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This report covers research conducted at RPI prior to the PI's relocation to Penn State, where the focus was on processing optimization for novel compositions fabricated by powder metallurgy. Alloys were fabricated with improved strength and hardness using alloying additions of Mo, Ta, and Re. These results were then applied to the fabrication of injection molded heavy alloys to illustrate the combination of high sintered properties within the context of net shaping without post-sintering deformation processing. Because ductility is sensitive to the processing conditions, special attention was given to identification of useful processing atmospheres. A three stage sintering atmosphere cycle was developed to optimize densification and properties, and demonstrated for times up to 10 h. For comparison, long time vacuum sintering was performed to illustrate the importance of hydrogen and dew point control for this system. Microstructural observations include a drop in the contiguity and the flattening of larger grains with long sintering times, indicative of coalescence contributions to coarsening.

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HIGH PERFORMANCE HEAVY ALLOYS BY ALLOYING & PROCESS CONTROL

for work conducted at Rensselaer Polytechnic Institute, Troy, NY

for the period to July 1991

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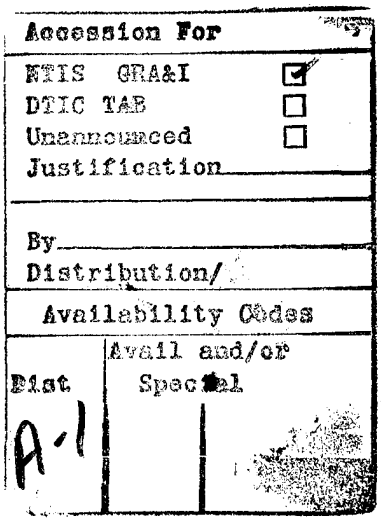

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Abstract

Tungsten heavy alloys have an attractive combination of mechanical and physical properties. This report covers research conducted at RPI prior to the PI's relocation to Penn State, where the focus was on processing optimization for novel compositions fabricated by powder metallurgy. Alloys were fabricated with improved strength and hardness. The classic approach to strength improvement through post-sintering deformation was abandoned in favor of novel alloying concepts to allow net shape processing. Theory predicts, as verified in this research, that Mo, Ta, and Re should act as strengthening additives. Compared to the baseline properties with no additions, the strength and hardness continuously increased with alloying, with a concomitant decrease in the sintered grain size and ductility. These results were then applied to the fabrication of injection molded heavy alloys to illustrate the combination of high sintered properties within the context of net shaping without post-sintering deformation processing.

Because ductility is sensitive to the processing conditions, special attention was given to identification of useful processing atmospheres. Residual porosity of more than 1% drastically reduces ductility. The sintering atmosphere plays a vital role and long sintering times (two hours or more) invariably result in higher residual porosity and poor ductility. Sintering for long times in a dry hydrogen results in the formation of entrapped gas blisters which degrade mechanical properties. A three stage sintering atmosphere has been developed to optimize densification and properties. Sintering for times around 10 h have been demonstrated with minimal blistering. For comparison, long time vacuum sintering has been performed to illustrate the importance of hydrogen and dew point control for this system. It is postulated that dissolved oxygen in the tungsten is released into the liquid matrix during grain growth by solution-reprecipitation, leading to vapor bubbles. These bubbles coalesce and form pores which grow during long time sintering to generate large blisters. Extended time vacuum sintering resulted in matrix vaporization. Interesting microstructural observations include a drop in the contiguity and the flattening of larger grains with long sintering times.

Research Overview

Powder injection molding (PIM) provide an exciting net shape manufacturing process which is currently the focus of intense interest. The process is used extensively to form complex shapes in high volumes in a high production environment. Tungsten heavy alloys modified with molybdenum additions can benefit from the net-forming capability of powder injection molding to form complex shapes. The effort conducted at RPI focused on developing the injection molding of a high strength, high hardness molybdenum treated heavy alloy (82W-8Mo-8Ni-2Fe) using a mixture of polyethylene and stearic acid as the binder. The properties of the injection molded alloy have been discussed and compared with the conventional press and sintered heavy alloy of similar composition. This investigation demonstrates the feasibility of producing net shape, high strength heavy alloys by powder injection molding. Additional impetus for this development is generated due to the success in improving the strength and hardness of the tungsten heavy alloys by alloying with other refractory metals. Prior to this development, higher strengths in tungsten heavy alloys were generated by post sintering mechanical deformation followed by aging. The process of mechanical deformation naturally does not lend itself to near net shape forming techniques.

