Production of Porous Refractory Metals with Controlled Pore Size

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Abstract:

High porosity Nb, Mo-Re, and Ir metals with controlled pore size have been produced in various shapes by a powder metallurgy method. Production of these materials involves tailoring the size of powders to attain the correct green pore size for a given packing density through various combinations of presintering, milling, or sieving. Powders were slurry cast into soft tooling to create complex shapes and test pellets, which were then debound and vacuum sintered to the desired density and pore size. With these techniques, densities as low as 35 % may be attained. In the case of spherical powders, the pore size can be accurately predicted using a particle packing equation. In the case of non-spherical powders, the equation predicts a pore size larger than measured.

Background:

The green pore size of a powder compact is a function of particle size, particle shape, particle size distribution, and packing density. Given the particle size *D,* and packing density *f*, the mean pore size *d* can be estimated by the following equation [1]:

$$d = \frac{2}{3} \cdot \frac{D \cdot (1 - f)}{f} \qquad \text{(eq. 1)}$$

This equation assumes that the particles are monosized spheres, but may be used as a first approximation of pore size. The equation may also be used to predict the pore size of a presintered structure, since particle shape is only slightly altered in the presintering process. In this case the sintered density replaces the packing density, *f*, in the equation.

Experimental Procedure

One Ir powder, two Nb powders, and one Mo-49Re powder were used in this study. Each powder was processed to alter its particle size distribution before sintering. The powders are listed in Table I with the particle size analysis in the as-received condition. It is important to note that the Ir powder and the 7μm Nb powder both contained amounts of agglomerated sub-micron particles, which were interpreted as discreet particles by laser scattering wet particle size analysis. This caused the particle size measurement to indicate a larger particle size than actually existed. Ultrasonics were used to decrease the severity of agglomeration prior to testing.

Powder Processing

Niobium

The 7μm Nb powder was first presintered by heating 5°C/min to 300°C, 2°C/min to 800°C for 1 h and 10°C/min to 1050°C for 1 h. This cycle served to dehydride and deoxidize the powder, and sinter the finest particles to the larger particles or to themselves, eliminating the agglomerated sub-micron particles. Presintering of the powder did not result in a hard cake. The soft cake was returned to powder condition upon removal from the sintering crucible. No significant changes in particle size were observed, however, the particle size was increased, since the agglomerated fine particles were eliminated. The -45 μm (-325 mesh) Nb powder was sieved to +/- 32 μm (450 mesh) to create 2 particle size distributions. The particle size analyses of all three powders are given in Table I.

Mo-49Re

The Mo-49Re powder was specified as -20μm (–635 mesh) in the as-received condition. Because of the powder's tendency to agglomerate, most of the powder would not go through a 635 (20μm) screen. Two new particle size distributions were obtained by sieving with a 450 (32μm) screen, and taking the +450 and –450 portions. The particle size distributions are given in Table II.

Iridium

The iridium powder as-received was highly agglomerated, much more so than the 7 μm Nb powder. In order to reduce the agglomeration and increase the particle size, the powder was presintered at 1000°C in 10^{-4} Torr vacuum tube furnace, resulting in a presintered powder cake. Break-up of the cake was performed by pushing the cake through a 20 mesh sieve with milling rods, then rod milling for 10 minutes. The particle sizes before and after this process are given in Table I. The particle size did not change significantly, however, the as-received particle size measurement was effectively measuring the agglomerate size.

Table I
Powder Characteristics

Sample	D_{10}	D_{50}	D_{90}	Shape
Ir, as received	3.7	8.5	16.8	Agglomerated
Ir, presintered at 1000°C and milled	3.6	8.4	17.5	Sintered agglomerates
Nb, 7 μm, as received	3.2	6.7	12.1	Rounded, irregular
Nb, 7 μm, presintered at 1000°C	3.3	6.4	10.9	Rounded, irregular
Nb, -45 μm, as received	23.1	39.5	63	Angular
Nb, –32 μm sieved	18.9	31.1	47	Angular
Nb, -45 μm, +32 μm sieved	31.2	45	66	Angular
Mo-Re, as received	5.3	9.8	15.6	Spherical
Mo-Re –32 μm sieved	7.2	13.7	20.3	Spherical
Mo-Re +32 μm sieved	9.2	16.6	28.1	Spherical

Slurry Casting

Slurry casting was used to produce the samples, to allow for low green density and shape complexity. In this process, powder is mixed with melted wax and poured hot into a rubber mold, avoiding the need for hard tooling. Some settling of the powder occurs before the wax solidifies. The resulting green density for each material is given in Table II. All slurry was cast at 110°C into a mold preheated to 80°C and allowed to cool at room temperature. The piece was ground down to the correct height, allowing for removal of the low density material on top due to powder settling. Cylinders with a diameter of 4 mm were cast for use in all green density, sintered density, and porosimetry measurements. Complex shapes produced were 7 cm diameter discs with and without circular surface corrugations.

