Title: Synthesis and Fabrication of Mo-W Components for Neutron Resonance Spectroscopy Temperature Measurement

Author(s): Sherri R. Bingert, MST-6
Paul Desch, NALCO Chemical Co.
Eralio J. Trujillo, MST-6

Submitted to: Proceedings of the 1999 International Conference on Powder Metallurgy & Particulate Materials
June 20-24, 1999
Vancouver, British Columbia, Canada
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
SYNTHESIS AND FABRICATION OF Mo-W COMPONENTS FOR NEUTRON RESONANCE SPECTROSCOPY TEMPERATURE MEASUREMENT

Sherri R. Bingert¹, Paul B. Desch², and Eralio Trujillo¹

¹Materials Science and Technology Division
Los Alamos National Laboratory
Los Alamos, NM 87545

²Nalco Chemical Company

ABSTRACT

A Molybdenum – $^{182}$Tungsten (Mo-$^{182}$W) alloy was specified for an application that would ultimately result in the measurement of temperature and particle velocity during the steady state time following the shock loading of various materials. The $^{182}$W isotope provides a tag for the analysis of neutron resonance line shape from which the temperature may be calculated. The material was specified to have 1.8 atom percent W, with W-rich regions no larger than 1 μm in size. Both the composition and W distribution were critical to the experiment. Another challenge to the processing was the very small quantity of $^{182}$W material available for the synthesis of the alloy. Therefore, limited fabrication routes were available for evaluation. Several synthesis and processing routes were explored to fabricate the required alloy components. First, precipitation of W onto Mo powder using ammonium metatungstate was investigated for powder synthesis followed by uniaxial hot pressing. Second, mechanical alloying (MA) followed by hot isostatic pressing (HIP) and warm forging was attempted. Finally, arc-melting techniques followed by either hot rolling or crushing the alloyed button into powder and consolidation were pursued. The results of the processing routes and characterization of the materials produced will be discussed.

INTRODUCTION

Measurement of the internal temperature in a system subjected to dynamic loading is of great interest in many areas of physics and chemistry and particularly in shock-wave physics. Previously, temperature measurements under these conditions have relied on optical techniques and internal probes; both of which have various inherent limitations. Neutrons are probes that can readily penetrate a sample to detect the temperature in its interior, and in dynamic loading experiments, ejecta products that may shield a sample optically are often transparent to neutrons. When neutrons from a pulsed white source pass through a sample, the time-of-flight (TOF) spectrum of the transmitted beam exhibits a series of dips caused by resonances in the cross section that are characteristic of the material’s nuclear properties. The resonance locations and lineshapes that appear in the TOF spectrum are unique to each isotope, and temperature determinations can be localized by properly positioning
the appropriate isotope in the sample. Neutron Resonance Spectroscopy (NRS) provides a nearly ideal means for probing the internal temperature of a material subjected to dynamic loading [1]. Figure 1 shows a schematic of the experimental set-up for the NRS experiments performed at the Los Alamos Neutron Scattering Center (LANSCE).

![Figure 1. Schematic of the set-up for the NRS experiments performed at LANSCE [1].](image)

The actual experiment and target were assembled within the containment vessel, and are shown schematically in Figure 2.

![Figure 2. Schematic of the multi-point initiator and launcher-target assembly [1].](image)
The $^{182}$W isotope addition to Mo was chosen in order to decrease the neutron cross section and result in a sharper TOF spectrum with an improved neutron flux over that of pure Mo. In the dynamic experiment, the Al flyer plate was accelerated and impacted the Mo target assembly to impart a planar shock to the target. This was accomplished through the use of a multiple point detonation system to initiate the propagation of a planar wave front through the explosive resulting in the acceleration of the Al flyer plate, see figure 2.

Figure 3a shows simulations of the time of flight (TOF) spectra for $^{182}$W under static and dynamic conditions while 3b shows the actual TOF spectra for the shocked Mo experiment illustrating both static and dynamic data. The position of the dip is determined by the bulk or particle velocity while the dip width is dependent on the internal temperature.

The challenges in this research were in fabricating the Indicator. Initially, the composition was specified to be Mo-1.0 atom % $^{182}$W. This composition was used for the first processing route investigated. The composition requirement was changed after some preliminary experiments with the first components to be Mo-1.8 atom % $^{182}$W (3.4 weight %W). This composition was used for the second and third processing routes investigated. The requirements for the indicator included fabrication of 6 to 10 discs that were 1 mm thick and 40+ mm in diameter. These discs were to be full density and chemically homogeneous. Tungsten-rich phases/regions were to be no larger than one micron. Several issues were immediately posed in addition to the technical requirements including a short delivery schedule and a very small quantity, 10 grams, of W isotope. Initially, the W isotope was only available in oxide, powder form. However, a second batch was eventually available in metal powder form. The small quantities of the tungsten isotope disallowed any consideration of processes that would involve thermomechanical processing of a larger batch size, therefore the alternative processing techniques described below were investigated.

