# Advances in Powder Metallurgy Rhenium

**T. Leonhardt, M. Hamister, N. Moore and J. Downs**

**Rhenium Alloys, Inc.**
**Elyria, Ohio 44036**

## Abstract

Several recent developments in powder metallurgy (PM) rhenium have significantly enhanced the uses and usability of rhenium and rhenium alloys. One of the developments was cold isostatic pressing (CIP) to a complex shape with traditional rhenium powder. CIPing to a complex shape with a one or two–part mandrel reduces the quantity of rhenium required to produce the component and significantly reduces the secondary machining. The CIP-to-complex shape method was developed for rhenium liquid-fueled apogee engine combustion chambers. The other major development was high-density spherical rhenium powder (SReP), which has excellent flow for use in traditional and advanced processes for PM rhenium. Several advanced consolidation techniques were investigated; vacuum plasma spraying (VPS); direct hot isostatic (D-HIP); and laser additive manufacturing (LAM) to produce near net shape components. All of the recent developments will lower the cost, reduce the processing time, and improve the yields when making powder metallurgy rhenium and rhenium alloy components.

## Introduction

Rhenium is one of the last naturally occurring elements to be found, and the discovery occurred in 1925 by Ida Tacke and Walter Noddak, and Otto Berg. They named it after Germany's Rhine River. Only a few milligrams of rhenium were produced in 1927, and the first full gram in 1928. It was not until the 1960's that rhenium was produced in a full-scale manufacturing operation (1,2). Rhenium is a heavy transition metal with a melting point of 3459 K, and has the highest modulus of elasticity of all the refractory metals. It does not form a carbide, even when exposed to graphite at very high temperatures. Further, rhenium also possesses a high electrical resistance across a wide temperature range (2,3). Additionally, powder metallurgy rhenium has consistently provided high yield and ultimate tensile strengths at both ambient and elevated temperatures, while maintaining excellent ductility and exceptional creep qualities as well as the low-cycle fatigue properties required by demanding high-temperature applications (4,5,6,7).

Rhenium metal powder (RMP) is an irregularly shaped, flaked powder with poor flow characteristics, and an oxygen concentration of 1000 ppm. The process of manufacturing hydrogen-reduced rhenium metal powder is described in reference 2. Rhenium Alloys, Inc. manufactures a powder metallurgical grade of rhenium that possesses a purity grade (99.99%). The –200 mesh RMP has an average particle size of 3.5 um and an apparent density of 1.84 g/cm$^3$ with a tap density of 3.03 g/cm$^3$ (Figure 1) (7).

SEM Courtesy of CTC

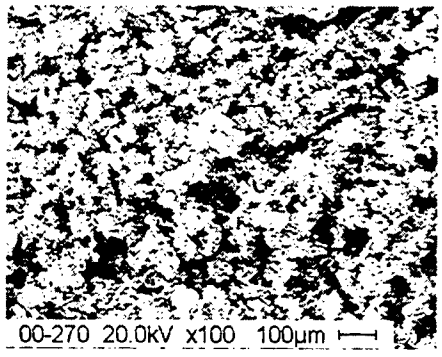



Figure 1: -200 mesh rhenium metal powder

## Thruster Procedure

Historically, rhenium has been produced in a variety of standard metal forms; rod, bar, plate and sheet, and these basic shapes underwent electrical discharge machining (EDM) methods to generate the specified shapes and sizes to indicated tolerances. The current method of consolidating powdered rhenium metal for rods is cold isostatic pressing (CIP). In CIP the technique rhenium metal powder is packed into a flexible mold with a "rigid container" to maintain the desired shape (Figure 2). Then the can/mold assembly is immersed in water contained within a CIP vessel. This "wet bag" process uses hydrostatic pressures of 210 to 410 MPa, which transfers the isostatic pressure to the mold and consolidates the rhenium metal powder into a "green" rhenium compact (8).