The higher strengths of the new alloys are due to the combined effect of solid solution strengthening and grain size refinement. Thus, the modified heavy alloys have the capability of utilizing the net shape manufacturing potential of PIM, while exhibiting the increased strength and hardness obtainable by moderate amount of deformation of the classic tungsten heavy alloys.

The process of powder injection molding involves mixing of a suitable binder (usually polymeric) with the metallic powder, granulating the binder-powder feedstock, injection molding into a die (oversized to account for the shrinkage) to generate the desired shape, removing the binder, and sintering. The possibility of successfully injection molding and sintering of classic tungsten heavy alloys has been demonstrated. Most importantly, this project allowed combination of the PIM route with new tungsten alloys to take advantage of net shaping while retaining the property combination of swaged and aged tungsten heavy alloys.

The properties of tungsten heavy alloys are extremely sensitive to processing conditions, impurities, and post-sintering treatments. Molybdenum was chosen as the alloying addition to the classic tungsten heavy alloy since it has complete solid solubility in tungsten and is capable of strengthening the alloy. Additionally, molybdenum is also soluble to a great extent in nickel and iron and could strengthen the matrix too. The alloy which was injection molded had a composition of 82W-8Mo-8Ni-2Fe as preliminary investigations have shown that this alloy has excellent strength and ductility combination. The present investigation addresses the key issues like mixing, injection molding, debinding, proper sintering and heat treatment schedule, evaluation and comparison of the injection molded tensile properties with classic press and sintered alloys, and microstructural analysis. The success of this investigation is expected to lead to the rapid and economic fabrication of complex shapes of high strength tungsten heavy alloys.

Ductility of the heavy alloys are extremely sensitive to the processing history and is adversely affected by residual porosity, impurity segregation, hydrogen embrittlement and intermetallic phase formation. Residual porosity of more than 1% can drastically reduce the ductility of these alloys. The sintering atmosphere plays a vital role and long sintering times invariably results in higher residual porosities and thus, poor ductilities. The development of a three stage sintering atmosphere have resulted in the first successful sintering of fully dense heavy alloys whose ductility is not drastically reduced with long sintering times (two hours or more). The salient features of the sintering cycle includes the pre-reduction hold at 800° C in dry hydrogen for 1 hour, followed by heat up to the sintering temperature (1480 to 1500° C). At around 1250 to 1300° C (before the liquid forms), the dry hydrogen is switched to wet hydrogen in order to suppress the in situ formation of water vapor. The final atmosphere switch from wet hydrogen to dry argon is made about 10 minutes before the end of the sintering cycle. This is done in order to remove the hydrogen embrittlement effect. To avoid solidification shrinkage pores, samples are cooled slowly from the sintering temperature to the temperature where the material is completely solid. A post sintering heat treatment of water quenching after a hour hold at 1100° C is carried out for reducing the impurity segregation effects. The detailed description of the sintering cycle is provided elsewhere.

Long sintering times, especially for heavy alloys with less than 90 weight percent tungsten content, in the past, have always resulted in poor sintered properties, especially in terms of the ductility. With increased sintering time, the residual porosity can coalesce and grow, causing a decrease in the final sintered density. This behavior becomes more acute with

increasing matrix content and low hydrogen dew points during the actual liquid phase sintering step. The three stage atmosphere cycle which uses wet hydrogen during the actual liquid phase sintering, is observed to alleviate this problem. Thus, for the first time the study of varying grain sizes and the corresponding properties of tungsten heavy alloys can be determined without the associated property degradation.

The varying grain sizes in tungsten heavy alloys can bring about a host of interesting microstructural variations. The observation that the large tungsten grains often have a tendency to flatten out for better accommodation, is in good agreement with the theoretical calculations. However, the decrease in the contiguity with long sintering times is a deviation from the general theory. More detailed investigations are required where the microstructural variables like the mean matrix layer thickness, the dihedral angle, connectivity, and the volume fraction are correlated with the grain size and properties of the tungsten heavy alloys. This paper discusses the preliminary research efforts, mainly in the direction of mechanical property variations with grain sizes varied by increased sintering times.

