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Plasma Alloying and Spheroidization Process and Development

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Elemental and blended refractory metal powders were processed using a plasma alloying and spheroidization (PAS) process. The powders were characterized to determine changes in chemistry and morphology after processing. Five refractory metal powders were evaluated during this investigation: (1) crystalline W, (2) spray dried Mo, (3) W-25 wt.% Re composite powder, (4) W-2 wt.% Re composite powder, and (5) Mo-40 wt.% Re composite powder. Benefits of the PAS process, such as a two-order of magnitude reduction in oxygen contamination, production of highly spherical powders for enhanced flow characteristics, and the ability to produce prealloyed powders were demonstrated.

Keywords plasma alloying, prealloyed powder, refractory metal powder, spherical powder, spheroidization

1. Introduction

Free-flowing powder feedstock is desired to improve process repeatability and handling for many applications. In addition, prealloyed powders are desired.[1-3] Until very recently, it has been difficult to manufacture certain alloy compositions, e.g., refractory metal alloys.[4] To address these concerns, a plasma alloying and spheroidization (PAS) process has been developed and evaluated, leading to the production of prealloyed, spherical powders.[5]

During PAS, powder feedstock is fed into a plasma stream where melting occurs and surface tension causes spherical droplets to be formed. It is during this molten stage of the process that alloying takes place. As the droplets pass out of the plasma, they rapidly solidify and are collected. To minimize oxidation of the feedstock during processing, the PAS process is conducted in a vacuum or an inert atmosphere for oxygen-sensitive materials. For less oxygen-sensitive materials, PAS processing can be performed at ambient conditions. If needed, auxiliary cooling gases can be used to enhance powder cooling.

An inert gas such as argon is typically used to form the plasma. Secondary gases can be used, such as hydrogen, to promote higher temperature plasma and a reduction of oxide scale on the powder feedstock surface.

2. Experimental Procedure

Five refractory metal powders were evaluated during this investigation: (1) crystalline W, (2) spray dried Mo, (3) W-25 wt.% Re composite powder, (4) W-2 wt.% Re composite powder, and (5) Mo-40 wt.% Re composite powder. Because refractory metals are sensitive to oxidation, these powders were PAS processed in vacuum and inert atmospheres. Detailed descriptions of the powders are given in Table 1.

To characterize the flowability of the powders, the Hall flow test was used. This test measures the time necessary for a given amount of powder to pass through a critical orifice as a result of gravity.

Both optical and scanning electron microscopy (SEM) techniques were used to examine the powders. Image analysis software was used to determine quantitative data about the powders, such as particle size, and the amount of melted and unmelted particles after PAS. In addition, electron dispersive spectroscopy (EDS), Leco oxygen analysis, and glow discharge mass spectroscopy (GDMS) were used to determine compositional data about as-received and PAS powders.

3. Results and Discussion

3.1 Flowability Analysis

Flowability of a powder is critical because it affects process repeatability, which in turn determines the scrap rate of a production technique. Highly flowable powders will result in good repeatability, thus reducing scrap. Several characteristics affect the flowability of a powder including, but not limited to, morphology, density, particle size/distribution, and electrical properties. For metal powders, morphology has a major influence

Table 1 Description of Starting Powders

Composition	Description	Particle Size, µm
W	Crystalline	−45
W-25Re	Composite(a)	−45/+15
W-2Re	Composite(a)	−45
Mo	Spray dried	−38
Mo-40Re	Composite(a)	−45/+15

(a) Elemental blend with 1-2% organic binder

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Table 2 Hall Flow Test Results for As-Received and PAS Powders

	Flowability, g/s	
Composition	As-received	PAS Processed
W	No flow (Failed)	100 g/10 s (Passed)
W-25Re	No flow (Failed)	100 g/10 s (Passed)
W-2Re	No flow (Failed)	100 g/11 s (Passed)
Mo	No flow (Failed)	50 g/20 s (Passed)
Mo-40Re	No flow (Failed)	100 g/15 s (Passed)

on flowability, with spherical shaped powder particles resulting in maximum flow characteristics.

Table 2 shows the results of the Hall flow tests. All five powders were tested in the as-received condition and after PAS processing. Note that all the powders in the as-received conditions resulted in no flow, i.e., failure of the test, which translates to inconsistent powder flow during processing. In contrast, all the PAS powders passed the flow test demonstrating excellent flow characteristics. Thus, PAS powders demonstrated the necessary improved flow needed for increased productivity and better repeatability during manufacturing.