EXPERIMENTAL

Three process routes were investigated to address the requirements and limitations set forth for the application. In the first, W was coated onto the surfaces of the Mo particles by precipitating ammonium metatungstate onto the Mo and reducing the AMT to WO$_3$ and then to W through a heat treatment of the powder. This powder was consolidated via hot pressing (HP) or hot isostatic pressing (HIP), and then rolled or forged. The second method involved mechanical alloying (MA) followed by
HIP'ing and forging. The third process included arc melting to form the alloy followed by hot rolling or crushing the alloyed button into powder, HIP'ing, and forging.

The Mo powder chosen for the work had low metallic impurities and good compaction characteristics compared to other Mo powders. This powder achieved reasonably high green densities when pressed between 10 and 80 ksi and sintered to 89-93% of theoretical density (\(\rho_{\text{th}}\)) at 1700°C in hydrogen and to 94-96% at 2350°C in vacuum. Some of its characteristics are given in Table 1. Normal tungsten powder was used for the development work for this project. The isotopic tungsten powder was not characterized due to the small quantity of the material available for the fabrication of the discs.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Density</td>
<td>2.43 g/cm³</td>
</tr>
<tr>
<td>Tap Density</td>
<td>3.48 g/cm³</td>
</tr>
<tr>
<td>Sedibal Surface Area</td>
<td>0.149 m²/g</td>
</tr>
<tr>
<td>Sedibal Average Particle Size</td>
<td>9.7 ± 4.8 μm</td>
</tr>
</tbody>
</table>

Table 1. Characteristics of the Mo powder used in this study.

Powder Coating, Consolidation, Thermomechanical Processing

For the coating process, ammonium metatungstate (AMT), \((\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}\), was dissolved in water. The solubility of AMT in water is 1.6 grams per centiliter. Excess water was used in order to provide enough solution to more uniformly coat the Mo powder and create a thick paste. The paste was dried under a heat lamp and stirred frequently during the drying process to ensure an even coating of the powder particles and minimize agglomeration. The dried powder was heat treated at 850°C for 2 hours in flowing hydrogen in order to completely decompose the AMT into tungsten oxide + ammonia and then reduce the tungsten oxide, \(\text{WO}_3\), decomposition product to tungsten metal, forming a very thin W film, on the surface of the Mo particles.

Two HP runs and one HIP run were completed to consolidate the coated powders. Hot pressing was performed in graphite dies. The punches and inner diameter of the die were coated using a boron nitride spray to prevent reaction of the graphite with the powder, and also to aid in reducing the friction between the punches and die. The powder was pre-compressed in the die to 1600 psi. The pressings were accomplished by heating to 2000°C and applying the load to achieve a pressure of 3000 psi pressure in a flowing Ar atmosphere. For the first set of pressings (HP1 parameters), a rapid heating rate of approximately 50°C/minute was used. This rate allowed the temperature to reach 2000°C within 2 hours. The second set of hot pressings (HP2) used Mo foil as a reaction barrier in addition to the BN coating and a slow heating rate of 15°C/minute during pressing. This allowed 2000°C to be achieved in about 4 hours. The HIP run (HIP1) was accomplished by pre-pressing the coated Mo powder into a cylinder and sealing the pressing inside a tantalum (Ta) can under vacuum using electron beam welding. The canned assembly was HIP'ed at 1600°C and 30 ksi for 2 hours.

Post-consolidation processing of the HP1 compacts included cold rolling and hot rolling by preheating the sample to approximately 1000°C. One of the pressings from this set of parameters was subsequently HIP'ed at 1600°C and 30 ksi for 2 hours following the hot press run to increase the densification. The HP2 sample was hot forged in a graphite die at 2000°C under Ar atmosphere. The HP2 compact was wrapped with Mo foil prior to forging to help retard excessive carburization of the compact. Some of the AMT coated powder was HIP'ed at 1600°C and 30 ksi for 2 hours. The first HIP of this powder was unsuccessful, the can leaked and the compact did not densify. The sample was recanned and HIP'ed again under the same conditions. This compact was subsequently warm forged in air on open platens at 500°C.
In order to manufacture a pre-alloyed powder for consolidation, mechanical alloying was investigated. Recall that the isotopic tungsten was purchased in the form of oxide powder. Since there was very little powder, it was not characterized and the compound was assumed to be primarily WO$_3$. The powder was reduced to the pure metal form prior to mechanical alloying (MA). To accomplish this, it was heated in flowing hydrogen at a rate of 4.5 cubic feet per hour. The reduction heat treatment included a hold at 625°C for 2 hours followed by a hold at 800°C for 1 hour [2,3]. After reduction the powder was transferred to a dry, inert atmosphere to minimize subsequent re-oxidation.