Experimental Techniques

Elemental tungsten, molybdenum, nickel and iron powders were mixed in the desired ratio which corresponded to a composition of 82W, 8Mo, 8Ni and 2Fe by weight. The mixing was carried out in a turbula mixer for one hour. The milling procedures for the powder were as follows: A stainless steel container of two liter capacity was filled to half of its capacity with 5 mm diameter tungsten-carbide-cobalt balls, and 1.5 kg of the tungsten-nickel-iron-molybdenum powder mixture was added. The container was then filled with heptane and sealed. Milling was performed for 16 hours at 60 rpm. The powder and milling media were subsequently separated by sieving, and the powder dried at 60° C for eight hours.

A wax based binder was used for the injection molding. The binder consisted of 30 wt.% polypropylene copolymer. This resin has a peak molecular weight of 42,600, a density of 0.89 g/cm^3, and a melting point of 142° C. The major binder component was 65 wt.% paraffin wax. This wax has a molecular weight of 350 to 420, a density of 0.90 g/cm^3, and a melting point of 59° C. The remaining 5 wt.% was stearic acid with a molecular weight of 285, a density of 0.941 g/cm^3, and a melting point of 74° C.

Mixing of feedstock was performed in two stages. Premixing was in a sigma blade mixer, and the feedstock was subsequently extruded and pelletized using the injection molding machine as an extruder. An oil jacketed sigma blade mixer was brought to a temperature of 150° C and all binder components introduced. Upon complete melting, the powder was gradually introduced over about 10 minutes. Mixing at maximum speed was performed for 20 minutes. The heat was then turned off and the mixer kept running at minimum speed during cooling. As the feedstock solidified, attritioning took place and spherical feedstock pellets were formed. The feedstock was then extruded using the injection molding machine. For this purpose, the check-ring at the screw tip was removed. A temperature profile of 107/118/118/95° C was used for the nozzle and three barrel heating zones. The feed area was chilled to 18° C. A screw speed of 80 rpm was used for the extrusion cycle with a 1.5 mm diameter nozzle and 22 mm diameter screw and barrel assembly. The feedstock was extruded and pelletized three times until the extrudates are very consistent.

Die inserts were designed for a modular mold set. A tensile bar was injection molded

for process optimization. Debinding was performed in two steps, with initial debinding using a solvent debinding route. Both solvent debinding by condensed vapor and immersion debinding were investigated. Debinding by immersion proved a better route for the projectiles, as 62% of the binder could be removed within 5 hours at 60° C. Debinding in condensed vapor at 80° C removed only 49% of the binder, and contour control was superior with the immersion route. The higher temperature necessary for condensation debinding softened the binder and allowed distortion.

Sintering was performed in a tube furnace in a hydrogen atmosphere using the following thermal cycle: 10° C/min ramp to 800° C, 60 min hold at 800° C, 10° C/ramp to 1500° C, 30 min at 1500° C, furnace cooling. Alumina supports were employed to avoid contamination. Typical atmosphere turnover was five to ten times per hour.

The molded tensile bars were lapped to a 240 grit surface finish after heat treatment. The sample dimensions and the densities were carefully measured. The hardness of the samples was then measured on the Rockwell A scale and an average of at least 18 values has been used as the final HRA value. The samples were pulled in tension using a crosshead speed of 0.004 mm/s. The elongation, yield and ultimate tensile strength of the samples were measured and the average of at least three specimens have been reported. On completion of the tensile tests, small pieces were sliced from the end of the fractured bars. The pieces were mounted, polished and etched and examined under an optical microscope. The injection molded properties of the alloy are compared with the classic press and sintered alloys of similar composition.

Significance of Results

With the increase in molybdenum content by the replacement of tungsten, the theoretical density of the composite will decrease. With increasing molybdenum additions, the elongation decreases and the strengths (both yield and ultimate) increases monotonically (at least for the range of compositions used). The hardness also shows a similar monotonic increment with increasing molybdenum content. The increase in strength and hardness is due to the combined effect of solution hardening and grain refinement brought about by molybdenum additions.