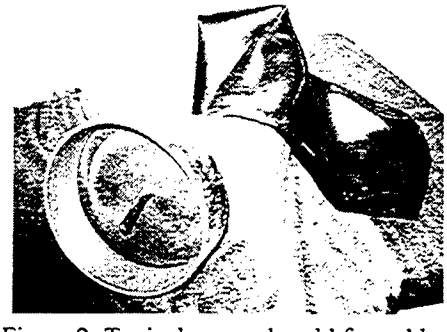


Figure 2: Typical can and mold for cold isostatic pressing

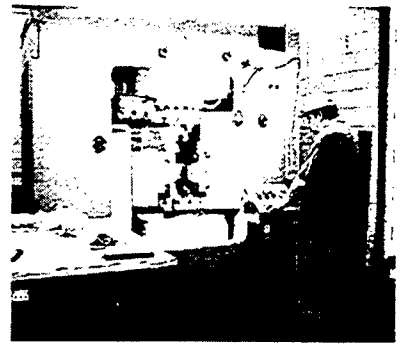


Figure 3: 1000-ton hydraulic press

The method of compacting rhenium into plate forms is open die compaction using a bi-directional 1000-ton hydraulic press Figure 3 (7,8). The green compact (plate) produced by the 1000 Ton hydraulic press has a high theoretical density of 48%. The plate is pre-sintered and sintered to an approximate size of 3.5" x 8.2" x 0.675" with a sintered density of 95%. The new plate size increases the amount of rhenium powder used from 2400 grams to 6500 grams. This innovation in plate size will produce cold rolled rhenium products with an approximate thickness up to 0.500".

Prior to Rhenium Alloys, Inc. undertaking a National Aeronautics and Space Administration (NASA) Phase II Small Business Innovative Research (SBIR) program, all complex parts and components based on PM were manufactured using a standard rod or a large diameter rod (ingot) that involved numerous machining operations. The initial powder metallurgy apogee thrusters were made from 15-40 kg rhenium ingots, and while this method worked well,

extensive machining was required to produce a high quality part (9). This led to our initial research into the area of powder metallurgy near-net shape manufacturing.

As part of the NASA Phase II SBIR, two (2) completed and "deliverable" thrusters of different and unique types were to be manufactured; one (1) each of the 440 Newton (N) and 490 N high performance bi-propellant liquid-fueled apogee rhenium/iridium thrusters. Both thrusters have rhenium as a substrate with iridium applied as an oxidation-resistant coating. Each of the thruster designs utilizes a conventional convergent-divergent design to produce thrust for use in low-earth orbit and/or a geo-stationary orbit for satellite positioning systems.

To produce a component possessing complex shape properties, the CIP tooling must have a design contour similar to that of the actual part, and will entail the use of a contour "can" and mold, as well as a one or two-part solid pressing mandrel. This method of using a pressing mandrel is known as the "collapsing bag technique" as described in ASM Handbook Vol. 7 (8). This technique was used to manufacture the thruster, with a two-part pressing mandrel, which generated a near-net shape "green" part. Because the thrusters are of a convergent-divergent cone design, it was necessary for the mandrels to be divided at their narrowest point. Also the mandrel was manufactured with a slight taper to allow it to be removed without scratching the inside of the "green" compacted part during the mandrel extraction process. In this method, the mandrel holds the thruster's inside diameter contour while maintaining the dimensional tolerances, (Figure 4). The flexible mold accepts the contour of the mandrel, and the green compact gets a contoured outside diameter matching the shape of the mandrel. In this technique the powder fill controls the wall thickness of the near-net shaped (NNS) part with contoured inside and outside surfaces, as shown in Figure 5.