3.2 Tungsten Crystalline Powder

To develop a baseline for the PAS process, the initial experiments were conducted with W crystalline powder. A SEM backscattered image of the as-received W crystalline powder is shown in Fig. 1. This figure shows the blocky, faceted powder morphology of the as-received powder. For comparison, Fig. 2 shows the W powder after PAS processing. In contrast to the faceted particles of the as-received W powder, the PAS particles are near perfectly spherical in shape, which results in excellent flow characteristics. The beneficial spherical shape is formed as a result of surface tension forces due to particle melting as it is fed into the plasma. As the particle passes out of the plasma, the particle solidifies rapidly, which prevents distortion of the spherical shape as the powder is collected.

3.3 W-Re Composite Powders

A SEM backscattered image of the as-received W-25Re composite powder is shown in Fig. 3. The composite powder comprises large W particles (blocky/faceted morphology), smaller Re particles (flake-like morphology), and an organic binder. However, as can be seen from Fig. 3, the as-received powder more closely resembles an elemental blend with few, if any, Re coated W particles. Figure 4 shows the same W-25Re powder after PAS processing. Similar to the W crystalline powder results, the PAS process produced highly spherical W-Re particles with excellent flow characteristics. Because Re and W have similar densities (ρ_{Re} = 21.0 g/cm^3 and ρ_W = 19.3 g/cm^3), EDS analysis was unable to determine the composition of individual powder particles. Similar results were obtained for the W-2Re material.

3.4 Spray Dried Molybdenum Powder

The spray dried Mo powder was evaluated to determine the effect the PAS process has on spray dried powder. Figure 5 shows a SEM backscattered image of the as-received spray dried Mo powder. Note that each powder particle is composed of many smaller particles that have been agglomerated as a result of a spray drying process. Although the agglomerated particles are primarily spherical in shape, the as-received powder possessed poor flow characteristics.

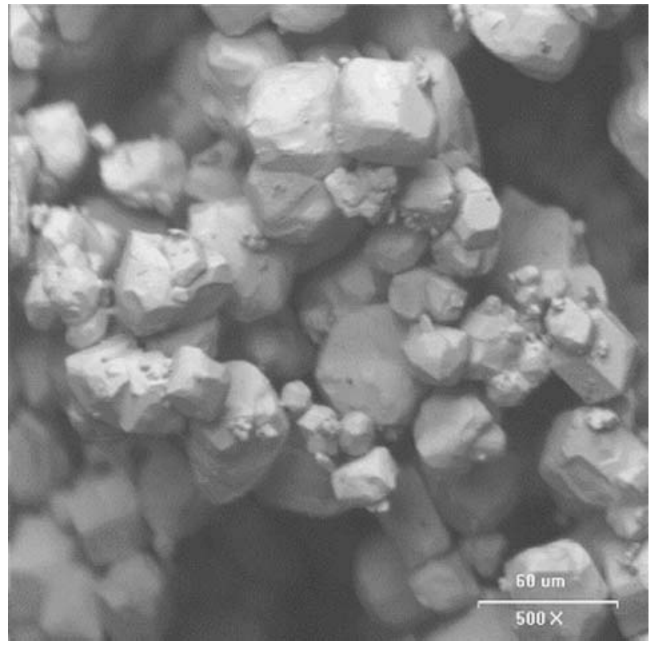

Fig. 1 SEM backscattered image of as-received tungsten crystalline powder showing blocky, faceted powder particles

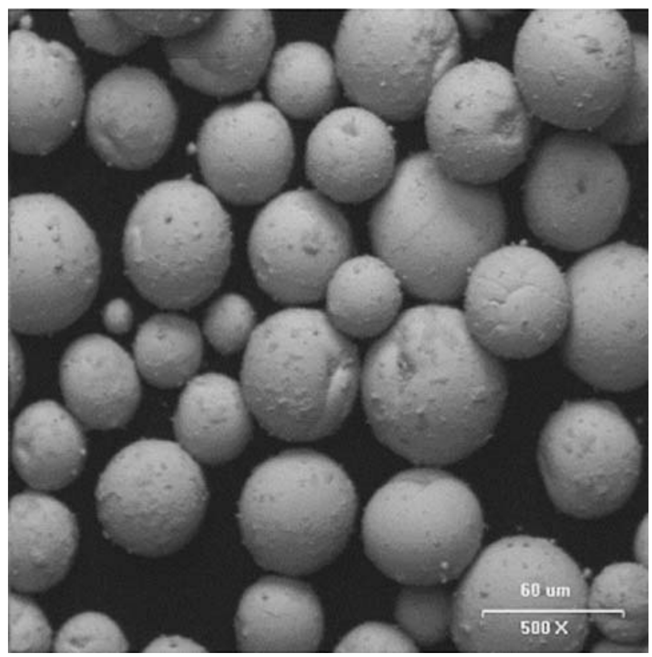

Fig. 2 SEM backscattered image of tungsten crystalline powder after PAS processing. Highly spherical powder particles were produced.

