Compacting of Powder of Molybdenum By Pressure Higher Than 2.0 GPa

Guerold S. Bobrovnitchii, Alan Monteiro Ramalho, Marcello Filgueira

State University of North Fluminense. Advanced Materials Laboratory.
Av. Alberto Lamego, 2000. 28015-620 Campos dos Goytacazes/RJ – Brazil

ABSTRACT. Compacting of powder of molybdenum was made in an anvil type device of superhigh pressure. The pressure of processing was within the limits of 2.0 – 6.0 GPa. Maximum density (99%) was achieved at 3.6 GPa. The heating to the temperature of 800°C has not changed this parameter. Durability of coupling of separate grain in a sample was estimated qualitatively by micro-hardness measurements. The maximum value of micro-hardness reached 4.000 MPa. The qualitative tendency of the micro-hardness curve is explained in terms of the physical enlargement of the X-Ray lines, received by the Debay-Sherer method.

Keywords: compacting, superhigh pressure, properties.

1. INTRODUCTION

Molybdenum (Mo) is a refractory metal of the VIB group, its melting point is 2626°C, which processing is mainly conducted through powder metallurgy. It is a metal widely used in the superconductivity field, in thermocouples protection, electrodes, crucibles, catalysts, aerospace industry, carbide synthesis, biomedical implants, micro-alloyed steels, and other special application.

The actual technology of the powder compacts processing (previous compacting – sintering – final conformation) allows obtaining Mo parts with density near the theoretical ones (10.22g/cm³) [1]. The disadvantages of this technique are the multistage processing and the duration (mainly in the high temperature conventional sintering of about 2000°C), grain growth during sintering that leads to mechanical strength reduction if the initial powder purity is not high, mainly in the point of view of oxygen content [2,3]. Beside this, in previous work it was noted that the yield strength limit diminishes as the grains grow [4].

The present work is proposed the use of high pressures (up to 2.0 GPa), with or without simultaneous heating of the treated material (Mo) as a perspective to obtain fine grained parts from the starting powder materials of hard dealing.

2. EXPERIMENTAL

Mo powder compaction by high pressure was carried out via use of an anvil type superhigh pressure device with spherical and toroidal concavity [5]. The device sketch is shown in figure 1. This device is composed of two anvils (1 and 2), supported by the multi-rings (3), and a calcite made gasket (4). Into the gasket cavity is put the pre-compacted Mo powder (5) and the discs (6) that acts as a thermal insulator and electrical conductor, simultaneously. The compaction was carried out in a press of 630 tons of force, model DO138B by Ryazantyashpressmash (Russia), in which is possible to generate pressure within the gasket in the order of 8.0 GPa, forming the compressive gasket (7). This device allows to compact the powder cylinders until diameters of 8.0 mm in diameter and 6.0 mm of height.
The Mo powder used in this work shows mean particle size of about 2.0 µm, that was pre-compact in a steel matrix to get the green powder cylinders. The mean green density obtained was of 8.0 g/cm³. The chamber assembly with cylinders and discs was carried out in other matrix. The high pressure was generated during the approximation of the anvils inside the press, promoting gasket’s deformations. Under 2.0 GPa of pressure into the compression chamber, the gasket extruded material closes the compression chamber. The posterior pressure increase occurs without the gasket plastic flux, already deformed. The pressure produced into the compression chamber was measured by using the well known methods which features the application of bismuth (Bi), thalium (Tl), and barium (Ba) based pressure sensors [6].

The Mo samples were heated by direct current flux passing through the anvils and discs, during the compaction into the high pressure device. The temperature was measured with Chromel-Alumel - K-type thermocouples (during the calibration) and by means of the current value (during the experiments). The compacting parameters are the following:

- Increasing pressure time until the desired value was of 10 to 20 seconds;
- Time of maintenance of pressure was of 40 seconds;
- Time of pressure reduction varied from 30 to 180 seconds;
- The temperature applied to heat the samples did not overcome 800°C. It was also accomplished the heating during the pressure increasing.

3. RESULTS AND DISCUSSION

The compaction results of the Mo samples are shown in the table 1. The relationship among the Mo density and pressure and compacting temperature are shown in figure 2. Under the pressure of 3.6 GPa, the Mo samples reached almost 99% of its theoretical density. During the posterior pressure (higher than 3.6 GPa) increase it could be observed the change of the density dependence in relation to the compacting pressure. The appearance of two very different compacting behaviour can be explained only by the different compression mechanisms. In the first part of the graph (fig.2) the density increase is related to the porosity closure, accompanied by the plastic deformation of the Mo particles. In the second part, saturation of plastic deformation of the Mo particles occurs, leading to the grain and particles fragmentation, which promotes the appearing of micro-cracks at the cylinder extremities. This effect is linked to the changes of compression conditions: axial tensions increase much more than the radii ones. The application of the heating temperature causes the partial density decrease, and peak displacement of the curve to 3.6 GPa. The analysis of the graph curves shows that the pressure of about 3.6 GPa may be considered as the optimum pressure for the compaction of Mo powder by high pressures, under the above mentioned conditions.
The cohesion strength of isolated grains of the sample was qualitatively evaluated through micro-hardness measurements. This relation is shown in figure 3. The micro-hardness increase up to 1900 MPa (as cast Mo) indicates the material strengthening in the plastic deformation process of the separated particles during the high pressure treatment (reaching at 2800 MPa for a pressure of 6.1 GPa).

The micro-hardness study at the longitudinal section of the samples revealed a relatively heterogeneous distribution of the results. This may be related to the pressure and temperature gradients into the compression chamber of the high pressure device [7]. To eliminate this effect, it is necessary to change the compressible medium of the gasket central part.