The mechanical alloying was accomplished in a dry, inert glove box using a high energy SPEX mill. Figure 4 shows a schematic of the MA process[4]. Mo and W will not actually alloy in the solid state under these milling conditions, however they will form a submicron lamellar structure. In order to accomplish this end, a composition of 7.59 g of Mo was milled with 6.05 g of $^{182}$W for 12 hours in a tungsten carbide container using a tungsten carbide ball. The resulting powder was divided into three parts. Each of these parts was then milled with another 20.07 g of Mo powder for 15 minutes. The three batches were screened to a size of less than $75 \mu m$. The $+75 \mu m$ fraction was milled further to reduce the size until it passed through the $75 \mu m$ screen. The milled powders were annealed at 800°C in vacuum for one hour to soften the powder and remove any residual hydrogen in the powder from the reduction step. Additional Mo powder was blended with the alloyed powder by jar rolling to dilute the alloy to the desired composition.

![Figure 4. Schematic of the cold welding/fracturing process that occurs during mechanical alloying.](image)

The MA and blended powder was pre-consolidated by cold isostatically pressing at 50 ksi. The pressing was sealed under vacuum in a Ta can using electron beam welding. The slug was HIP'ed under an Ar pressure medium at 1600°C and 30 ksi for 1.5 hours.

The faces of the Ta can were machined parallel prior to forging, however the sides of the Ta can were left on the pressing to minimize the oxidation of the Mo alloy during preheat in an air furnace. The consolidated part was forged in a single motion at a temperature of about 540°C to a thickness of 1.6 cm. The discs were electrodischarged machined (EDM) out of the forged slug.
Arc Melting followed by Rolling, or Crushing, Hot Isostatic Pressing, and Forging

In preparation for melting, hydrogen reduced powders were blended in the appropriate proportions to achieve the required 1.8 atom % W composition for 4 hours and pressed into 100 gram pellets. The arc melting required some development and included melting under the following conditions:
1. partial vacuum backfilled with Ar to a static pressure of 450 torr,
2. partial vacuum backfilled with He to a static pressure of 450 torr,
3. He-6%H₂ mixed gas flowing at a rate of 0.5 liters/minute, with the chamber being constantly evacuated.

Rolling development was accomplished under the following conditions:
1. preheat button in air to 600°C,
2. preheat button contained in stainless steel foil in flowing Ar to 600°C,
3. preheat buttons in flowing Ar to temperatures ranging from 600-1350°C.

Ultimately, the arc cast buttons were hand crushed using a tungsten carbide lined mortar and pestle and screened through a 40 mesh screen (-425 μm). All of the -40 mesh powder was pressed in a steel die at 90 ksi to preconsolidate it prior to canning in Ta and HIP’ing at 1600°C and 30 ksi for 2 hours.

The HIP’ed compact was machined on the faces to yield flat and parallel surfaces for forging. The compact was preheated to approximately 600°C and open-die forged to a thickness of 1.5 cm and diameter of 5.0 cm. The finished discs were EDM machined to finish dimensions of 1 mm thick by 43 mm diameter.

Characterization

Characterization of intermediate products and the finished discs included: immersion density measurement per ASTM Test Method B31-93 [5], light microscopy to evaluate porosity and microstructure, scanning electron microscopy to evaluate the morphology and chemistry of second phase constituents, and wet chemistry analysis to determine the final composition.

RESULTS AND DISCUSSION

Precipitation/Coating, Consolidation, Thermomechanical Processing

Coating the Mo particles with W was successful using this technique. Initially, the composition was specified to be 1.0 atom % W. The measured pycnometer density was 10.28 g/cm³ and very near the calculated theoretical density of 10.35 g/cm³.

The first hot press runs (HP1) yielded compacts with densities of 93% ρₚ. This lower density may be due to pores remaining in the compact as well as a reduction in density from the formation of lower density reaction products. The BN coating did not prevent the Mo and graphite from reacting, and actually produced a moderately thick, very brittle shell surrounding the compact. The formation of Mo₃B and Mo₃C may be expected above 1300°C based on examination of the ternary Mo-B-C phase diagram. There was a great deal of reaction within the compact as well. The HP2 run resulted in increased densification prior to reaction. This compact demonstrated a density of 96% ρₚ. Although this run was performed at slower ramp rates it seemed to have less reaction products, probably due to the use of the additional Mo foil barrier. Figure 5 shows a typical HP microstructure with Mo-rich areas surrounded by a Mo-C eutectic structure. Figure 6 shows the verification that the eutectic structure is principally Mo and C with the C x-ray dot map illustrating the areas with high C.
concentrations. There were no other significant impurities detected in the SEM chemical analyses performed on these compacts.