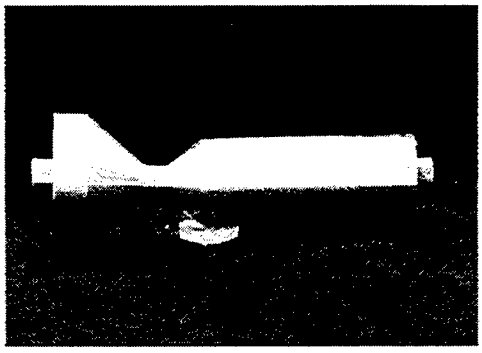


Figure 4: Mandrel used for cold isostatic pressing of NNS thruster

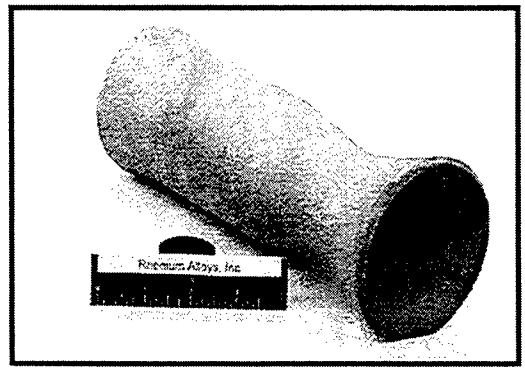


Figure 5: "Green" near net shaped rhenium thruster

**Thuster Results**

The 440 N thruster was the first near-net shaped chamber produced using the "CIP-to-NNS" process, and it reached a final density of 99.4 %. The hot processing methods applied produced a fine-grained microstructure with micro-porosity inside the grains (Figure 6). This thruster (Figure 7) was delivered to NASA Glenn Research Center in Cleveland, Ohio, and was coated with iridium to provide oxidation resistance. The thruster will be hot-fire tested for flight hardware certification in the near future.

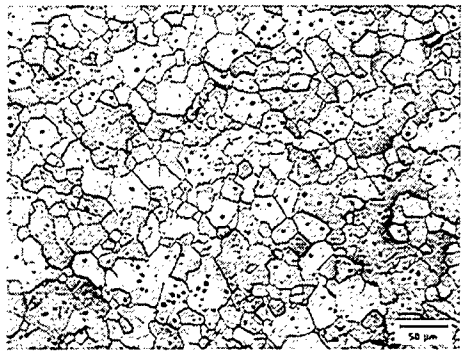


Figure 6: Microstructure of the 440 N rhenium thruster

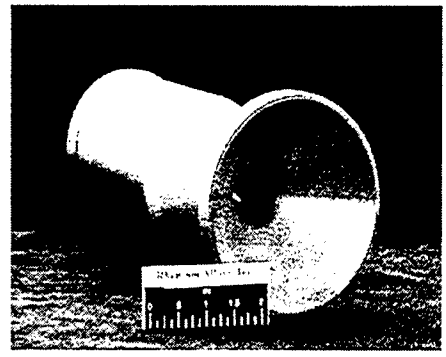


Figure 7: 440 N rhenium thruster before iridium coating

The 490 N thruster was the more challenging of the two thrusters to manufacture because of the large exit cone and smaller barrel section when compared to the 440 N thruster. The parameters for making the 490 N thruster were similar to those used for the 440 N thruster except for a higher compaction pressure. The completed 490N thruster (Figure 8) had a density of 99.9 %, with a fine grain microstructure (Figure 9).