Debinding and Sintering

Niobium

Debinding and presintering were performed by surrounding the part in 10 μm alumina powder and heating at 2°C/min to 120°C for 1 h, 2°C/min to 250°C for 1 h, 1°C/min to 450°C for 1 h, 5°C/min to 1125°C for 1 h, and 10°C/min to 20°C in high purity argon. The parts were removed from the alumina packing and heated at 5°C/min to 1350°C or 1450°C for 1 h in 10^{-5} Torr in an all-metal construction vacuum furnace with Mo heating elements.

Mo-49Re

Debinding was performed by surrounding the parts in 10 μm alumina powder and heating at 2°C/min to 120°C for 1 h, 2°C/min to 250°C for 1 h, 1°C/min to 450°C for 1 h, 5°C/min to 1200°C for 1 h, and 10°C/min to 20°C in high purity argon. The parts were then presintered in the alumina packing at 1500°C for 4 h in 10^{-5} Torr.

Iridium

Debinding and presintering were performed by surrounding the parts in 10 μm alumina powder and heating at 2°C/min to 120°C for 1 h, 2°C/min to 250°C for 1 h, 2°C/min to 450°C for 1 h, 5°C/min to 1100°C for 1 h, and 10°C/min to 20°C in high purity argon. Parts were removed from the alumina before heating at 5°C/min to 1200°C or 1300°C for one hour in 10^{-5} Torr.

Sample Evaluation

Green density and sintered density were measured by Archemedes technique, while sintered pore size was evaluated by mercury porosimetry.

Results

Table II summarizes the sintered samples and their properties. Pore size was predicted based on equation 1, substituting the sintered density for the packing density, and using the average particle size. Since the samples are all in the presintered state, this is a reasonable approximation. During the presintering stage, the pore size and particle shape do not change significantly, since surface diffusion is dominant [2]. There is a small increase in density from the green to sintered condition, and this is a combination of constriction of the compact as wax is removed in debinding, and sintering shrinkage. Metallography indicates that no real particle morphology changes have occurred, only sintering necks have been formed. In general, the predicted pore size is larger than the measured pore size. Only the Mo-Re powders are spherical. It is observed that the best agreement with the equation is observed with the Mo-Re powders. The worst agreement is observed with the 31 μm and 45 μm Nb powders that are very angular in shape.

Table II
Sintering Results

Material	**D_{50} Particle Size, (μm)**	**Green Density, (%)**	**Sintering Condition**	**Sintered Density, (%)**	**Measured Average Pore Diameter, (μm)**	**Predicted Average Pore Diameter, (μm)**	**Predicted/ Measured Ratio**
Mo-49Re	9.8	45	1500°C 4 h	61	3.4	4.1	1.21
Mo-49Re	13.7	48	1500°C 4 h	56	5.8	7.2	1.24
Mo-49Re	16.6	44	1500°C 4 h	57	7.9	8.2	1.04
Nb	6.4	34	1350°C 2 h	43	3.5	5.6	1.63
Nb	6.4	33	1450°C 2 h	52	2.5	3.8	1.52
Nb	31	46	1450°C 2 h	52	10.2	19.0	1.87
Nb	45	44	1450°C 2 h	49	13.2	31.2	2.37
Ir	8.4	33	1200°C 1 h	35	5.8	10.2	1.77
Ir	8.4	33	1300°C 1 h	46	3.4	6.4	1.87

Discussion

The findings indicate that equation 1 may be used to predict the presintered pore size if the particles are spherical or near spherical. The sintered density is substituted for the packing density. In the case of the Ir, where agglomerates were sintered, a bimodal pore size resulted because the pores within the agglomerates were smaller than those between the agglomerates. Since the measured particle size reflects the size of the agglomerates, the porosity within the agglomerates is not accounted for in the prediction of pore size. This would explain why the predicted pore size is larger than the measured pore size by a factor of 1.77 at 1200°C and 1.87 at 1300°C. It is observed that as the Nb particle size increases, the particles become less spherical and more angular. Correspondingly, the predicted pore size becomes increasingly oversize as the particles become less spherical.

Conclusions

This investigation shows that porous Nb, Mo-49Re, and Ir may be produced by slurry casting into soft tooling and vacuum sintering. The pore size and density can be controlled by adjusting the particle size, packing density, and sintering temperature. In the case of spherical or near spherical powders, the pore size can be accurately predicted by a particle packing equation.

References

1. R. M. German, *Particle Packing Characteristics*, Metal Powder Industries Federation, pp. 298-300, 1989.

2. R. M. German, *Sintering Theory and Practice*, John Wiley & Sons, pp. 12-13, 1996.