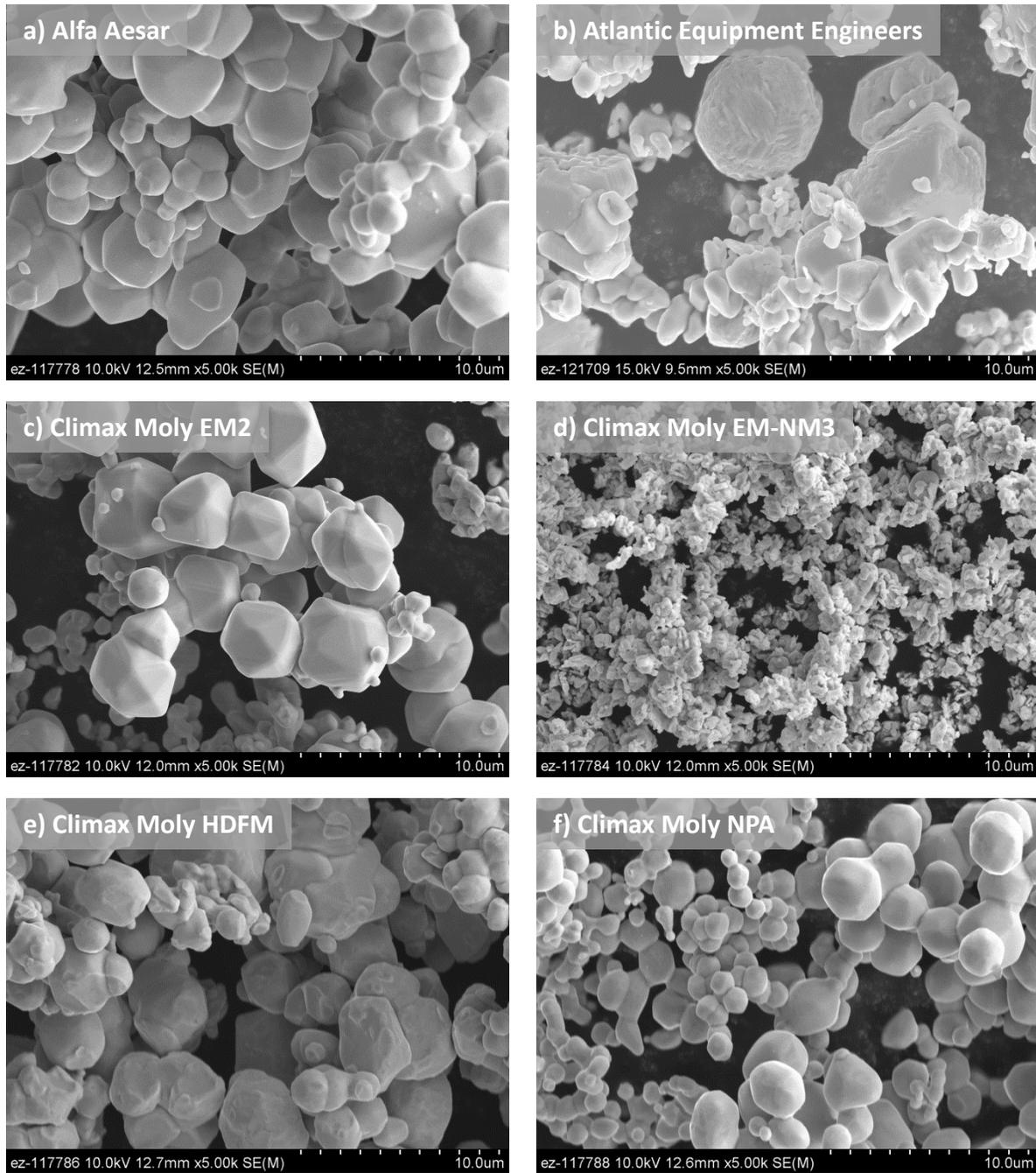


Figure 1. SEM micrographs showing the morphology of the various Mo powders. Primary particles sizes range from submicron to $>5 \mu\text{m}$. Particle agglomerates are clearly evident.