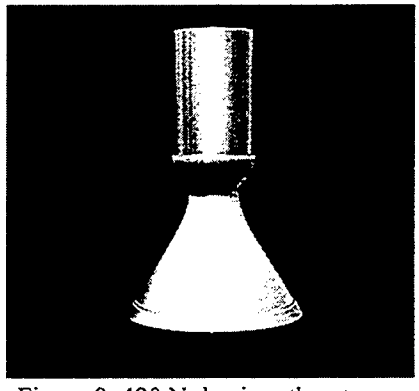


Figure 8: 490 N rhenium thruster

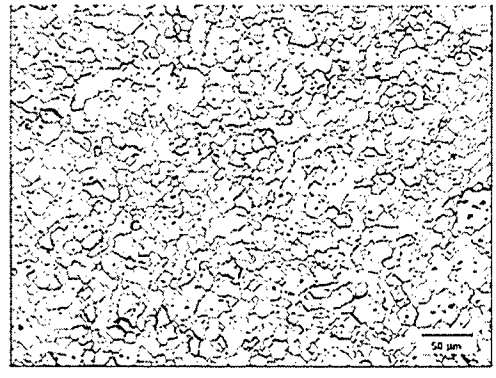


Figure 9: Microstructure of the 490 N rhenium thruster

**SReP Procedure**

The next step in rhenium near-net shape (NNS) manufacturing techniques is to produce the components in large quantities at lower cost, with faster turn-around times, while using less material. This can be accomplished through the use of NNS techniques that include: vacuum plasma spraying (VPS); direct-hot isostatic pressing of powder (D-HIP); directed light fabrication (DLF); and metal injection molding (MIM). The enabling technology that promotes the usage of these extremely effective techniques will be the continued development of high density, low oxygen, spherical rhenium powders (*SReP*) in a wide range particle sizes.

To produce and develop spherical rhenium powders, Rhenium Alloys, Inc. undertook an extensive, in-depth research program, partially funded by a Ballistic Missile Defense Organization (BMDO) Phase I Small Business Innovative Research (SBIR) program. The program's goal was to produce a spherical rhenium powder possessing low-oxygen content with less than 50 ppm. Additional required characteristics included: a tap density of 12 g/cm$^3$; with an apparent density of 11 g/ cm$^3$; and a flow rate of 4 second /50grams.

### Rotating Electrode Process

The BMDO Phase I goal for this project was to manufacture spherical rhenium powder (*SReP*) by the rotating electrode/plasma rotating electrode process (REP/PREP/GA-REP)(8,10). This process utilizes a rhenium rod rotating at 15,000 rpm's in an atmosphere of argon, while a high-velocity plasma torch melts the rhenium into droplets. The gas-assisted rotating electrode process (GA-REP) was investigated as a means to reduce the droplet size. Typical particle size for the rotating electrode process is 200-600 microns, with a bi-modal distribution (10).

### Plasma-Atomized Process

Through a self-funded program, Rhenium Alloys, Inc. created and developed the plasma-atomization process (PA) to produce spherical rhenium powder *(SReP)*. During the initial phase of this program a fine particle size of less than 40 microns was produced, however a wide range of particle size; ranging from 5-80 microns, can also be produced with this process (10).

## SReP Results

### Rotating Electrode Process

In all, a total of 96 kilograms of rhenium rods were used during the rotating electrode/plasma-rotating electrode process, and from this 56 Kg of *SReP* was collected, with the balance being melted rod end pieces, as seen in Figure 10. The desired goals of this phase of the project included; achieving an oxygen content of less than 50 ppm; a tap density of 12.5 g/cc or greater; and the production of spherical rhenium powder particle possessing high flow characteristics. As shown in table 1, the tap density, apparent density, and flow data is listed by specific particle sizes. In table 2, image analysis was used to determine particle size vs. the diameter of the starting rod, and, as illustrated, the larger the diameter of rod, the smaller the diameter of the *SReP* produced. For the rotating electrode process, the average sizes of particles are: 128 micron for the 50mm diameter rod; 161 micron for 38mm diameter; and 241 micron for the 30.5 diameter. In addition, the majority of the *SReP* was in a 100 to 300 micron diameter range, with both the tap and apparent densities being very similar. This is typical for most spherical metal powders.

