



Spherical Rhenium Metal Powder

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Summary

The development of a high-density, spherical rhenium powder (*SReP*) possessing excellent flow characteristics has enabled the use of advanced processing techniques for the manufacture of rhenium components. The techniques that were investigated were vacuum plasma spraying (*VPS*), direct-hot isostatic pressing (*D-HIP*), and various other traditional powder metallurgy processing methods of forming rhenium powder into near-net shaped components. The principal disadvantages of standard rhenium metal powder (*RMP*) for advanced consolidation applications include: poor flow characteristics; high oxygen content; and low and varying packing densities. *SReP* will lower costs, reduce processing times, and improve yields when manufacturing powder metallurgy rhenium components. The results of the powder characterization of spherical rhenium powder and the consolidation of the *SReP* are further discussed.

Keywords: Rhenium, spherical metal powder, powder metallurgy, vacuum plasma spray, hot isostatic pressing, laser additive manufacturing

Introduction

Rhenium is one of the last naturally occurring elements to be found, and the discovery occurred in 1925 by Ida Tacke, 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 3453 K, and has the highest modulus of elasticity of all the refractory metals. It does not

form a carbide, even when exposed to methane and 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 of 99.99%. The -200 mesh RMP has an average particle size of 3.5 μm and an apparent density 1.84 g/cm^3 with a tap density 3.03 g/cm^3 (Figure 1) (7).

Due the inherent characteristics of rhenium metal powder (RMP), products made from rhenium have only been manufactured in a few basic forms to include: rod; bar; plate; sheet, foil and wire (Figure 2). To produce complex shapes, basic rhenium products are machined to specified dimensions and tolerances. A significant amount of scrap rhenium is created to produce a single complex component. Numerous attempts involving the use of RMP in advanced NNS techniques have met with very limited success (8,9), so a need has risen to exam other, more effective and more efficient means of manufacturing rhenium metal powder.

SEM Courtesy of CTC

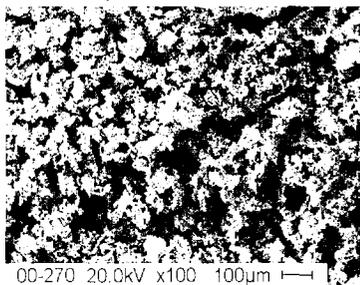


Figure 1: Rhenium metal powder

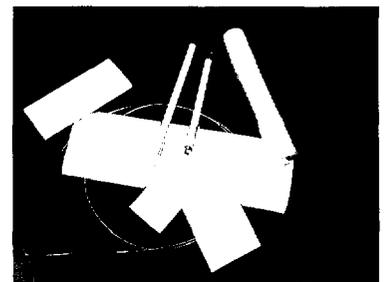


Figure 2: Rhenium products, plate, rod, sheet, foil and wire

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 of particle sizes.

Procedure:

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/cm³ with an apparent density of 11 g/cm³, 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/gas-assisted rotating electrode process (REP/PREP/GA-REP)(10,11). 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 GA-REP was investigated as a means to reduce the droplet size and can be described as a secondary atomization process (11). Typical particle size for the rotating electrode process is 200-600 micrometers, with bi-modal distribution (11).

To produce *SReP* by rotating electrode/plasma rotating electrode process (REP/PREP/GA-REP), Rhenium Alloys, Inc began with 96 Kg of 16 (30.5 mm), 7 (38 mm), and 4 (50 mm) rhenium rods. These rods were fed into the centrifugal atomizer through a collet and melted down to a length of 60 mm. To evaluate the particle sizes produced by different diameter rhenium rods the powder was individually collected by rod diameter size, and placed into separate containers.

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 micrometers was produced, but a wide range of particle size, ranging from 5-80 micrometer, can also be produced with the PA process (11).