Table 1- Relation among the pressure and temperature imposed to the molybdenum cylinder powder and its density.

<table>
<thead>
<tr>
<th>Pressure, GPa</th>
<th>Temperature, °C</th>
<th>Density, g/cm³</th>
<th>Average density, g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2</td>
<td>20</td>
<td>9.32; 9.36; 9.38</td>
<td>9.35</td>
</tr>
<tr>
<td>2.2</td>
<td>400</td>
<td>9.45; 9.49; 9.43</td>
<td>9.46</td>
</tr>
<tr>
<td>2.2</td>
<td>800</td>
<td>9.86; 9.83; 9.84</td>
<td>9.84</td>
</tr>
<tr>
<td>3.6</td>
<td>20</td>
<td>10.12; 10.34; 10.13</td>
<td>10.13</td>
</tr>
<tr>
<td>3.6</td>
<td>400</td>
<td>10.11; 10.09; 10.12</td>
<td>10.11</td>
</tr>
<tr>
<td>3.6</td>
<td>800</td>
<td>10.06; 10.07; 10.03</td>
<td>10.05</td>
</tr>
<tr>
<td>4.8</td>
<td>20</td>
<td>9.95; 9.92; 9.91</td>
<td>9.94</td>
</tr>
<tr>
<td>4.8</td>
<td>400</td>
<td>9.98; 9.99; 10.01</td>
<td>9.99</td>
</tr>
<tr>
<td>4.8</td>
<td>800</td>
<td>10.02; 10.00; 10.04</td>
<td>10.02</td>
</tr>
<tr>
<td>6.1</td>
<td>400</td>
<td>9.91; 9.88; 9.93</td>
<td>9.91</td>
</tr>
<tr>
<td>6.1</td>
<td>800</td>
<td>9.96; 9.94; 9.98</td>
<td>9.96</td>
</tr>
</tbody>
</table>

The internal tensions intensity (or the dislocation density) caused by the heterogeneity of the hardness along the section, was determined by the lines enlargement in the X-ray diffraction obtained by the Debay-Sherer method [8].

In conformity with the reference [9], the dislocation density is given by the relation shown below:

\[
\alpha = A \beta^2
\]

Where:

\(A\) – coefficient dependent on the elastic characteristics of the material, dislocation characteristics. For Mo, \(A = 2.10^{16} \text{ cm}^2\);

\(\beta\) - measured line enlargement (physical).

The \(\beta\) dependence on the compacting pressure was also considered and plotted in the graph of the figure 3. One can observe the qualitative coincidence of this curve with the microhardness ones. The substitution of \(\beta\) measured values in the equation 1 gives the result of dislocation density of \(\alpha = 10^{13} \text{ cm}^2\). These so high \(\alpha\) magnitudes are linked to the \(\beta\) increase in the result of the micro-tensions influence, and also due to the size effect of current dispersion blocks (of the Mo grains). It was established the current dispersion is responsible to about 65% of the physical line enlargement observed, considering that the blocks sizes in the (321) plane is almost 660 \(\text{Å}\), and the square mean deformation of the lattice in the same plane is \(\varepsilon = 7.10^{-4}\), which corresponds to the degree of deformation of the 65 to 75% range.

During the compaction with heating to 800°C, the Mo samples showed hardness in the range of 3000 to 4000 MPa. This may be explained by the fact that in this compaction stage with use of the thermobaric treatment operations consequences (increase of pressure simultaneously with
increase of temperature, parameters maintenance, temperature reduction to 20°C, and pressure reduction), occurs the material plasticity limit reduction accompanied by the compactability improvement simultaneous with the deformation degree increase and, consequently, with an increase of the Mo particles consolidation degree (strength).

![Graph showing the dependence of Mo cylinder powder density on pressure and temperature.](image)

**Figure 2-** Dependence of the Mo cylinder powder density on the pressure and temperature of the thermobaric treatment.

The strength attained by this deformation is preserved under heating until the recrystallization temperature (1200°C), what is related to the high dislocation density influence on the diffusion processes locking during the recrystallization. The posterior treatment of the Mo samples obtained by high pressures under vacuum ($10^{-5}$ mmHg) and temperature of 1400°C for 20 minutes caused a rapid micro-hardness reduction, and the appearing of the high plastic Mo properties. For example, the compacted samples under pressure of 3.6 GPa and temperature of 20°C after the vacuum heat treatment under the above mentioned conditions deformed very easily during a single cycle of deformation (deformation degree of 2.2) without further crack appearing, because under these conditions the Mo samples are completely recrystallized, with an elevated degree of dislocations annihilation, resulting in a high ductility, which is a characteristic of the Mo (body centered cubic lattice metal).
Figure 3- Dependence among micro-hardness and line semi-enlargement in the (321) plane, and pressure and temperature of the thermobaric treatment. The dashed line indicates the as cast Mo micro-hardness.

4. CONCLUSIONS

This work has shown that it is possible to obtain high density Mo with fine structure through the hot and cold treatment under pressures in the 2.0 to 6.0 GPa range, being an alternative to the Mo parts processing. It is also shown the following aspects of the experiments:
1. It was determined the optimum compaction pressure under the conducted conditions of 3.5 GPa;
2. The treatment temperature during the compressions did not influenced considerably in the Mo compacts density, because the used temperatures (20 to 800°C) are still low to cause further change into the Mo structure;
3. The Mo compact strength obtained was in the range of 1.6 to 2.0 times higher than the as cast Mo ones;
4. The vacuum assisted thermal treatment of the Mo compacted samples allowed the attainment of a ductile material (plastic), by using a shorter time of treatment than that usually used in the conventional Mo sintering.

REFERENCES