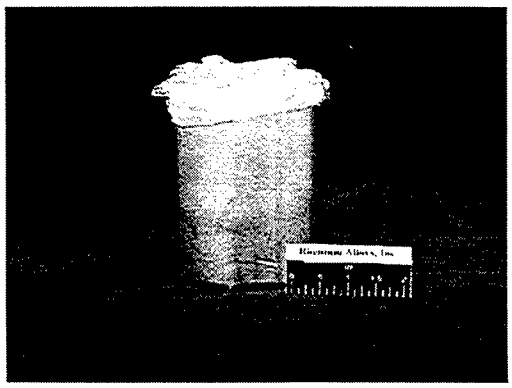


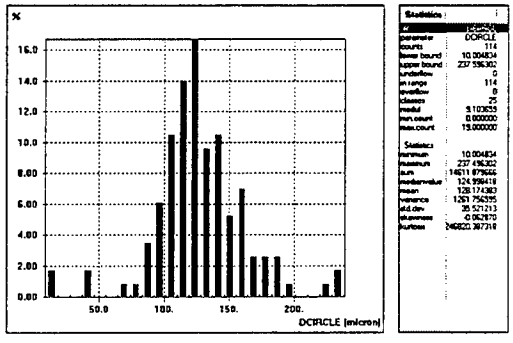
Figure 10: Two-inch diameter melted rhenium rod from the Plasma rotating electrode method.

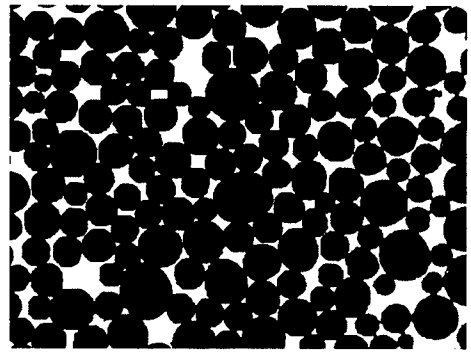
Table 1: Characterization of SReP by particle size

| Mesh | Micron | Tap Density g/cc | Apparent Density g/cc | Flow sec/50g |
|---|---|---|---|---|
| +50 | 300 | 13.111 | 12.782 | 6.244 |
| -50 +100 | 300-150 | 13.532 | 12.4564 | 4.955 |
| -100 +120 | 150-125 | 13.184 | 12.232 | 4.968 |
| -120 +140 | 125-106 | 13.336 | 12.191 | 4.902 |
| -140 +200 | 106-75 | 13.514 | 12.252 | 4.623 |
| -200 +325 | 75-45 | 13.130 | 12.529 | 4.123 |
| -325 +400 | 45-38 | 13.513 | 11.845 | 4.204 |
| -400 +450 | 38-32 | 13.144 | 10.256 | 4.081 |
| -450 +500 | 32-25 | 12.496 | 10.665 | 3.985 |
| -500 +635 | 25-20 | 12.074 | 10.485 | 5.81 |
| -635 | -20 | 12.263 | 9.169 | NF |

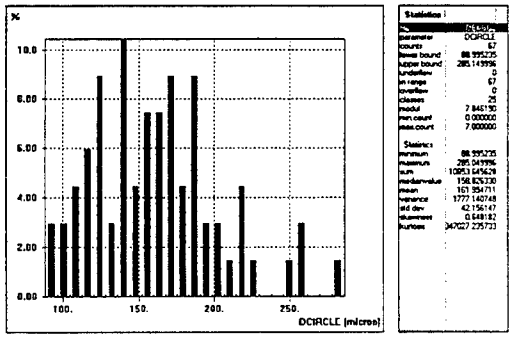
Table 2: Image analysis of Rotating Electrode processed SReP by rod diameter

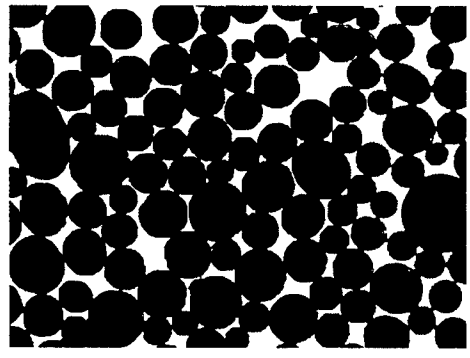
2"