Advance Consolidation Methods

Two (2) non-traditional methods of producing NNS rhenium objects were examined, as was the traditional die compaction method with the use of *SReP*. The first process investigated was that of vacuum plasma spraying (VPS). VPS is an excellent choice for metals that readily oxidize, and/or have high melting points. Under VPS conditions, the chamber is evacuated and then the chamber is back-filled with argon, or an argon/hydrogen mixture. Thus, by the use of a reducing atmosphere, the plasma will decrease the amount of oxygen present, and increase the heat transfer to the powder. Due to the high heat transfer of the VPS method, the powder is melted and at a high velocity contacts the substrate to form a splats structure that produced a dense coating.

The second method investigated was direct-hot isostatic pressing (D-HIP) (11). In this method, a high-temperature metal container capable of being formed into complex shapes is used as a containment vessel for the powder. The *SReP* can be poured directly into the HIP container. The container is then evacuated and sealed. After HIPing the can is removed from the rhenium part. The high-density and the low-oxygen content of the *SReP* will produce a high quality rhenium parts.

Traditional die-pressing was also examined to help increase our understanding of the properties of *SReP*. Several compactions were produced to examine particle interaction as well as particle size distribution in the compact, and further understand how these compaction parameters influences both the green and sintered densities of the compacts. Predictably, die-compactions of *SReP* were of particular interest, due to the enormous potential for highly complex, high-volume precision parts and components being manufactured by this method.

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 3). 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/cm³ or greater; and the production of spherical rhenium powder particle possessing high flow characteristics. As shown in table 1, the tap, apparent densities and flow data are 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 micrometer for the 50mm diameter rod; 161 micrometer for 38mm diameter; and 241 micrometer for the 30mm diameter. In addition, the majority of the *SReP* was in a 100 to 300 micrometer diameter range, with both the tap and apparent densities being very similar. This is typical for most spherical metal powders.

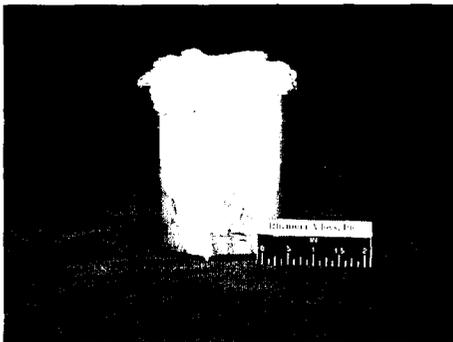
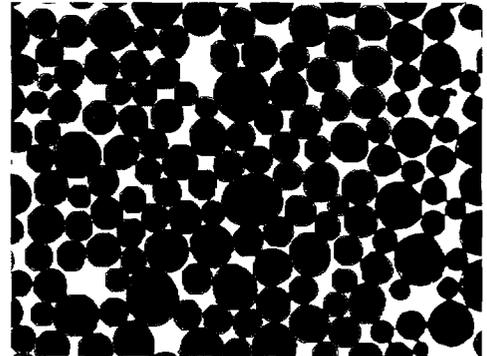
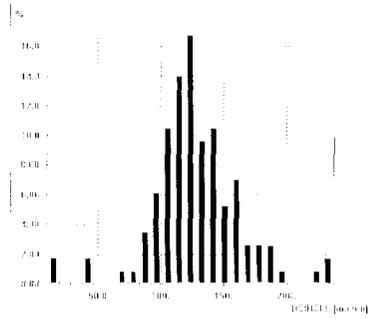


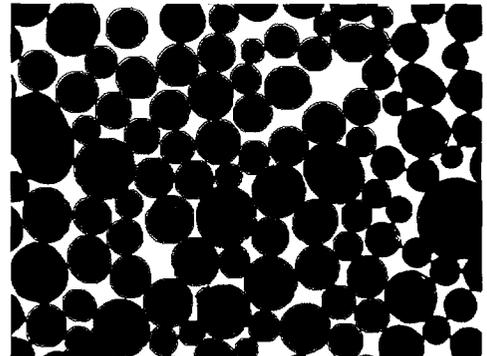
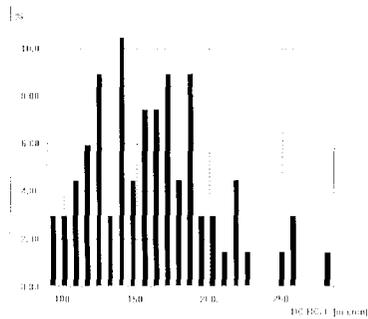
Figure 3: A melted rhenium rod 50 mm diameter from the Plasma rotating electrode process.

