Modeling of fine molybdenum powder for press-and-sinter processing

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Abstract

Fine molybdenum powder processing offers the opportunity to produce fine-grained microstructures that are expected to have superior material properties. However, to maintain the advantages of the fine particle powder, the powder processing route must be carefully designed. A model that links press-and-sinter process route to final material properties is established for fine molybdenum powder. This model is characterized through existing data and experimentation. Key processing windows are identified for press-and-sinter opportunities by using the model. The final property predictions are verified through experiments.

1. Introduction

Nanograined materials are predicted to deliver improved mechanical properties such as strength and hardness. However, processing of nanograined materials is a challenging task. When using nanoscale powders to produce parts through powder processing routes, generally the sintering process results in significant grain growth during which the desired nanograined microstructure is lost.

The first task directed at producing nanograined materials is identifying the ideal process windows. This is accomplished by developing process models for the press-and-sinter manufacturing route. These models can then be used to design optimal processes. German has developed such models for tungsten [1], finding that fine microstructures can be attained through non-conventional press-and-sinter processing at very high compaction pressures (>2GPa) and at lower sintering temperatures for shorter sintering times. In this work, we extend the applicability of these models to molybdenum, training the molybdenum models through reported data and experiments. These models are used to identify ideal processing parameters for fine molybdenum powder (D_{50}=1.2 \mu m by BET surface area).

2. Experimental work

Due to the limited availability of nanoscale molybdenum powder, the smallest available powder was used for the experiments. The powder characteristics of the -325 mesh molybdenum powder (Alldyne) are shown in Table 1. The powder is irregularly shaped and agglomerated as can be seen from the SEM photo of the powder shown in Figure 1.

Table 1 reports the average green density measured out of 20 samples pressed at each compaction pressure. The green density was calculated from the green mass and measured dimensions, and is reported relative to the powder pycnometer density.

![Figure 1. SEM photo of the molybdenum showing agglomeration](image)

Table 1. Powder characteristics

<table>
<thead>
<tr>
<th>particle size</th>
<th>laser diffraction, wet measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET (mean)</td>
<td>D_{10}</td>
</tr>
<tr>
<td>1.2 \mu m</td>
<td>2.4 \mu m</td>
</tr>
</tbody>
</table>

Table 2 reports the average green density measured out of 20 samples pressed at each compaction pressure. The green density was calculated from the green mass and measured dimensions, and is reported relative to the powder pycnometer density.
Table 2. Green density at compaction pressure

<table>
<thead>
<tr>
<th>compaction pressure</th>
<th>green density</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPa</td>
<td>relative std. dev.</td>
</tr>
<tr>
<td>280</td>
<td>20 62.7% 1.4%</td>
</tr>
<tr>
<td>560</td>
<td>40 72.8% 0.9%</td>
</tr>
<tr>
<td>840</td>
<td>60 78.5% 1.1%</td>
</tr>
<tr>
<td>1120</td>
<td>80 85.0% 0.8%</td>
</tr>
<tr>
<td>1400</td>
<td>100 87.8% 0.6%</td>
</tr>
<tr>
<td>1960</td>
<td>140 91.0% 0.4%</td>
</tr>
</tbody>
</table>

The green samples were sintered in flowing hydrogen (0.5 l/s flow rate, -40°C dewpoint) at either 1000°C for 1h, or 1200 or 1400°C for 1 or 4h, ramping to the peak temperature at 5°C/min. The sintered density was measured using the Archimedes water immersion method and is reported relative to the theoretical density for molybdenum, 10.2 g/cm³. The measured density results of the compaction and sintering experiments are shown in Figure 2.

Figure 2. Density results of compaction and sintering experiments

3. Process Modeling

Reported data for molybdenum [4-11] as well as the experimental data presented is used to characterize models linking powder properties, such as particle size and apparent density, and process parameters, such as compaction pressure, sintering time and temperature, to final properties, such as sinter density.

3.1. Apparent density model

German [1] suggested a power-law relationship between apparent density, \( \rho_A \), and particle size, \( D \) for tungsten,

\[
\rho_A = \rho_0 D^n \tag{1}
\]

In Equation 1, \( \rho_0 \) is a model parameter relating to the apparent density at 1μm and \( n \) is the exponent. Apparent density is reported relative to the theoretical density for molybdenum. The particle size used to fit the data is calculated from the BET surface area measurement as an equivalent spherical diameter. Fitting available data for molybdenum to Equation 1 results in \( \rho_0 = 0.1654 \) and \( n = 0.4461 \), with the coefficient of determination \( R^2 = 0.6456 \). The poor fit of the data, seen in Figure 3, can be attributed to the wide scatter in reported data.

![Figure 3. Apparent density data and model](image)

3.2. Compaction model

Compaction models are based on the assumption that as a powder is compacted, it approaches full density, and that as it approaches full density, it requires increasing levels of pressure to increase its density [2]. In other words, the rate of change of green density, \( \rho_G \) with respect to compaction pressure, \( P \) is directly proportional to the remaining porosity,

\[
d\rho_G \over dP = k(1 - \rho_G) \tag{2}
\]

Integrating Equation 2 shows that green density has an inverse exponential relationship with compaction pressure.