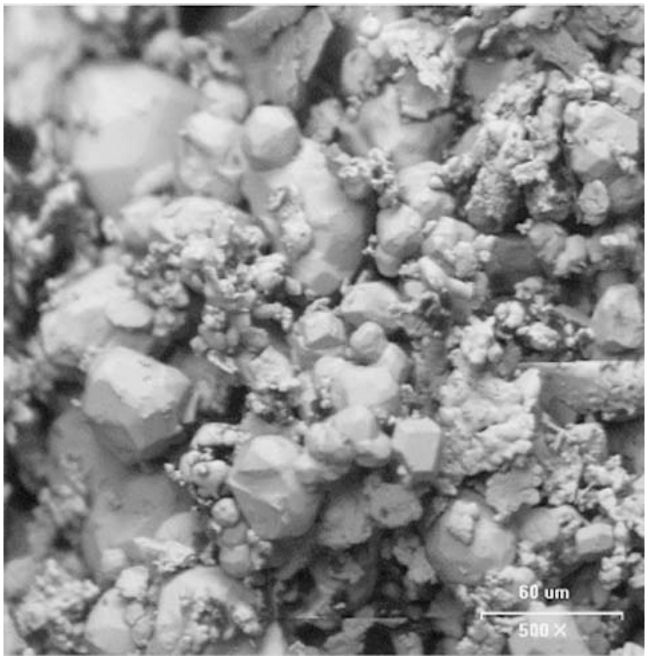

Fig. 3 SEM backscattered image of W-25Re composite powder in the as-received condition. The composite comprises blocky, faceted W particles, flake-like Re particles, and a 1-2% organic binder.

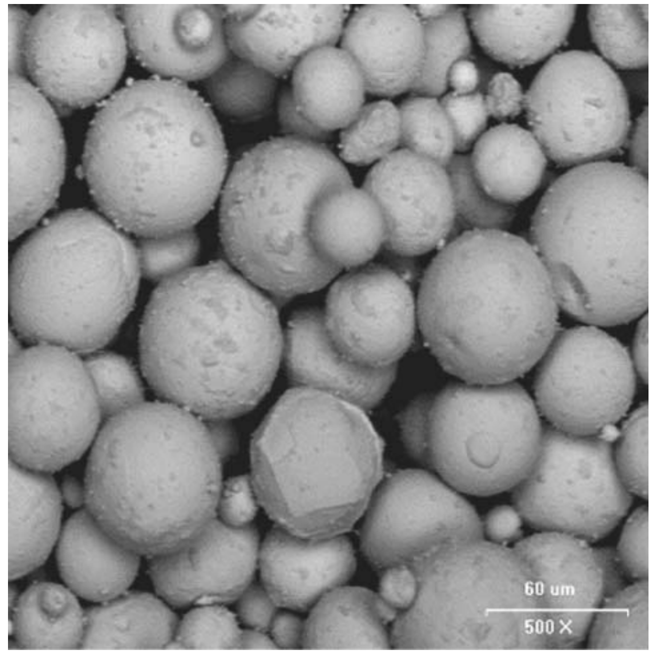

Fig. 4 SEM backscattered image of W-25Re powder after PAS processing. The PAS process produced highly spherical W-25Re powder particles.

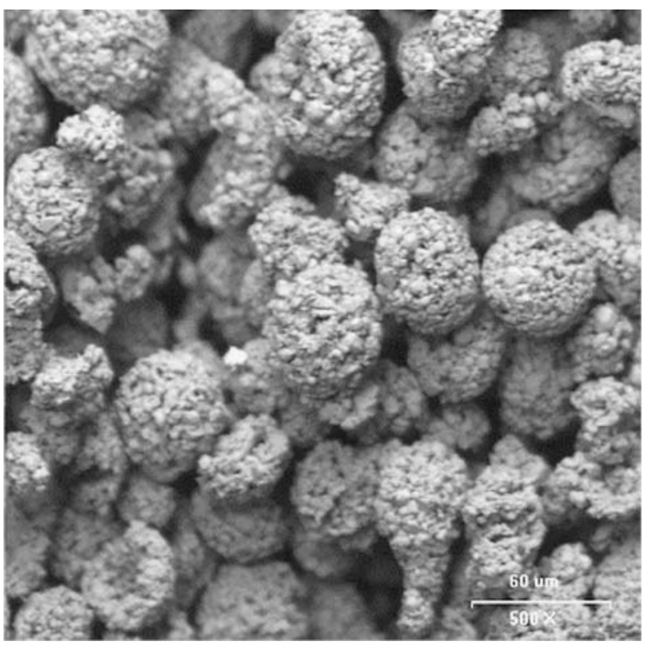

Fig. 5 SEM backscattered image of spray dried Mo powder in the as-received condition. Each spray dried particle comprises smaller (<10 μm particle diameter) agglomerated particles.