It is evident from the binary phase diagrams of Mo-Ni and Mo-Fe that Mo has a fair amount of solubility at 1300° C in both Ni (38 wt.%) and Fe (24 wt.%). Tungsten and molybdenum exhibit complete solid solubility in each other over the whole range of compositions. Thus, addition of molybdenum to the classic tungsten heavy alloy system results in a situation where molybdenum is shared between the tungsten grains as well as the matrix, and it can thereby strengthen both by solid solution.

Due to the solutioning of molybdenum into the matrix alloy, the matrix can no longer dissolve the usual amount of tungsten. This in turn causes a modification in the solution-reprecipitation step which is responsible for grain growth in tungsten heavy alloys. During this stage, the smaller tungsten grains are preferentially dissolved and reprecipitated on the larger ones. With the molybdenum addition to the system, solutioning of tungsten is hindered, resulting in grain size refinement.

The choice of the final material composition for powder injection molding was selected to be 82W-8Mo-8Ni-2Fe. This composition exhibited property combinations which was comparable to a swaged classic tungsten heavy alloy (around 8 to 10% reduction in area).

The role of uniform mixing plays a key role in the proper realization of the optimum injection molded properties. The first signs of improper mixing can be obtained from the deviation between the calculated and experimental theoretical density values before the critical loading has been attained. It was observed that mixing for 15 minutes in the double planetary vacuum mixer resulted in mixture densities substantially less than the calculated ones. When mixing under vacuum was carried out for an hour, the calculated and the theoretical densities were almost identical. High volume fraction of solid loading (0.6 or more) would not be possible due to the rough surface characteristics of the powders.

Debinding of the fine powders proved to be quite difficult as the samples tend to crack and form pores under various debinding conditions. The samples were always embedded in alumina to allow faster debinding conditions. In the first case where the samples were heated at 10 K/min to 450° C and held there for 60 minutes before cooling, resulted in very fragile and porous material. The debinding conditions in this case was obviously too fast, which resulted in large pressure build up in the sample causing pores on the debound pieces. In the second debinding condition, where the sequence was 10 K/min to 150° C, hold for 120 minutes; 10 K/min to 180° C, hold for 120 minutes; 10 K/min to 200° C, hold for 120 minutes; 10 K/min to 250° C, hold for 120 minutes; 10 K/min to 350° C, hold for 120 minutes; furnace cool to room temperature; resulted in samples which showed large surface cracks. Through a few other debinding experiments, the conclusion was that a hold at around 300° C was crucial for proper debinding of the specimens. Thus the successful debinding cycle consisted the following sequence : 10 K/min to 250° C, hold for 30 minutes; 10 K/min to 300° C, hold for 30 minutes; 10 K/min to 325° C, hold for 30 minutes; 10 K/min to 350° C, hold for 30 minutes; 10 K/min to 375° C, hold for 30 minutes; furnace cool to room temperature. This resulted in debinded samples with no apparent flaws like cracks or pores. The hold times between 300 and 350° C was critical for obtaining good quality debinded samples. These samples were then pre-sintered at 900° C for 60 minutes in dry hydrogen atmosphere.

The debinded and pre-sintered samples were sintered according the schedule developed earlier. Three sintering temperatures (1475, 1500, and 1530° C) were used. The sintered samples exhibited densities which were greater than 99.5% of theoretical, thus proving the success of the sintering schedule. The as sintered microstructure of an injection molded alloy of 88W-8Mo-8Ni-2Fe is similar to the press and sintered material of the same composition. As expected, the sintered strength increased and the elongation decreased with lower sintering temperatures. Thus, modification in the properties of the alloys is also possible by variation in the sintering conditions. For actual comparison, the properties of a 82W-8Mo-8Ni-2Fe alloy and a classic 90W-8Ni-2Fe alloy processed by press and sinter method, is also included in the table. It can bee seen that the injection molded properties compare very well with the press and sintered alloys. Thus, it is possible to produce net shape parts of high strength heavy alloys (comparable properties as swaged heavy alloys) by powder injection molding.