German [1] suggested the following model,

\[
\rho_G - \rho_A = 1 - \rho_A \exp \left( - \frac{B}{C} P \right) \tag{3}
\]

where the model parameter \( B \) is related to the particle size and \( C \) is related to the material strength.

Ge [3] suggests the following relationship

\[
\rho_G = 1 - (1 - \rho_A) \exp \left( -E \cdot P^n \right) \tag{4}
\]

based on a slightly more complex form of Equation 1 which includes an inverse power-law relationship for the compaction pressure and an additional power-law relationship for the green density.

Panelli and Filho [3] noted that wide scatter and uncertainty is reported apparent density values can make determination of the model constants challenging. For this reason, only the experimental data presented here is used to characterize these models. Regression analysis using the experimental data for molybdenum is performed on German and Ge’s models, resulting in the following model parameters: \( B = 0.8554; C = 5000\text{MPa} \) for German’s model with a mean error of 0.032 relative density, and \( E = 0.5629; F = -1.5024 \) for Ge’s model with a mean error of 0.006 relative density. Both the data from literature along with the experimental data is plotted in Figure 4, showing that Ge’s model in particular shows good correlation to reported and measured data.

In German’s work on nanoscale tungsten [1], the parameter \( B \) in Equation 3 is dependent on particle size. However, the best fit to the combined experimental data and data from literature for molybdenum was found with \( B \) taken as a constant. The same was found for the parameter \( E \) in Equation 4 when performing regression analysis on the available data.
Figure 4. Correlation between green density data and compaction models

3.3. Sinter model

The initial stage sintering equation,

\[ Y_P = B_s t^w \exp\left(\frac{Q}{T}\right) \]  

(5)

is frequently used to estimate sintering shrinkage, \( Y_P \) as a function of time, \( t \), temperature, \( T \), particle size, \( D \), and activation energy, \( Q \). \( B_s \) is a material dependent model constant. Initial stage sintering is roughly bounded by a neck size ratio of 0.3 at which point very little sintering shrinkage has occurred, therefore applying this equation throughout the entire sintering regime results in over prediction of sintering shrinkage in the intermediate and final stages of sintering. However, German found that applying a sigmoid function correction to the initial stage sintering model results in accurate prediction of sintered density. This is exercised through the following equation

\[ \frac{\Delta L}{L_G} = f_1 + \frac{f_2}{1 + \exp\left(\frac{f_3 - Y_P}{f_4}\right)} \]  

(6)

where \( L_G \) is the green dimension, \( \Delta L \) is the change in dimension during sintering and constants \( f_i \) define the shape of the sigmoid curve fit. The sintered density, \( \rho_s \) can be determined from Equation 6 by a conservation of mass calculation under the assumption of isotropic shrinkage,

\[ \rho_s = \frac{\rho_G\left(1 - \frac{\Delta L}{L_G}\right)^3}{\left(1 - \frac{\Delta L}{L_G}\right)^3} \]  

(7)

The available reported and experimental sinter was fit to the sinter model using the following model parameters: \( B_s = 0.71; w = 0.13; v = 0.85; Q = 8477K; f_1 = 0.034; f_2 = 0.220; f_3 = 0.110; f_4 = 0.035 \). The model is evaluated by comparing the predicted and measured values for sintered density. If the model is accurate, the data should show a linear fit with a unity gradient, as shown in Figure 5. Unlike for the compaction model, both the reported data from literature and data from the experiments conducted in this study were used to characterize the model. The reason for this is because the experimental data did not yield a wide enough range of sinter density for full characterization of the model.

4. Discussion

The models for apparent density, green density as a function of compaction pressure, and sintered density presented have reasonable correlation to data from experiments and literature. This work therefore provides simple models through which the press-and-sinter process for molybdenum can be designed. Similarly to the research conducted on tungsten [1], it was found that a press-and-sinter process involving a high compaction pressure, and low sintering time and temperature hold the most promise for delivering good sintered density. Further research to evaluate grain size and mechanical properties is expected to show that the high sinter density relates back to good mechanical properties. Macrohardness tests on the sintered samples was performed, but it was found that due to the ductility of molybdenum, almost all the samples were at the HRB limit of 100 despite variations in sinter density.

One of the limitation of the sinter model presented here, is that the predicted sintering shrinkage is independent of the green density of the porous body. As can be seen from Figure 2, for a given sinter cycle combination of time and temperature, a range of sinter densities is found based on the initial green density of the powder compact. Further work to develop this model in this regard is planned.

5. Conclusions

Simple press-and-sinter process models, that can be used to design manufacturing routes, have been developed for fine grained molybdenum powder in the range of 1 – 8μm. It has been shown that higher sintered density can be achieved through use of high compaction pressures at lower temperatures and for shorter times than conventional processing that involves low (<500MPa) compaction pressures combined with long sintering times (+4h) at high temperatures (1400°C).

References