Compacts which were pressed following the HP1 parameters were subsequently cold rolled, hot rolled and HIP'ed. The cold rolled sample failed catastrophically by cracking, and was not characterized further. The sample that was hot rolled at 1000°C failed by edge cracking. However, the bulk of the sample resulted in a product of 98.7% ρₙ. The sample that was canned and HIP'ed had a density of 98.1% ρₙ after processing. This sample was not processed any further.

Figure 5. Typical an as-pressed microstructure resulting from the hot pressing of AMT coated Mo powders in graphite dies. SEM backscattered image.

Figure 6. Shows a) a higher magnification view of the Mo-C eutectic region and b) a carbon x-ray dot map illustrating the locations high in C composition.

Compacts that were pressed following the HP2 parameters were subsequently hot forged in a flowing Ar atmosphere at 2000°C. The forging was performed inside the hot press inside a graphite die. This forged compact demonstrated significant carburization following both the hot pressing and the forging.
A portion of the AMT/Mo powder was HIP'ed and reached a density of 98.8% \( \rho_{th} \) following the second HIP run. This sample was then preheated to 500°C and open die forged successfully in a single stroke. In this process, the can did not rupture and the compact did not crack.

Although the AMT coating on the Mo powder was deemed successful, the \(^{182}\)W isotope was not available in an AMT compound. Therefore recognizing the time constraints, synthesis of the AMT compound from W powder was not pursued, and this coating technique for the powder preparation was abandoned. However, should this technique be used in the future, it should be noted that the film of tungsten that forms on the AMT treated powder is very thin and the amount of W is small compared to the large surface area of the Mo powder. Because of this, the diffusion that would occur during the high temperature consolidation should homogenize the alloy in a much shorter time than blended or MA powders making this process more efficient and advantageous than other routes.

In general, the hot pressing process was not successful for this material. The formation of reaction compounds was much too pronounced, and could not be avoided. However, some improvements may have been made with modifications to the process. During the pressing sequence, there was no additional ram movement under the maximum pressure for the graphite dies above 1550°C. Therefore, most of the consolidation had already taken place by that time in the process and the higher temperatures used were probably not necessary. Hot pressing at lower temperatures may help to minimize the formation of the reaction compounds while still achieving high densities. Finally, had the \(^{182}\)W been available in the form of AMT, this powder synthesis route would have been acceptable when combined with the HIP and forge processes. Therefore, these processes were applied to the other investigations.

Mechanical Alloying, Hot Isostatic Pressing, and Forging

It was assumed that the as-received powder was principally WO\(_3\). The powder was seen to lose 17.17% of its starting weight during the reduction process. This number is slightly less than the expected weight loss for a pure WO\(_3\) powder. This implies that the powder may have been slightly off stoichiometry in the as-received condition. Regardless, it was determined that the powder was essentially fully reduced to metal prior to mechanical alloying.

The milling process resulted in 0.09 g of agglomeration on the ball and container used for milling, an extremely small weight loss. There was no indication of any abrasion or erosion of the milling ball or container. Scanning electron micrographs taken in backscattered image mode show the fine lamellar structure of the 50Mo-50W powder in Figure 7. These images were taken prior to the second milling step and blending with the pure Mo powder.

Prior to HIP'ing, the milled and blended powders were cold isostatically pressed (CIP'ed). The powder was vibrated into the PVC pressing sack to a density of approximately 38.1% \( \rho_{th} \). In this case, the alloy was specified to be Mo-1.8 atom % \(^{182}\)W with a theoretical density of 10.47 g/cm\(^3\). Following pressing to 50 ksi, the compact demonstrated a density of ~70.5% \( \rho_{th} \). The compact was sealed in a Ta can and HIP'ed. The can cracked during processing resulting in incomplete densification. The density of the compact inside the can was estimated at ~80% \( \rho_{th} \), indicating that some densification occurred prior to the can failure. Since Ta is typically extremely ductile, and this lot of material had been used for prior HIP work, it was suspected that the can cracking was due to hydrogen embrittlement. It was hypothesized that some hydrogen was retained in the powder after the reduction processing, and may have been released at temperatures above 800°C (the temperature of the vacuum anneal for the MA powder). The compact was recanned and HIP'ed again for a shorter time. The can appeared to have contracted considerably during the second run cycle indicating densification of the part. Since the can was not removed prior to forging, and the can shrunk somewhat non-uniformly during HIP'ing, density
determination was not made at this point in the process. Also, preheating the HIP'ed compact with the Ta can still in place appeared to protect the Mo from the severe oxidation that was observed in the other two methods thermomechanical processing steps.