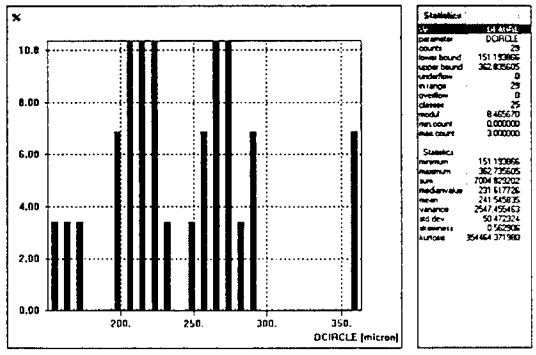



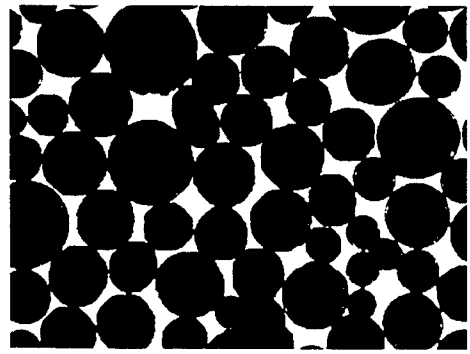
1.4"



1.2"



**Plasma Atomized Process**

The plasma-atomized, spherical rhenium powder had a particle size of 37 microns ± 17 microns for type A (Figure 11) and 25 microns ± 8 microns for type B (Figure 12). The apparent density for type A was 10.27 g/cm$^3$ and for type B 10.37g/cm$^3$. The tap density for type A was 11.60g/cm$^3$ and for type B 12.12 g/cm$^3$. These densities are similar to the rotating electrode process illustrated in table 1. In addition, as illustrated in table 1, the smaller the size of the particle the more likely that the flow characteristics are reduced. In contrast to the SReP, the traditional rhenium metal powder has an apparent density of 1.84 g/cm$^3$ and a tap density of 3.03 g/cm$^3$, which are significantly less when compared to the SReP densities.

SEM Courtesy of CTC

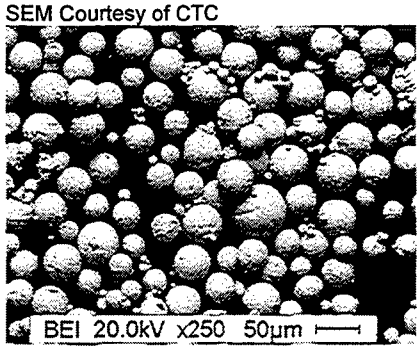



Figure 11: Type A, PA-SReP

SEM Courtesy of CTC

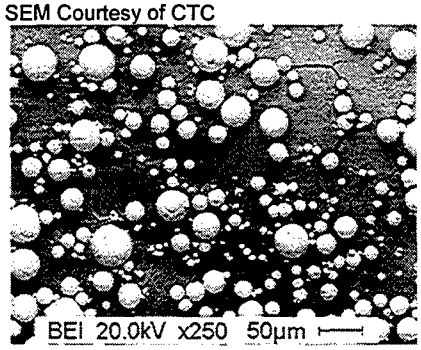



Figure 12: Type B, PA-SReP

**Advanced Consolidation Methods**

The first experiment conducted was to vacuum plasma spray (VPS) type A. *PA-SReP*. Several experiments were performed to optimize the VPS parameters, deposition rate, and density of the rhenium coatings. As shown in Figure 13, a flat coupon and a tube were VPS-ed to a maximum thickness of 5mm. In (Figure 14) the microstructure of the VPS-ed PA-*SReP* is displayed.