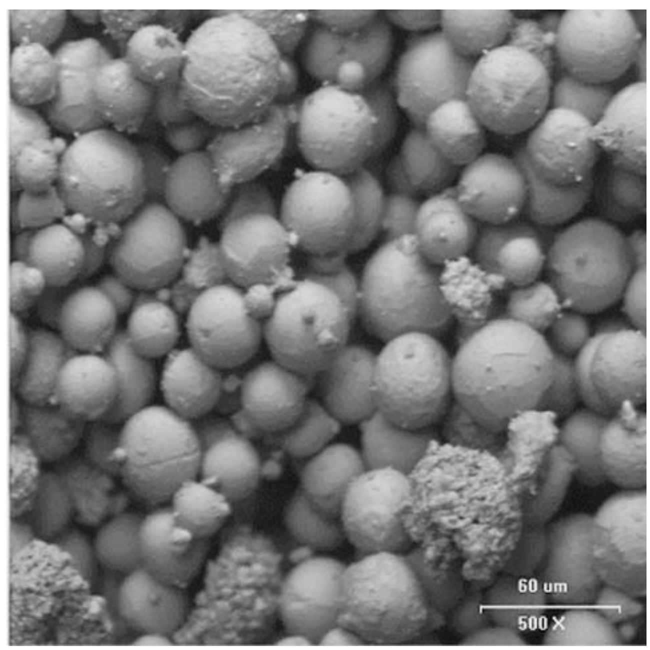

Fig. 6 SEM backscattered image of spray dried Mo powder after PAS processing. Note the agglomerated particles of the as-received powder have been converted to solid Mo particles, which significantly reduces the overall surface area and the level of oxygen contamination.

Figure 6 is a SEM backscattered image of the spray dried Mo powder after PAS processing. PAS processing eliminated the agglomerated particles and replaced them with solid Mo particles. Because each spray dried particle is composed of many smaller powder particles (<10 μm diameter), the amount of surface area is significantly more for an agglomerated particle than for a solid particle of the same size. With oxygen-sensitive materials such as the refractory metals, more surface area results in more oxygen contamination. Therefore, a spray