Table 2: Image analysis of Rotating Electro Processed SrP by rod diameter

50 mm



38 mm



30 mm

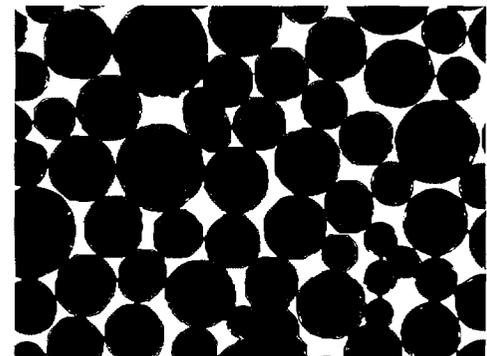
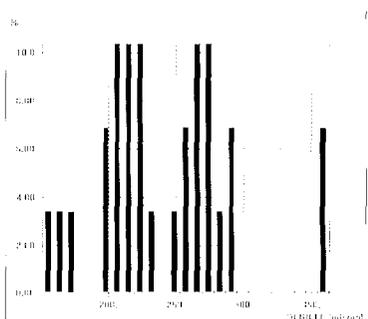


Table 1: Characterization of SReP by particle size

Mesh	Micrometer	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

Plasma Atomized Process

During the initial phases of the experimentation with plasma atomization of SReP, two experimental powders were produced, type A and type B.

The plasma-atomized spherical rhenium powder had a particle size of 37 micrometers \pm 17 micrometers for type A (figure 4) and 25 micrometers \pm 8 micrometers for type B (figure 5). The apparent density for type A was 10.27 g/cm³ and for type B 10.37g/cm³. The tap density for type A was 11.60g/cm³ and for type B 12.12 g/cm³. 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 the flow characteristics are reduced. In contrast to the SReP, the traditional rhenium metal powder has an apparent density of 1.84 g/cm³ and a tap density of 3.03 g/cm³, which is significantly less than the SReP.

SEM Courtesy of CTC

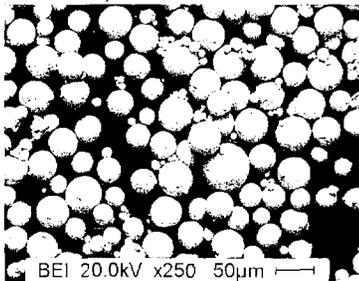


Figure 4: Type A PA-SReP

SEM Courtesy of CTC

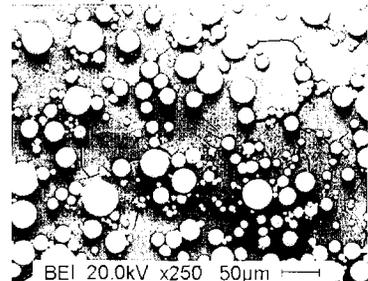


Figure 5: Type B PA-SReP

Advance 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 6, a flat coupon and a tube were VPS-ed to a maximum thickness of 5mm. In (figure 7) the microstructure of the VPS-ed *PA-SReP* is displayed.



Figure 6: VPS flat coupon and tube

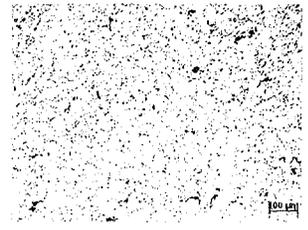


Figure 7: microstructure of VPS rhenium tube

The second experiment conducted involved the direct-hot isostatic press (D-HIP) of the B type *PA-SReP* into a 19mm diameter rods. Hot isostatic pressing containers were filled with *SReP*, evacuated, and then sealed (figure 8). A density of 98% was achieved using the D-HIP process for the *PA-SReP*. As shown in (Figure 9), the microstructure of the direct hot isostatic pressed rod had a larger grain size and illustrated final sintering.