Four of the natural Mo powders that were evaluated reached a density greater than 90% of theoretical when die pressed at 1379 MPa (200 ksi). The as-pressed densities of Mo-100 powders from different lots are shown in Fig. 4. At a given die pressing pressure, the density shows some lot-to-lot variation. It is also seen, that even when pressed at 1724 MPa (250 ksi) the Mo-100 sample did not reach 90% density.

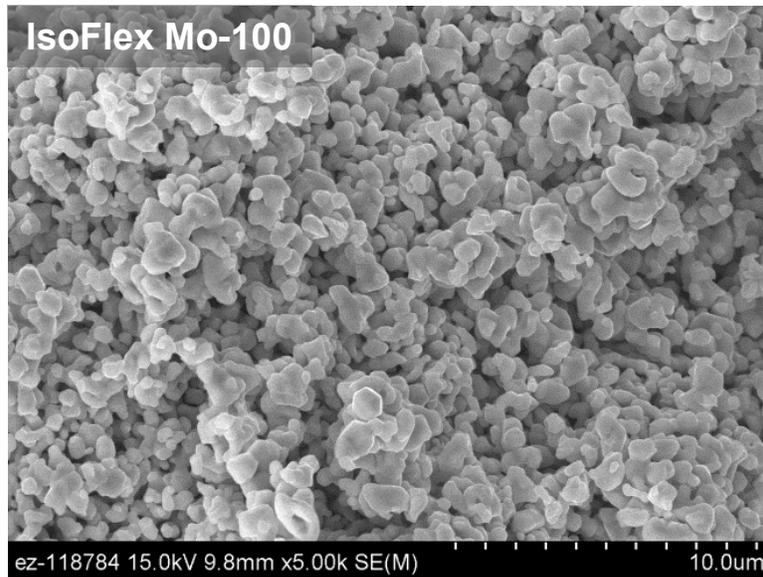


Figure 2. SEM micrograph of a typical Mo-100 powder lot.

Table 2. Measured characteristics of Mo powders.

Molybdenum Supplier	Mo Grade	Laser Median Particle Size, μm	BET Surface Area m^2/g	BET Spherical Equivalent Size, μm	SEM Primary Particle Size, μm
Alfa Aesar	10030	17.8	0.13	3.7	1-5
Atl. Equip. Eng.	MO-103	-	0.36	1.8	0.5-4
Climax Moly	EM2	10.3	0.15	4.0	0.5-4
Climax Moly	EM-NM3	2.1	2.83	0.2	0.1-1
Climax Moly	HDFM	6.6	0.09	6.6	1-7
Climax Moly	NPA	11.0	0.45	1.5	0.5-4
IsoFlex USA	Mo-100	-	0.80-1.17	0.5-0.7	0.4-1.0

Sintering

The relationship between the as-pressed and sintered density for 3 different natural Mo powders is shown in Fig. 5. The disks were die pressed at pressures up to 690 MPa (100 ksi) and then sintered at 1600°C for 1 hr. Both the as-pressed density and the sintered density are plotted in the graph. It is not surprising to see an increase in sintered density for individual powders as the as-pressed density increases. What is more interesting is to see the degree to which the powders vary in terms of sintering kinetics. Remarkably, the Climax Molybdenum Grade EM-NM3 powder sintered to 92.6% of theoretical density even though the as-pressed density was only 35%. In contrast, the Alfa Aesar Grade 10030 powder showed an increase of only 6.4 to 9.5 percentage points between the as-pressed and sintered densities.