Figure 7. MA powder imaged in SEM backscattered mode to show the bright W-rich phases and the gray Mo-rich phases.

Density was determined for each of the discs using an immersion density technique. The average immersion density was found to be 99.5% \( \rho_b \). However, there was a consistent density variation from disc to disc which was traced back to the locations in the original forged piece from which the discs were machined. It appeared that discs from one end were higher in density than discs from the other end of the original forged part. The only conclusion that could be drawn from this finding was that segregation of the higher density alloyed particles occurred during the vibratory loading of the CIP sack and, despite expected homogenization due to diffusion during the HIP process, this resulted in a density gradient in the work piece prior to machining.

One disc was sacrificed for microstructural characterization and chemical analysis. Light microscopy showed that there were second phase particles uniformly distributed in the Mo matrix as illustrated in Figure 8. These inclusions ranged in size from 1-10 \( \mu \text{m} \). Closer examination via SEM of the polished cross section showed that the second phase inclusions were nominally 15 weight \( \% \) W and no lamellar structure was seen internal to those particles. It appeared that the high stored energy from the milling process and the additional HIP process conditions allowed both the homogenization of the W and Mo in the MA particles, as seen in Figure 9, and also allowed the diffusion of W into the Mo matrix.

Chemical analysis of the finished product indicated that the only significant changes in the chemistry from the starting powders was a final oxygen content of 6100 ppm, nitrogen of 70 ppm, and hydrogen of 11.1 ppm. These levels of oxygen and nitrogen are not uncommon for MA powders, and the hydrogen is probably residual from the hydrogen reduction steps in the process. These levels of impurities did not seem to affect the final application. The W composition in the final product was 1.57 weight \( \% \) which corresponds to 0.84 atom \( \% \) W. It is not understood why the W composition is lower than expected except the possibility that a lower density (therefore lower in W content) sample was taken randomly for the analysis. Also, EDS analysis showed the overall chemistry of the sample to lie in the range of 4.4 weight \( \% \). Finally, the density measurements are consistent with a composition in the range of 1.8 atom \( \% \) W. Therefore, taking into account the uncertainty of each measurement technique the composition may be in the range desired. There were no significant increases in other metallic impurities noted.
Figure 8. Light micrograph of a cross-section of a finished disc following the MA, HIP, and forge approach to fabrication.

Figure 9. Scanning electron micrograph illustrating the morphology of the second phase particles and the lack of any internal structures remaining from the MA portion of the process.

In general, this fabrication route was acceptable for the application, however modifications could be made to improve the end product. For example, more microstructural homogeneity was desired. The presence of the second phase was not optimal. Finally, density gradients through the forged part thickness resulted in varying densities for the individual components. These concerns could be overcome by modifying the milling methods. Those modifications may include:
1. Pre-alloying the entire powder batch by milling (MA) rather than blending and not using a vibratory table for the loading of the pressing sack.
2. MA, heat treat at high temperature to allow interdiffusion of the two elements, and MA again to break up the sintered agglomerate prior to consolidation,
3. MA for longer times to achieve a finer alloyed structure. There are disadvantages to this method in the possibility of increased contamination and processing time.

**Arc Melting, followed by Rolling, or Crushing, Hot Isostatic Pressing, and Forging**

The first melting experiment was performed on powders that were simply blended and pressed into 100 g pellets. The furnace was evacuated and backfilled with Ar prior to melting. This melt spattered significantly and produced considerable quantities of soot probably due to trapped gases and interstitials in the powders. The second batch of powder was hydrogen reduced prior to melting. In this melt the soot and spattering were significantly reduced. However, complete melting of the button was difficult and the resulting button quality was poor. This was likely due to the poor thermal conductivity of Ar. All subsequent melts used hydrogen-reduced powders. The third melt was produced using a He backfill gas. This atmosphere allowed better heat transfer and resulted in a larger melt pool, more complete melting/alloying, and a higher quality cast button. Finally, a mixed gas of He-6%H₂ was used. The hydrogen not only increased the heat transfer, but also aided in the reduction of any residual oxygen during melting. This atmosphere resulted in a large penetration melt pool and a high quality arc cast button. Figure 10 shows the improvement in the microstructure between the melt produced in static He and that produced in the flowing He-6H gas. Note the decrease in inclusions, principally oxides, at the grain boundaries.