PIM provides an economic advantage in the mass production of complex shaped parts of tungsten heavy alloys. An additional impetus for this study results from the success in improving the strength and hardness of the tungsten heavy alloys by incorporation of refractory metals like molybdenum, rhenium, and tantalum [6]. Prior to this development, higher strengths in tungsten heavy alloys were generated by post-sintering mechanical deformation followed by heat treatment. The process of mechanical deformation naturally does not lend itself to net-shape forming techniques. The higher strengths of the new alloys

are due to the combined effect of solid solution strengthening and grain size refinement. Thus, the modified heavy alloys have the capability of utilizing the net-shape manufacturing potential of PIM, while exhibiting the increased strength and hardness previously obtained by deformation and aging. A major advantage is then attained by delivery of high performance levels in a net-shaping process. Thus, the former route to high performance was,

mix powder → compact → sinter → anneal → deform → aging → machine

while the new approach is,

mix powder → mold → debind → sinter → anneal.

The process of powder injection molding involves the mixing of a suitable binder (usually a polymeric thermoplastic) with the desired powder, granulating the binder-powder feedstock, injection molding into a shaped die (oversized to account for the shrinkage), removing the binder (termed debinding), and sintering the material to the desired density. The PIM processing of tungsten heavy alloys has already been demonstrated. This study goes further by examining the application of PIM to the formation of complex shapes while attaining the unique property combination of swaged and heat treated tungsten heavy alloys. Since the properties of tungsten heavy alloys are extremely sensitive to processing conditions, impurities, and post-sintering treatments, attention was focused on developing a process with competitive properties and good shape control.

Testing was performed on the molded and sintered tensile samples using slow strain rate testing. Several different mechanical property combinations were of interest. A summarization of sintered tungsten heavy alloy mechanical properties is given below. Almost all of the tests being performed on injection molded materials except for the two formed by "P & S" which denotes press and sinter, the classic approach to heavy alloys.

Properties of Some Injection Molded Heavy Alloys

alloy	processing at 1500° C	strength MPa	elongation %
90W-8Ni-2Fe	P & S	918	36
82W-8Mo-8Ni-2Fe	P & S	1048	24
82W-8Mo-8Ni-2Fe	PIM	1115	20
98W-1.4Ni-0.6Fe	PIM	708	1.5
98W-1.3Ni-0.7Co	PIM	772	2.7
97W-2Ni-1Cu	PIM	659	2.6
98W-1.3Ni-0.7Cu	PIM	696	3.5
98W-1.5Ni-0.5Mo-0.5Fe	PIM	890	1.4

P & S = press and sinter, PIM = powder injection molded

The mechanical properties are very attractive and compare favorably with previous reports on injection molded heavy alloys. The addition of molybdenum is effective in increasing the as-sintered strength to levels approaching that attained with swaged and aged alloys. Note the focus in this work was on very high tungsten contents, leading to drastic reductions in ductility. For many applications the performance is most dependent on density and strength, with little affect from ductility.

An important additional aspect of the research was optimization of the sintering atmosphere and investigation of long sintering times on tungsten heavy alloys. Heavy alloys with a variety of tungsten contents were sintered under optimal conditions of a dry-wet hydrogen atmosphere. A 88W alloy was sintered for 600 minutes using the atmosphere cycle, which starts wet hydrogen atmosphere before the liquid forms and maintains it till the last 10 minutes of the 600 minute hold. This resulted in samples which were 99.9% dense.

The fracture elongation was very sensitive to sintering time. The success of the three stage sintering atmosphere is clearly demonstrated for sintering times of 120 and 600 minutes. The elongation value of 14% exhibited by the 95W alloy sintered for 10 hours in this study is unique and not matched by any other investigations. The grain size variation with time follows the general cubic dependence reported in literature. The variation in the contiguity of the sintered samples shows with extended sintering. The limitation in mechanical properties was traced to water vapor formation within the matrix. If water vapor molecules are produced too rapidly, they coalesce and form stable bubbles are entrapped in the bulk material. If the rate is slow, the water vapor exits through the surface. The rate of this water vapor formation is controlled by the hydrogen atmosphere dew point. Thermodynamically, water vapor formation will continue even at high dew points (+ 20° C) but the rate of formation is slower.

Vacuum sintering of a 90W heavy alloy for 30 minutes resulted in fully dense samples with moderately good sintered properties. However, when the same alloy composition was sintered in vacuum for 10 hours, the final measured sintered density of the alloy exceeded the theoretical density by a substantial margin. The final sintered density was closer to a 92 weight percent tungsten alloy rather than a 90 weight percent tungsten alloy with which the sintering run was started. The volume fraction of tungsten which is around 0.78 for a normal fully dense 90W alloy was found to be around 0.84 for the 10 hour vacuum sintered sample. This is the direct consequence of the lower melting point and lower density constituent of the heavy alloy preferentially vaporizing and, thus, resulting in an increase in the tungsten content. Thus, long time vacuum sintering would not afford samples from which the true dependence of large grain size on sintered properties could be determined.