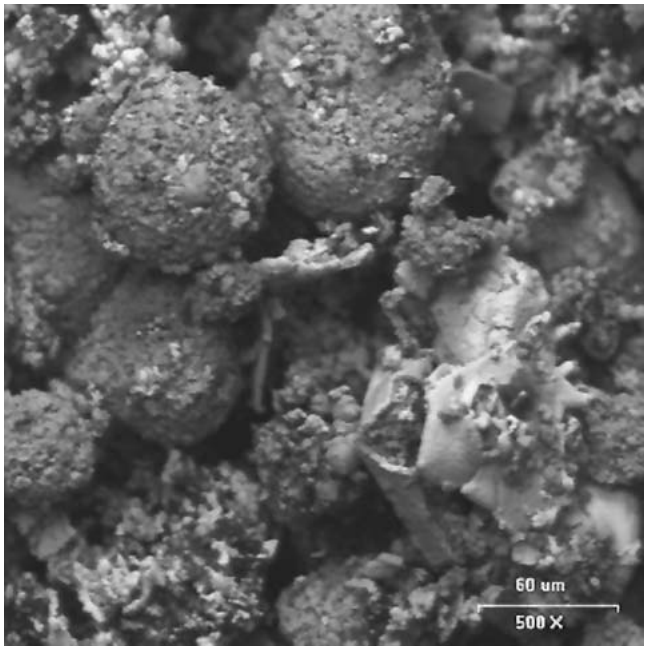

Fig. 7 SEM backscattered image of as-received Mo-40Re composite powder

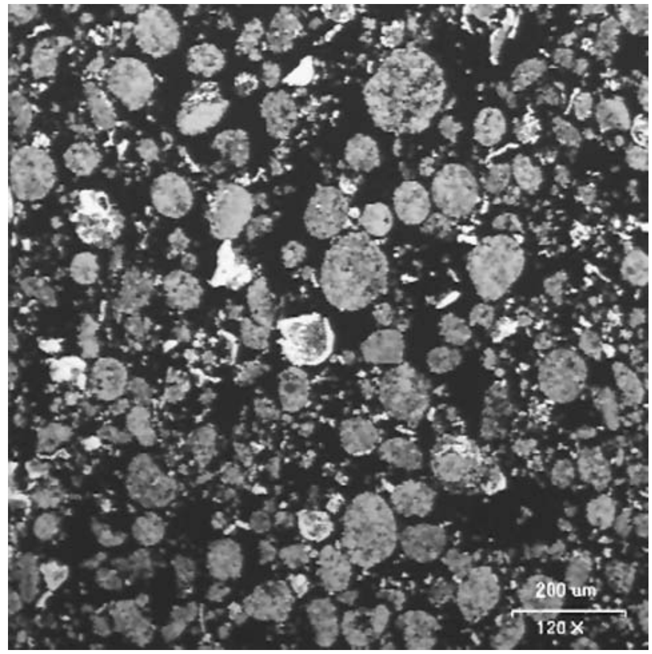

Fig. 8 SEM backscattered cross-sectional image of as-received Mo-40Re composite powder showing the nonuniform contact of the Re flakes with the spray dried Mo particles

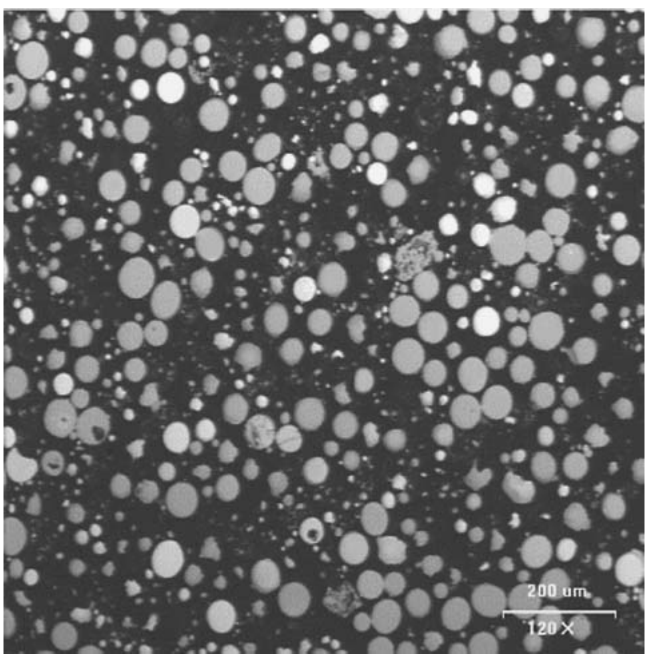

Fig. 9 SEM backscattered image of cross-sectional view of Mo-40Re powder after PAS processing showing highly spherical, dense particles produced with the PAS process

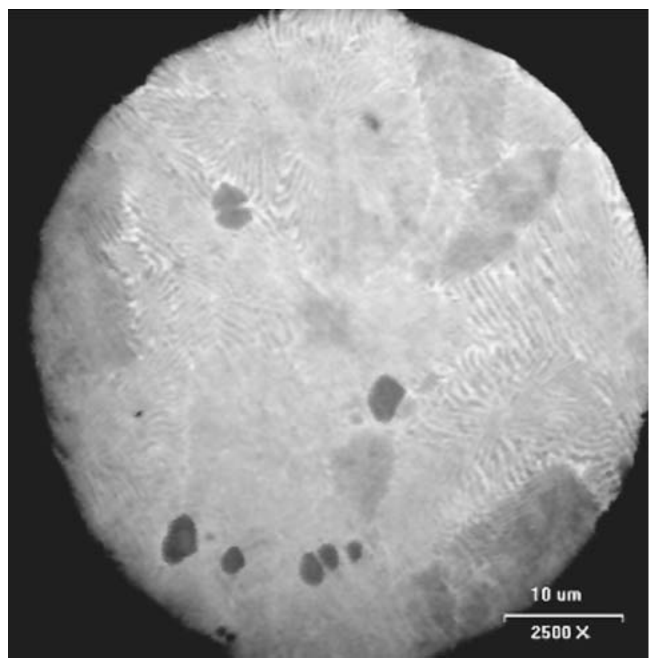

Fig. 10 High-magnification (2500×) SEM backscattered image of Mo-40Re powder after PAS processing showing evidence that Re and Mo are present in each particle

dried Mo particle will have much higher oxygen content than a solid Mo particle of the same diameter. The next section will detail lower oxygen content for PAS Mo-40Re powders. Thus, components made with the PAS powder will have lower oxygen contents, which translate into better properties and improved performance.