![Figure 10. Microstructure of the Mo-W arc cast button after melting in a) static He and b) in flowing He-6H. Light micrograph.](image)

The rolling studies were performed on the melt development buttons. When the button was preheated to 600°C in air it oxidized considerably and failed by edge cracking during the first pass. The button encapsulated in the stainless steel did not oxidize until the second or third pass when the stainless steel foil perforated and the hot button was exposed to air. It also failed due to edge cracking. Several additional rolling experiments were performed by preheating the buttons up to temperatures of 1350°C in a flowing Ar atmosphere to minimize the oxidation. Ultimately, each of the buttons oxidized on exposure to air in the rolling mill and all of the samples failed due to edge cracking. This was not completely unexpected as the formation of Mo oxides occurs above about 500°C, MoO₃ begins to volatilize above 600°C, and actually melts at temperatures above about 815°C [6]. The edge cracking occurred regardless of the amount of reduction taken on the rolling pass. The edge cracking was attributed to a combination of the high tensile stresses that the button experiences at its edges as it
passed through the rolls, and the large columnar grains resulting from the melting operation. In order to minimize these effects, several procedures may be used, but were not applied to this work due to time constraints. Also, recall that there was a limited amount of the $^{182}$W available for the work and all of the thermomechanical process solutions would require some material loss. First, the columnar grains may be broken up by upset forging the cast button in a constrained die. Second, the button may be machined on the edges to change the geometry and minimize the tensile stresses during rolling. Finally, if rolling could be accomplished in a hydrogen atmosphere, the oxidation may be reduced.

Ultimately, a combined melting/powder metallurgy approach was taken to fabricate the second batch of discs. In this case the alloyed arc cast button was crushed by hand in a tungsten carbide lined mortar and pestle to ~40 mesh. That powder was die pressed to a density of 82.9% $\rho_{th}$. After HIP'ing, the density of the part was calculated to be 100% $\rho_{th}$. The part was then warm forged successfully without cracking or oxidation and discs were EDM machined out of the forged piece. The sequence of this process is illustrated in Figure 11.

![Illustration of the successful process route for the production of Mo-1.8 atom % $^{182}$W discs used for neutron resonance spectroscopy.](image)

Density measurements were performed on all of the discs. Immersion density averaged 10.41 g/cm³, or 99.4% $\rho_{th}$ for a Mo-1.8 atom % W alloy. In this case no density variations were noted from disc to disc. One disc was again sacrificed for microstructural examination and chemical analysis. Light microscopy showed a clean, homogeneous microstructure with minimal porosity. This result is shown in Figure 12. SEM illuminated no tungsten rich regions in the sample. EDS analysis in several regions of the sample showed uniform W composition of 3.4-3.7 atom %W. However, the chemical analysis performed on the sample showed 1.74 weight %, or 0.92 atom %W. Again the W content as determined by wet chemistry analysis is consistently lower than that determined or inferred by other measurement techniques.
Figure 12. Light micrograph of Mo-W alloy manufactured via the melt and powder metallurgy approach. In this product there are not W-rich inclusions, and porosity has been minimized as a result of the processing.

CONCLUSIONS

A variety of conclusions may be drawn from this work.

1. Synthesis of W coated Mo Powders using ammonium metatungstate was successful.
2. Uniaxial hot pressing of coated powders in graphite dies resulted in unacceptably high carbon contamination and formation of reaction products. Using a cold press/HIP process for consolidation of coated powders is recommended for the future.
3. Mechanical alloying for powder synthesis and consolidation by powder metallurgy routes was satisfactory. However, second phase Mo-W rich particles and density gradients from disc to disc were not desirable. Milling smaller quantities of powders for longer times to achieve greater homogeneity and blending the alloyed powders together for consolidation is recommended for future processing. The use of a vibratory table for loading the powders is not recommended.
4. Melting to achieve the desired alloy was successful. Melting must be accomplished under a He-H₂ cover gas.
5. Rolling the arc cast buttons was unsuccessful. This may be improved by additional pre-rolling processing.
6. The melting-powder metallurgy process route was successful. The densification may be improved by crushing to a finer particle size prior to HIP’ing. A post-forge anneal is recommended prior to machining.