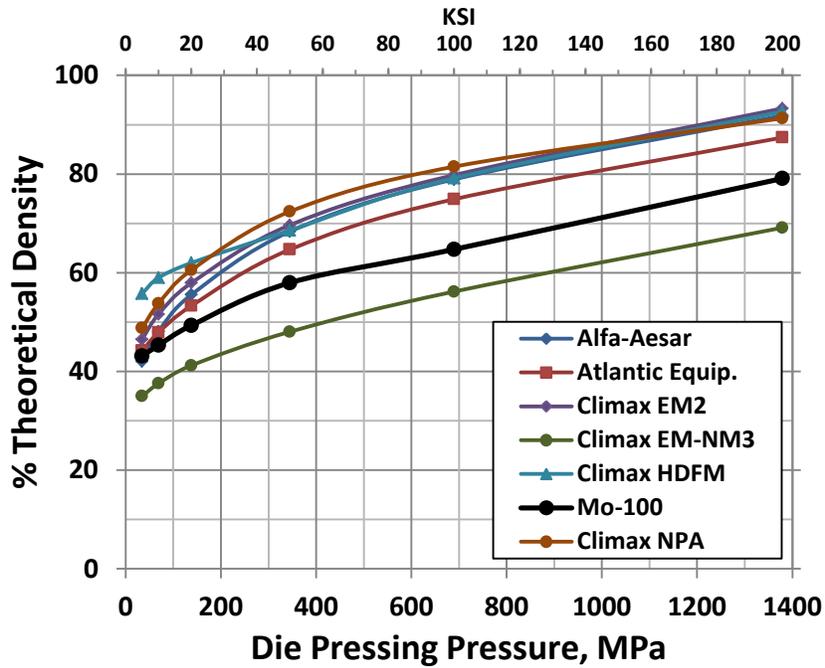


Figure 3. Relationship between the die pressing pressure and the as-pressed density of disks made from various types of Mo powder.

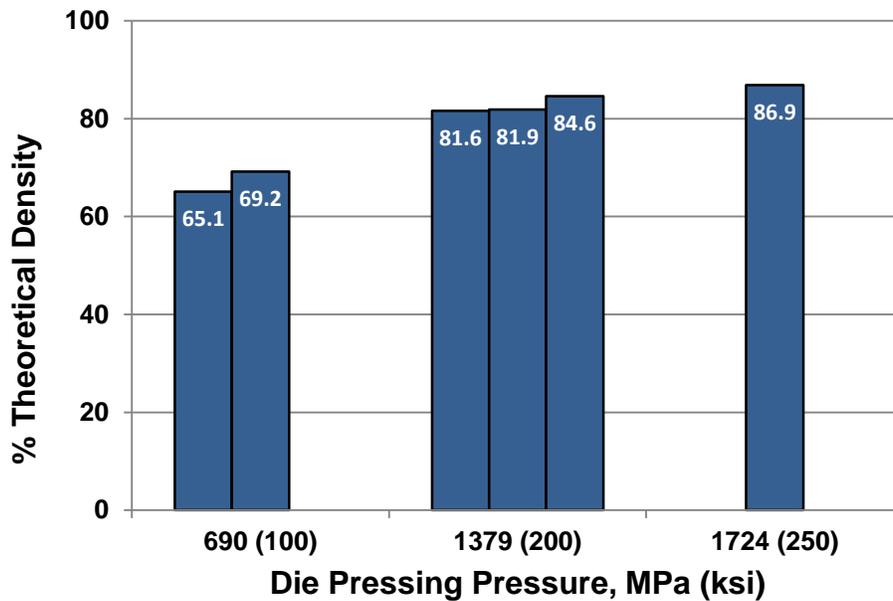


Figure 4. As-pressed density of disks made from various lots of Mo-100 powder. The data show some variability between the different lots of material.

The observed differences in the sintering kinetics that are shown in Fig. 5 can be attributed to the differences in powder particle size and surface area. These same characteristics also have an effect on the response of the powders to changes in the sintering temperature. This is illustrated

by the data shown in Fig. 6, where the percent theoretical density is plotted versus sintering temperature for disk samples that were die pressed at 690 MPa (100 ksi). The slope of the sintered density curves shows the degree to which the pressed powders respond to a change in sintering temperature. Once again, the response scales with particle size and surface area.