The next phase of the experiments used the three stage atmosphere cycle described earlier (Cycle 3). The 88W alloy sintered for 600 minutes resulted in samples which were 99.9% dense. The sintering of 88W alloy for the normal sintering time of 30 minutes did not result in badly slumped samples. However, with sintering times of 600 minutes, the sintered sample which in the green state was a dogbone tensile bar, totally slumped with the bottom part of the sample becoming much larger than the top. The effect of gravity alone would not be enough to account for the large slumping with increased time. It is felt, and has been verified (discussed later for the 95W sintering) that the contiguity of a sample is lowered with increasing hold times during actual liquid phase sintering. The 88W alloy which had a large volume of liquid to start with, had a low contiguity of 0.2 for samples sintered for the normal 30 minutes. With increased sintering time, due to melt penetration at the tungsten-tungsten interfaces, the contiguity should be lowered still further causing the samples to slump. Note

however, that the increased sintering time even to 10 hours, did not result in the large increase in the retained porosity as evident in similar samples sintered for only 2 hours. The tensile properties of the samples could not be determined due to the sample slumping.

The most interesting results emerged from the study of the sintering time effects on the properties of the 95W heavy alloy sintered according to Cycle 3 (the three stage atmosphere cycle). Firstly, the density of the samples are not decreased for the wide range of sintering times used for the present investigation (1 to 600 minutes). Secondly, and perhaps the most noteworthy result is that the mechanical properties, especially the ductility, does not drop off drastically, which is the case in all previously reported heavy alloys sintered for times in excess of one hour. As a direct comparison with an alloy of similar composition reported in the literature, it can be observed that sintering for 2 hours using the three stage atmosphere cycle, resulted in elongation values which are double of that reported in literature and for a sample sintered for 10 hours, it is more than a order of magnitude higher.

The grain size variation with sintering time follows the general cubic law where the cube of the grain size varies linearly with sintering time. The grain size for the least sintering time has not been considered as the grains did not have a chance to properly round off and form the normal grains that one observes in tungsten heavy alloys. Sintering times of 30 minutes resulted in fully dense samples whose microstructure reveals the usual rounded grains. The grain growth continued with increasing times. The sample sintered for 10 hours had an extremely interesting microstructure. Careful observation of the microstructure reveals that in lot of grains, contact flattening has occurred for shape accommodation. However, the most interesting observation is that very often, there is a very thin layer of the matrix that is observed to separate two grains, especially where the contacts have flattened. Thus even very large grains can often have a very small contiguous area in contact with another tungsten grain. It is evident that with increased sintering time, liquid matrix has penetrated the tungsten- tungsten contacts, and in some cases have totally separated the two contiguous grains by a thin film of liquid infiltration. It is conceivable that the penetration of the liquid will be more in the interfaces where the tungsten grains are favorably oriented. This is the reason for the sharp drop in the contiguity of the 95W alloy sintered for 10 hours. There is a continuous drop in the yield strength with increasing grain size which is normally expected. Thus, the present sintering cycle, for the first time, offers investigators the ability to measure the true effect of varying grain sizes on the properties of tungsten heavy alloys. The effect of large grain sizes on the dynamic properties of heavy alloys will be of great interest in determining the ballistic performance of these alloys.

Conclusions

This research has successfully employed new alloying concepts in tungsten heavy alloys to tailored mechanical properties in the context of net shaping via powder injection molding. The combination has implications for several applications.

With increasing molybdenum content, the ultimate tensile strength, yield strength and hardness of the heavy alloys go up while the elongation, grain size and theoretical density decreases. The increase in the strength and hardness with molybdenum additions is attributed to both solid solution hardening and tungsten grain refinement. The properties of a 82W-8Mo-8Ni-2Fe alloy are comparable to swaged classic 90W heavy alloys. This provides an alternate route of processing high strength heavy alloys to near net shape by powder injection molding.

The net shaping capability is demonstrated by successfully sintering injection molded alloys to full density and properties comparable to the classic press and alloys of similar composition.

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