ACKNOWLEDGMENTS

The assistance of C. Ragan for physics, V.D. Vargas, C. Kise, P. Dunn, F. Garcia, D. Hammon, H. Martinez, S. Atencio, S. Quintana for processing, J. Bremser and C. Haertling for density determination, A.M. Kelly for metallographic preparation, P. Kotula, for electron microscopy, and H. Sheinberg for insightful discussions is gratefully acknowledged. This work was conducted under the auspices of the U.S. Department of Energy under contract W-7405-ENG-36.
REFERENCES


SYNTHESIS AND FABRICATION OF Mo-W COMPONENTS FOR NEUTRON RESONANCE SPECTROSCOPY TEMPERATURE MEASUREMENT

Sherri R. Bingert¹, Eralio J. Trujillo¹, Paul Desch²,
¹ Los Alamos National Laboratory
² Nalco Chemical Company
Acknowledgments

- C. Ragan - Physics
- V. Vargas, C. Kise, P. Dunn, F. Garcia, D. Hammon, H. Martinez, S. Atencio, S. Qunitana - Processing
- A. Kelly - Light Microscopy
- P. Kotula - Electron Microscopy
- J. Bremsner, C. Haertling - Immersion Density
- H. Sheinberg - Insightful Technical Discussions

Work funded by the U.S. Department of Energy

Materials Science and Technology: Metallurgy

Los Alamos
Outline

• Application, Requirements, and Issues
• Fabrication Routes and Results
  – Ammonium Metatungstate coating of Mo Powders, Hot Press, Rolling or Forging
  – Mechanical Alloying, Consolidation, and Forging
  – Melting/Alloying, Rolling or Consolidation, and Forging
  – Conclusions
Application, Requirements, and Issues

• Application

• Requirements
  – Discs: 1 mm thick and 40+ mm diameter
  – 6-10 each
  – Full density
  – Chemically homogeneous

• Issues
  – Short delivery time frame for development and fabrication
  – Very small quantity (due to cost) of $^{182}$W isotope available in metal or oxide powder form, therefore can only produce small quantities of material for fabrication into parts
  – All development performed using natural W
**Ammonium Metatungstate (AMT) Coating of Mo Powders and Hot Pressing**

- **Coating Process Summary**
  - Dissolve AMT $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$ in H$_2$O
  - Blend with Mo powder and dry
  - Heat powder to 800°C in flowing H$_2$ to reduce the coating on the Mo particles to W metal coating

- **Hot Press Conditions**
  - Cold Press to 1600 psi
  - Hot Press in graphite die to 2000°C and 3000 psi in flowing Ar atmosphere
  - Run 1 - coated die with BN and used fast heat ramp rate
  - Run 2 - BN coating + Mo foil as reaction barrier and slow heat ramp rate

Los Alamos

Materials Science and Technology: Metallurgy
Thermomechanical Processing of Hot Pressed AMT Coated Powders

AMT Coated Mo Powder

- HP1
  - Cold Rolling
  - Hot Rolling 1000°C
    - Failure by Cracking
      - Failure Edge Cracking 98.7% $\rho_{th}$
- HP2
  - HIP 1600°C 30 ksi 2 hr
  - HIP 1600°C 30 ksi 2 hr
    - HIP 98.1% $\rho_{th}$
    - Significant Carburization
- HIP 1600°C/30 ksi/2 hr
  - Density 98.8% $\rho_{th}$
  - Warm Forge 500°C/Air
    - Successful

Materials Science and Technology: Metallurgy

Los Alamos
Results of AMT/Hot Press Approach

- **Results and Conclusions**
  - Achieved $\sim 94\% \rho_{th}$ for both HP trials
  - At that time, could not obtain $^{182}$W in AMT solution and no time to synthesize chemically
  - Hot pressing in graphite resulted in high carbon levels and undesirable eutectic microstructure, also observed formation of $B_xC$ shell on outside of pressing and other rxn products
  - Subsequent processing not successful
  - HIP/Forge successful
Mechanical Alloying, Consolidation, and Forging

Reduce WO₃ powder at 800°C in flowing H₂

Mechanical alloy (MA) Mo-50 % W by weight
12 hours in WC container in dry Ar glove box

Mill with additional Mo to achieve a
Mo-6.4 wt.% W composition milled powder

Anneal MA powder at 800°C to stress relieve the powder

Blend MA Powder with Pure Mo to Result in 3.18 wt.% W Composition
Jar roll 30 minutes in dry Ar

Cold Isostatic Press (CIP) at 50 ksi to ~70.5%ρₜ₉

Electron beam weld in Ta can
Hot Isostatic Press (HIP) 30 ksi, 1600C, 2 hours

Forge at 600°C to final dimensions

Electron Discharge Machine (EDM) to finish discs
1 mm thick X 40 mm diam.