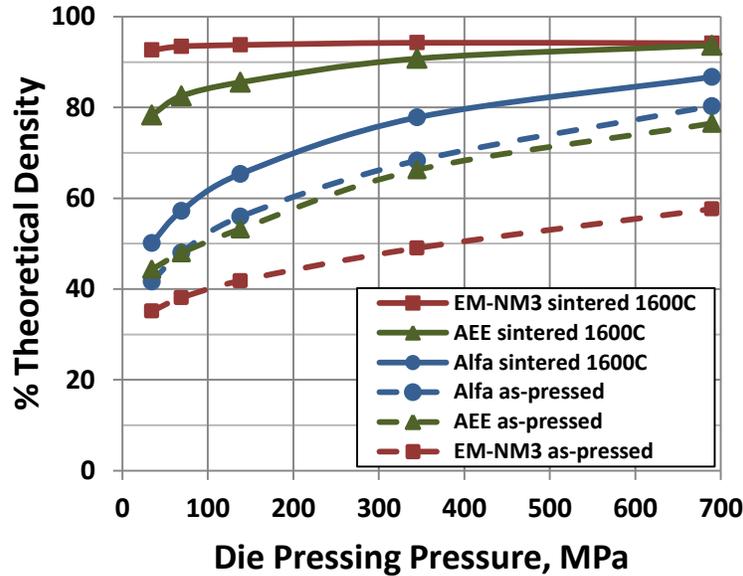


Figure 5. As-pressed and sintered densities of Mo disks die pressed at different pressures and subsequently sintered at 1600°C for 1 hr. The powders show significantly different sintering kinetics.

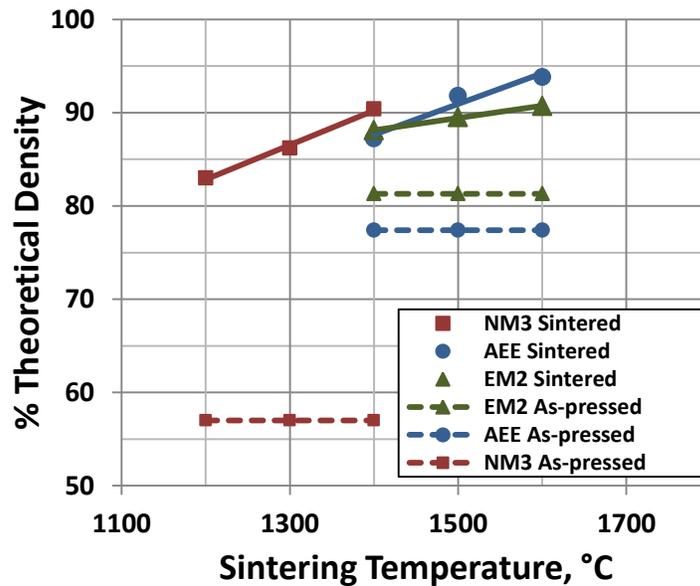


Figure 6. As-pressed and sintered densities of Mo disks die pressed at 690 MPa (100 ksi) and subsequently sintered at various temperatures. The powders show significantly different sintering kinetics and response to temperature change.

The results of sintering pressed disks made from Mo-100 powders is shown in Fig. 7. Due to the very high cost of Mo-100 isotope powder, a full range of tests could not be conducted. Disk samples which were die pressed as shown in Fig. 4, were sintered at various temperatures to evaluate how well the powders would sinter. As shown in Fig. 7, 90% density was reached using a sintering temperature as low as 1000°C. Sintering at 1600°C and 1650°C resulted in densities that were higher than desired. From these results, it is apparent that the Mo-100 powders that were tested are more difficult to die press to high density than most of the natural Mo powders, but they show very good sintering kinetics, similar to what was seen for the Climax Molybdenum Grade EM-NM3 powder.