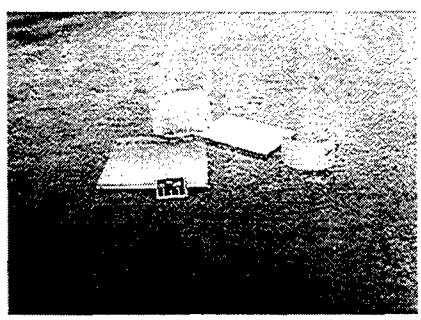


Figure 13: VPS flat coupon and tube

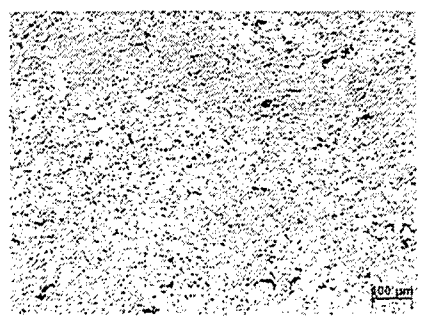


Figure 14: microstructure of VPS rhenium tube

The second experiment conducted involved the direct-hot isostatic pressing (D-HIP) of the B type *PA-SReP* into 19mm diameter rods. Hot isostatic pressing containers were filled with *SReP*, evacuated, and then sealed (Figure 15). A density of 98% was achieved using the D-HIP

process for the PA-*SReP*. As shown in (Figure 16), the microstructure of the direct hot isostatically pressed rod had a larger grain size and illustrated final sintering.

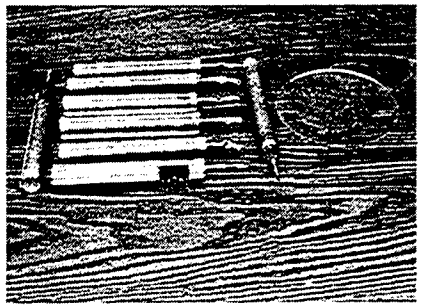


Figure 15: D-HIP container, filled and sealed with type B PA-SReP

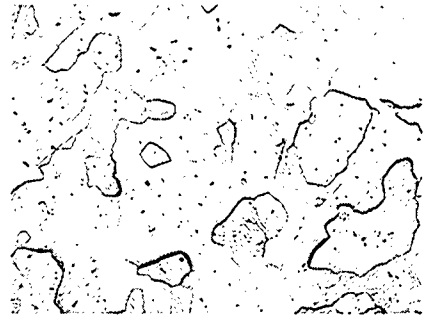


Figure 16: Microstructure of D-HIP experiment with Type B PA-SReP

The vacuum plasma spraying and hot isostatic pressing of PA-*SReP* were performed at NASA Glenn Research Center, Cleveland, Ohio, in cooperation with the Great Lakes Industrial Technology Center under NASA Space Act Agreement funded by Rhenium Alloys, Inc.

Additional experiments with the PA-*SReP* were performed utilizing traditional die pressing methods, with a two-way die. Several pellets were produced using type A and B powders. The small 20g pellets had an "as-pressed" density of 78% with a pre-sintered density of 85%. The microstructure of the pre-sintered pellet illustrates the deformation from die compaction of the spherical powder, and some necking of the powder particles after pre-sintering (Figure 17). Further, the sintered pellet achieved a density of 95.5%, with its microstructure showing intermediate sintering properties, as well as a fine grain size (Figure 18).

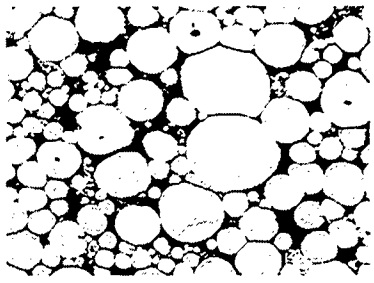


Figure 17: Microstructure of pre-sintered pellet

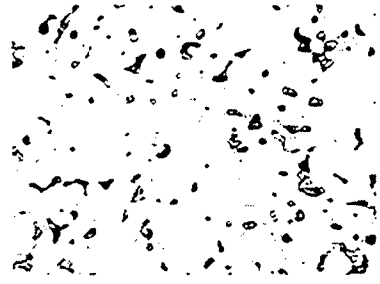


Figure 18: microstructure of a sintered pellet

**Discussion**

This paper describes the progress made in PM rhenium during the last 1.5 years and also describes the increase in traditional plate size with the product improvement due to the re-build of our 1000- ton hydraulic press. Through the use of this bi-directional press versus a uni-directional unit we were able to improve the consistency of the density throughout the thickness of the starting bar. This results in an improved, finished, cold-rolled plate with higher yields, and at a lower processing cost. The recent advancements in near-net shape PM rhenium using traditional powders show great promise for cost, time, and raw material savings. The successful

NASA Phase II SBIR development work will allow an increase in the use of advanced PM rhenium satellite propulsion chambers due to the lower cost and the improved deliveries.