Characterization:
Immersion Density
Light Microscopy
Scanning Electron Microscopy
Wet Chemistry

Los Alamos

Materials Science and Technology: Metallurgy
Scanning Electron Micrographs of MA Mo-W Powder

Materials Science and Technology: Metallurgy
Characterization of Finished Discs

Average Immersion Density = 99.5\% \rho_{th}
Density variations observed disc to disc

Inclusions nominally 15 wt\% W
Sizes ranging from \sim 1-10 \mu m
Process conditions allowed the diffusion of W into the Mo matrix and homogenization of the 2nd phase MA particles

Materials Science and Technology: Metallurgy
Conclusions on Mechanical Alloying Process Approach

• Acceptable for the application
  – met requirements for W isotope dispersion

• However...
  – more homogeneity desired in future
  – second phase not optimal
  – density gradients through forged part thickness resulted in varying densities for the individual components
    • density gradients due to the use of vibratory table during powder loading into die for CIP and segregation of tungsten rich second phase particles
Solutions to MA/Post Process Concerns

- Pre-alloy the entire powder batch by MA rather than blending MA powders with pure Mo
  - MA, Heat treat at high temperature to anneal and allow interdiffusion of Mo and W, MA again
  - Disadvantage: possible additional interstitial pick-up during extended MA

- Do not use vibratory table for loading powders prior to pressing
Melting and Post Processing Approach

- Powders were prepared for melting by heat treatment in flowing $\text{H}_2$ to reduce surface oxide, blended and pressed into pellets

- Melting Development
  - P/M pellets were melted under three different atmospheres
    - Static argon at 450 torr
      - Poor melt quality, limited pool depth and overall unsatisfactory button quality
    - Static Helium at 450 torr
      - Larger melt pool and higher quality button
    - Flowing He-6H
      - Gas flowed at rate of 0.5L/min and chamber was continually evacuated
      - Excellent melt pool volume, high quality cast button
Melting Quality

Static He

Flowing He-6H

Typical Arc Melted Button

Materials Science and Technology: Metallurgy
Rolling Development

• Pre-Heat Conditions
  - Air at 600°C
  - Flowing Ar at 600°C with button continued in stainless steel foil
  - Flowing Ar at temperatures ranging from 600-1350°C

• Results
  - Stainless steel foil failed during 1st pass
  - Buttons consistently edge cracked along large arc cast grain boundaries for all conditions
Possible Solutions to Rolling Issues

• Each option required additional material or waste
  – Cast thicker button
  – Machine into right circular cylinder
  – Upset forge to break up large, cast grain structure
  – Roll in H₂ environment

• Could not accomplish due to limited material to produce discs
  – Recall - only 10 grams of $^{182}$W available for fabrication of discs
Melting/Powder Metallurgy Approach

• Reduce Mo and W powders in flowing H₂ to reduce surface oxidation
• Weigh and blend for 4 hours, then die press into pellets for melting
• Arc melt in He-6H atmosphere to maintain/improve material cleanliness
• Crush cast buttons in WC mortar and pestle to -40 mesh
• Die press crushed alloy at 90 ksi to achieve 82.9% ρₜ₉
• Can in Ta using electron beam welding
• HIP at 1600°C and 30 ksi for 2 hour hold
• Warm forge in Ta can at 600°C to 1.5 cm thick
• EDM to final disc dimensions 1 mm thick by 43 mm diameter
Melting and P/M Approach

Arc Cast Button → HIP'ed + Compacts → Forged Component

Crushed and Pressed Alloy Powder → HIP'ed + Compacts → Finished Discs

Materials Science and Technology: Metallurgy
Characterization of Final Parts

- **Immersion Density**
  - Averaged 10.41 g/cm³ (99.4% $\rho_{th}$) for nine samples

- **Light Microscopy**
  - Showed clean, homogeneous, as-forged microstructure with minimal porosity

- **Scanning Electron Microscopy**
  - No W rich regions evident in backscattered illumination
  - EDS analysis of W content showed very consistent W composition in several regions of the sample


Materials Science and Technology: Metallurgy
Summary and Conclusions

- Synthesis of W coated Mo Powders using AMT - Successful.

- Uniaxial hot pressing of coated powders in graphite dies resulted in unacceptably high carbon contamination and formation of reaction products.
  - Recommend using cold press/HIP for consolidation of coated powders in the future.

- Mechanical alloying for powder synthesis and consolidation by PM routes was satisfactory. However, second phase (Mo-W rich) particles and density gradients from disc to disc not desirable.
  - Mill smaller quantities of powders for longer times for greater homogeneity, blend alloyed powders together for consolidation, do not use vibratory table for loading powder in die.
Summary and Conclusions Continued

- Melting to achieve alloy successful.
- Rolling unsuccessful.
  - May be accomplished by first forging in a closed die to break up large, cast grain structure.
- Melting-P/M Successful
  - Densification and grain structure may be improved by crushing to finer particle size prior to consolidation. Also recommend post-forging anneal prior to machining.