3.5 Mo-40Re Composite Powder

Due to the large difference in densities of Mo and Re (ρ_{Mo} = 10.2 g/cm^3 and ρ_{Re} = 21.0 g/cm^3), compositional information was obtained from SEM backscattered images and EDS analysis for the Mo-40Re powder. Figure 7 is a SEM

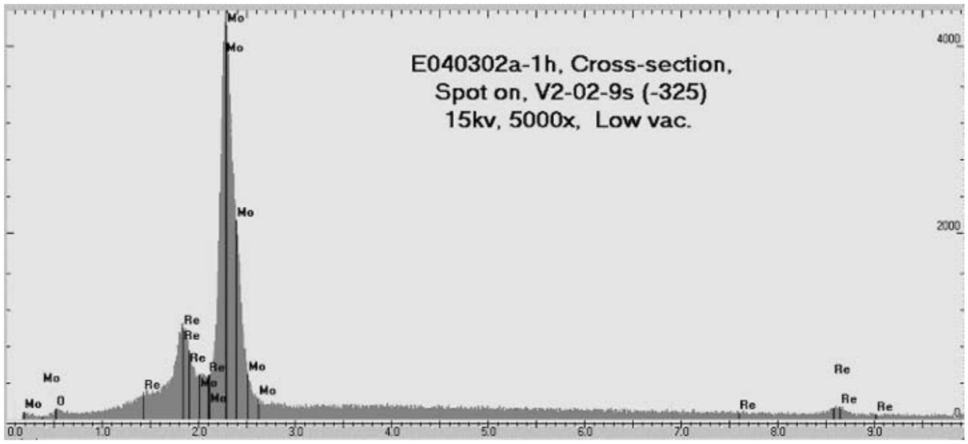

Fig. 11 EDS spectrum for a dark gray Mo-Re particle after PAS processing; estimated particle composition of Mo-19Re

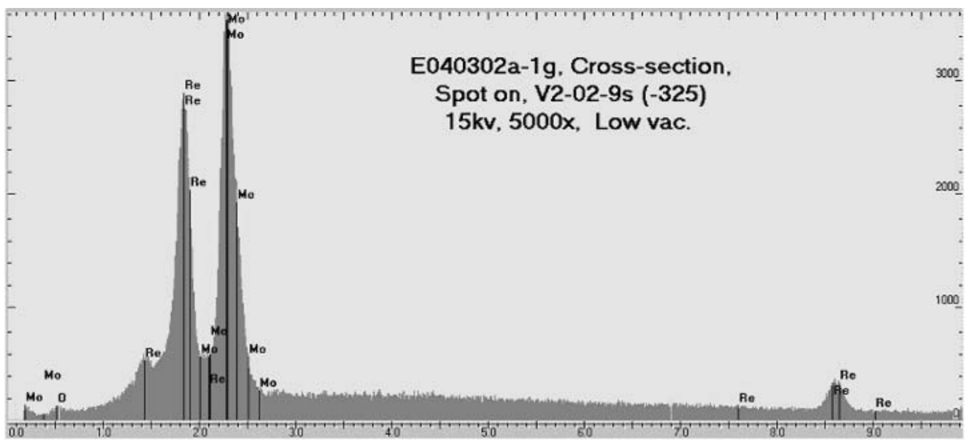

Fig. 12 EDS spectrum for a medium gray Mo-Re particle after PAS processing; estimated composition of Mo-45Re

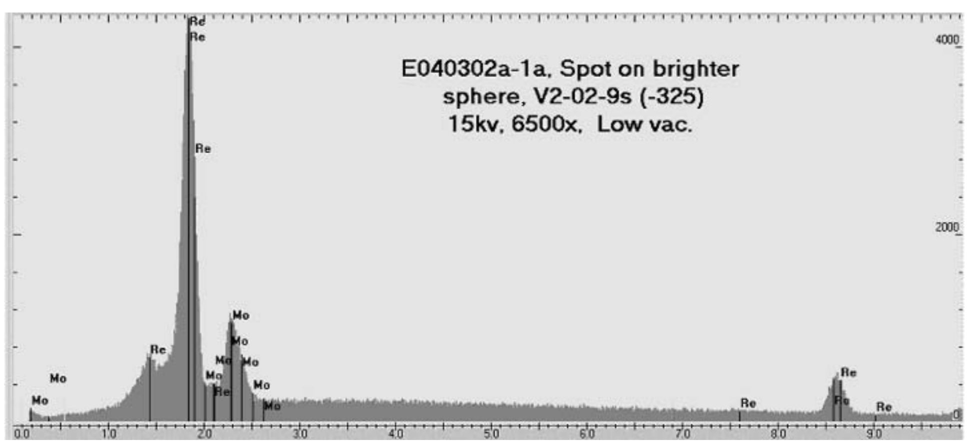

Fig. 13 EDS spectrum for a light gray Mo-Re particle after PAS processing; estimated composition of Mo-78Re

backscattered image of the Mo-40Re composite powder in the as-received condition. The lighter gray, flake-like particles are Re, while the darker gray, agglomerated particles are Mo. Figure 8 is a SEM backscattered image of a cross section of the as-received Mo-40Re powder. The cross-sectional image clearly shows the presence of porosity in the agglomerated Mo particles and a nonuniform distribution of the smaller, flake-like Re. The latter case will have a significant effect on the ability to produce individual prealloyed particles with the proper chemical composition.