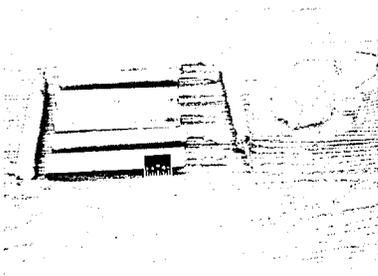


Figure 8: D-HIP container, filled and sealed with type B *PA-SReP*

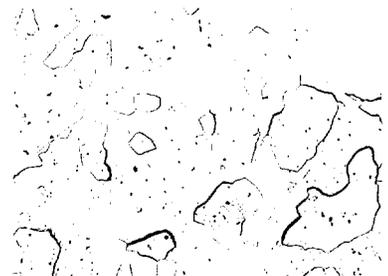


Figure 9: Microstructure of D-HIP experiment with Type B *PA-SReP*

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 a 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 displayed in (figure 10) illustrates the deformation from die compaction of the spherical powder, and some necking of the powder particles after pre-sintering. 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 11).

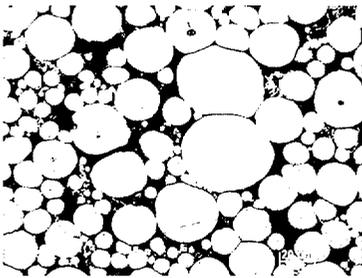


Figure 10: microstructure of pre-sintered pellet



Figure 11: microstructure of sintered pellet

Discussion

The experiments with REP/PREP/GA-REP produced SReP, but the yields were only 58% and the particle sizes, ranged from 100-300 micrometers in diameter. The size is too large for a majority of NNS applications. The REP-SReP particle size is too large for vacuum plasma spray applications because the residence time in the plasma will not be long enough to melt the large particle. If too large of a particle is used, the coating will either be extremely porous with non-melted powder particles or the powder particles will bounce off the substrate.

Typically, the particle size range for VPS is 10 to 50 micrometers, which is what the plasma atomization process provides, while direct-hot isostatic pressing can use small percentages of the REP *SReP* in bi-modal or multi-particle size blends with the smaller powder from the PA-*SReP*. Again, smaller particle sizes are preferred to produce a high-density (D-HIP) part, but to increase flow a small percentage of larger powder particles can be used.

The larger particle sizes produced by the REP/PREP/GA-REP are excellent for Directed Light Fabrication (9) and Laser Additive Manufacturing (12), which require a particle size of 100 to 300 micrometers. In these processes, a laser melts the rhenium powder to build up a 3-Dimensional rhenium part or component.

The *SReP* from the plasma atomization process is better suited for a majority of the applications for these types of advanced consolidation techniques. The overall cost of PAP-*SReP* is less than that of *SReP* made by the REP/PREP/GA-REP process, the *SRePs*' made by either process has excellent properties that include low oxygen content, high density and flow characteristic of 5 sec/50 grams of powder.

Conclusion

The REP/PREP/GA-REP processes produce *SReP*, but presently the yields are too low to ensure a successful production environment and economy. Further, the REP-*SReP* has limited uses due to its larger particle sizes. The powder is being used in experiments involving Laser Additive Manufacturing (12), which requires a powder possessing high flow characteristic and particle size range of 100 to 300 micrometers. However, if these experiments prove to be successful, and it is found that the plasma atomization process can not provide powder particles of the sizes required for the and LAM methods, a more economical means of processing rotating electrode process should be developed.

Fortunately, the PA-*SReP* manufacturing method can be fine-tuned to provide the user with the ideal particle size for the unique and diverse material requirements and process specifications mandated by the various advanced consolidation techniques presently in use today. Further, PA-*SReP* presents an additional economic benefit in that it is the more effective, more efficient

and much less costly method for the processing and production of *SReP*, far surpassing the levels achieved by the REP/PREP/GA-REP manufacturing technique.

Acknowledgements

The Authors would like to acknowledge 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, James J. Downs, 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 spherical rhenium power program.

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