The most significant advancement in PM rhenium is the development of the spherical, free-flowing, low oxygen, rhenium metal powder. This enabling technology will allow the use of advanced PM techniques that are currently being utilized for many other materials. The PM rhenium industry has been limited to relatively small size components in PM rhenium for 40 years due to equipment restrictions, the cost of producing large solid ingots and machining the finished parts, as well as the financial risk during processing. The development of SReP by Rhenium Alloys, Inc. will enable the military/aerospace community to enlarge the vendor base for PM rhenium components, improve competition, produce much larger near-net shape nozzles, and will also reduce overall costs.

## Conclusion

The field of PM rhenium has changed considerably in a short period and we look forward to an exciting future. The advancements in conventional powder processing with larger, higher density plates, near-net shape manufacturing, and improvements in other processing equipment have allowed us to be able to meet many of the challenges provided by today's design engineers. We look forward to producing rhenium components at a lower cost, in a wider variety of configurations, and with improved properties. The development of our spherical rhenium powder and the use of advanced PM techniques will enable us to utilize this relatively rare refractory metal even more effectively in many applications.

The unique properties of rhenium make it the material of choice for extreme service conditions such as tactical missile and launch vehicle throats, pintles, satellite thrusters, divert systems, large gun barrel liners, and nuclear applications. Until recently we have been unable to produce PM rhenium components large enough to be considered for many of these applications and the cost of using traditional methods was prohibitive. We will now be able to re-think how many of the components were produced in the past and look at new, more cost and material effective ways of producing them. The requirement in the near future for production quantities of many of these components demands that these advanced methods be developed. It will now be possible to accomplish that goal.

## Acknowledgements

The authors would like to acknowledge James Biaglow for his support and funding of Rhenium Alloys Inc. NASA Phase II SBIR and Dr. Carole L. Trybus of Concurrent Technologies Corporation for her technical assistance in characterizing and evaluating of powders. The Authors would also like to acknowledge Frank C. Danek, for their technical expertise, and advice in rhenium. The authors would like to thank Eric Blankenship for his editorial services, and finally the author wants to acknowledge Jan-C. Carlén for his support of the NNS and the spherical rhenium power program.

## References:

1. Davenport, W H, "Rhenium Sources and Methods of Extraction and Refining." American Institute of Mining, Metallurgical and Petroleum Engineers, February 1964
2. Bryskin, BD and Danek, FC, " Powder Processing and the Fabrication of Rhenium", JOM, Vol. 43, No. 7, July 1991 pp. 24-26

3. Grobstein, T., R Titran and J. R. Stevens, "Rhenium", Metals Handbook.
4. Chazen, ML, "Materials Property Test Results of Rhenium", AIAA Paper 95-2938, July 1995
5. Chazen, ML, and Sicher, D. " High Performance Bipropellant Engine", AIAA paper 98-3356, July 1998
6. Biaglow, JA, " High Temperature Rhenium Materials Properties", AIAA paper 98-3354, July 1998
7. Leonhardt, TA, and Carlén, JC, " Deformation Hardening and Process Annealing as Fundamental Elements in Rhenium Forming Technology", AIAA paper 98-3353, July 1998
8. ASM Handbook Vol. 7, Powder Metal Technology and Applications, 1998
9. Leonhardt, TA, Hamister, M. and Carlén, JC, " Near-Net Shape Powder Metallurgy Rhenium Thruster", AIAA paper 2000-3132, July 2000
10. Randall M. German, Powder Metallurgy Science, 2nd ed. 1984,pp110-117