A SEM backscattered image of a cross section of PAS Mo-40Re is shown in Fig. 9. Similar to the previous discussions, the PAS process produced highly spherical, dense Mo-40Re particles. Due to the density difference between Mo and Re, the backscattered image also reveals compositional information about each powder particle; i.e., light gray particles are Re-rich, dark gray particles are Mo-rich, and medium gray particles have a composition between that of the light and dark particles. Figure 10 is a high-magnification image of an individual particle. This figure demonstrates that each particle contains both Re and Mo.

To get an estimate of the amount of Re and Mo in the individual particles, EDS analysis was performed on a dark gray particle, a medium gray particle, and a light gray particle. The spectra produced from this analysis are shown in Fig. 11-13. A comparison of the resulting peak heights can be used as a qualitative estimate for the chemical composition of each particle. Thus, the estimated chemical compositions for the dark gray, medium gray, and light gray particles are Mo-19Re, Mo-45Re, and Mo-78Re, respectively. The most plausible explanation for these chemistries being off the bulk composition of Mo-40Re is due to the nonuniform distribution of Re in the individual starting composite powder, i.e., variations within the nominal Mo-Re batch. However, even without a uniform Re distribution, the analysis revealed significant amounts of Re alloyed with Mo in each PAS particle.

3.6 Chemical Analysis of PAS Powders

Because the PAS process was performed in a stainless steel chamber and W-Cu electrodes were used to form the plasma, there was concern regarding powder contamination from impurities. However, GDMS and oxygen analysis showed no major pickup of impurities for the Mo-40Re PAS powder as compared with the as-received material (Table 3). A comparison of the oxygen contents of the as-received Mo-40Re to PAS processed Mo-40Re showed a two-order magnitude drop in oxygen content. This reduction in oxygen content was due to processing in a vacuum and using reducing plasma.

Similarly, there was no significant pickup of impurities for the W-2Re material PAS processed in an argon atmosphere (Table 4). However, in contrast to PAS-processed Mo-40Re that resulted in a significant reduction of oxygen content from the starting feedstock, no significant reduction in oxygen content was observed for the PAS processed W-2Re material, albeit there was no significant pickup of oxygen either.

Table 3 Results of Chemical Analyses Showing Impurities in Mo-40Re Powders

	Composition, ppm						
Mo-40Re	W	Ni	Cu	Cr	Al	Fe	O
As-received	1000	300	100	100	<100	700	13 000
PAS(a)	1300	300	<100	200	<100	600	400

(a) Average of four measurements

Table 4 Results of Chemical Analyses Showing Impurities in W-2Re Powders

	Composition, ppm					
W-2Re	Ni	Cu	Cr	Fe	C	O
As-received	88	3.6	120	230	16	345
PAS(a)	64	5.8	140	130	30	639

(a) Average of four measurements

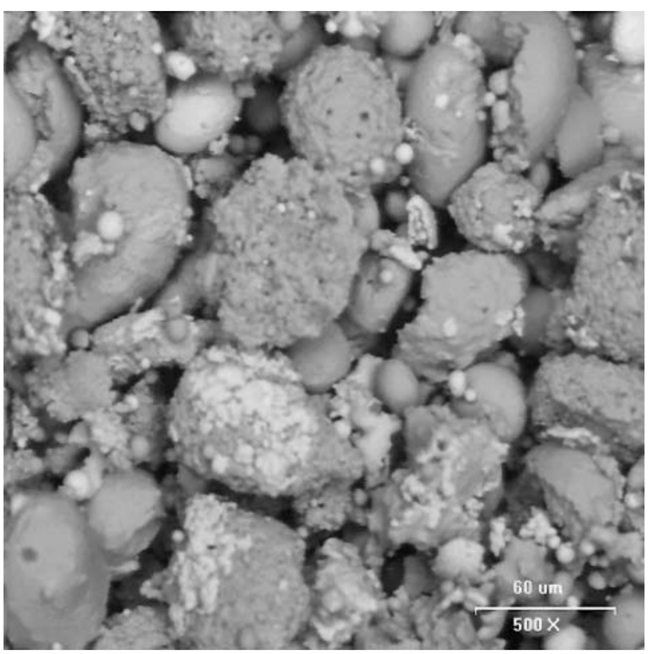

Fig. 14 SEM backscattered image of Mo-40Re powder after PAS processing at 30 torr