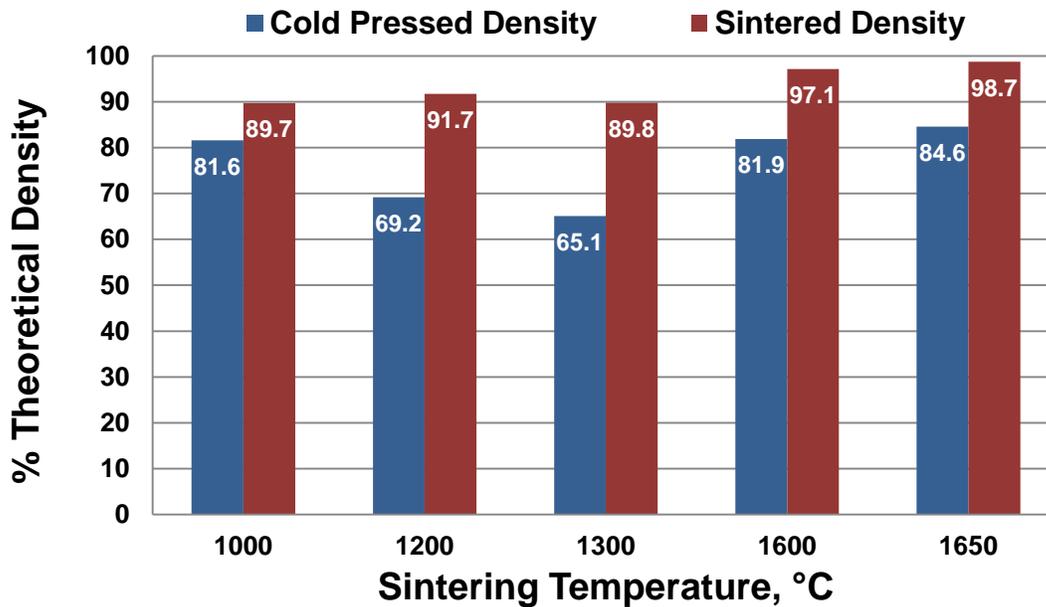


Figure 7. As-pressed and sintered densities of Mo-100 disks that were sintered at various temperatures. All of the disks sintered to $\geq 90\%$ density.

Table 3 shows a compilation of test results that summarizes the processing conditions that are needed to achieve a density that is 90% of theoretical for all of the Mo powders that were evaluated. For most of the natural Mo powders, this could be done by die pressing at 1379 MPa (200 ksi); no sintering was required. For Mo-100 powder, a very low sintering temperature can be used to reach 90% density.

Conclusions

1. Mo powders of different types show variations in powder characteristics, such as: particle size, particle shape, surface area, and degree of agglomeration. This was found to be true for Mo powders having a natural isotope ratio and for Mo-100 isotope powders.
2. These powder characteristics have an effect on both the as-pressed and sintered density of compacted disks. They can also be linked to sintering kinetics, where fine particle size and high surface area promote rapid sintering and increased response to changes in the sintering temperature.

3. Many of the natural Mo powders were cold pressed directly to 90% density or greater without any need for sintering.

4. All of the Mo powders that were investigated, including 5 different lots of Mo-100 powder, could be sintered to 90% density or greater at temperatures ranging from 1000°C to 1600°C.

Table 3. Summary of minimum conditions required to reach 90% density.

Molybdenum Supplier	Mo Grade	Pressing Pressure, MPa (ksi)	Sintering Temperature, °C	Theoretical Density, %
Alfa Aesar	10030	1379 (200)	-	90.0
		690 (100)	1600	88.8
Atl. Equip. Eng.	MO-103	1379 (200)	-	88.3
		690 (100)	1500	91.3
Climax Moly	EM2	1379 (200)	-	91.4
		690 (100)	1600	90.7
Climax Moly	EM-NM3	1379 (200)	-	67.4
		1379 (200)	1200	90.0
		690 (100)	1400	90.4
Climax Moly	HDFM	1379 (200)	-	90.7
		690 (100)	1600	91.6
Climax Moly	NPA	1379 (200)	-	91.7
		690 (100)	1600	89.9
IsoFlex USA	Mo-100	1379 (200)	-	84.6
		1379 (200)	1000	89.7
		690 (100)	1300	89.8

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