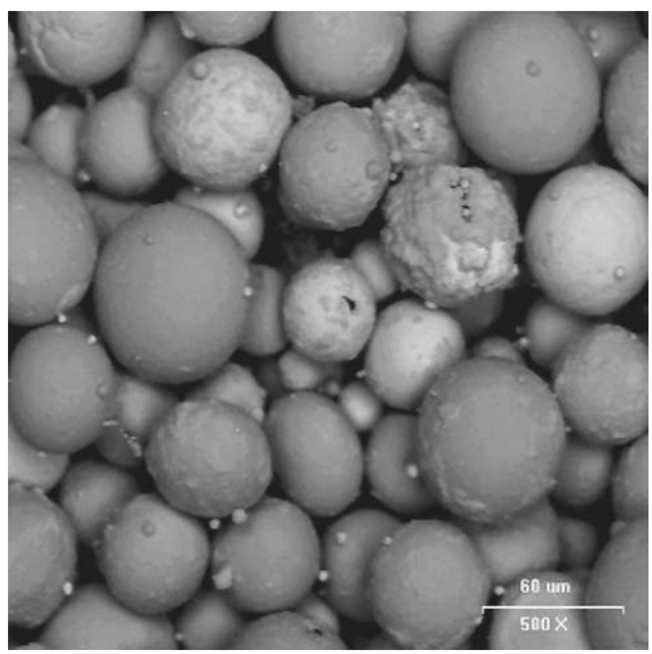

Fig. 15 SEM backscattered image of Mo-40Re powder after PAS processing at 250 torr

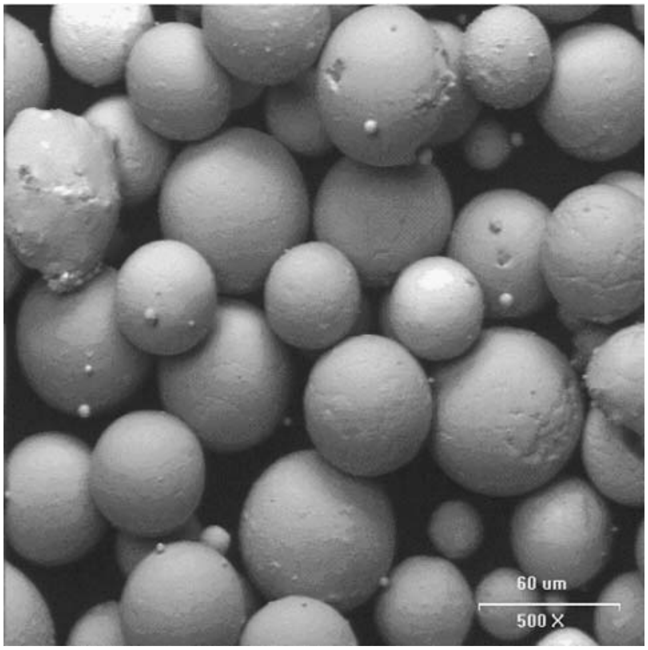

Fig. 16 SEM backscattered image of Mo-40Re powder after PAS processing at 500 torr

3.7 Effect of Chamber Pressure

To identify the effect of chamber pressure and plasma length, e.g., dwell time in the flame on the PAS process, the Mo-40Re composite powder was processed at three pressures, i.e., 30, 250, and 500 torr. Lowering the processing pressure causes the plasma to extend, which results in a slightly increased dwell time for the powders, but it also reduces the intensity of the plasma. In contrast, raising the processing pressure causes the plasma to contract, which results in a higher intensity plasma but leads to a reduced dwell time.

Figures 14-16 show the results of changing the PAS processing pressure on the resulting Mo-40Re powders. Processing at a pressure of 500 torr (the baseline processing pressure) resulted in dense, highly spherical particles with very few partially melted particles (Fig. 16). In contrast, the powders processed at 30 torr (Fig. 14) and at 250 torr (Fig. 15) resulted in many partially melted particles. Using quantitative microscopy techniques, the percentage of partially melted particles was determined to be 92.5% at 30 torr, 24.6% at 250 torr, and 3.4% at 500 torr. These results are shown graphically in Fig. 17 along with the plasma length as a function of pressure.

4. Summary and Conclusions

Highly spherical refractory metal powders were produced, possessing excellent flow characteristics when using the PAS process.

Prealloyed powders can be produced using the PAS process.

Key processing parameters, such as processing pressure, and the need for a uniform distribution of constituents in the powder feedstock were identified.

Reduction in oxygen content of PAS processed powder as compared with starting feedstock is possible when reducing plasma is used.

No significant pickup of impurities from the electrodes was observed for PAS processed powders.

Benefits of the PAS process, including a two-order magnitude reduction in oxygen contamination, production of highly spherical powders for enhanced flow characteristics, and the ability to produce prealloyed powders.

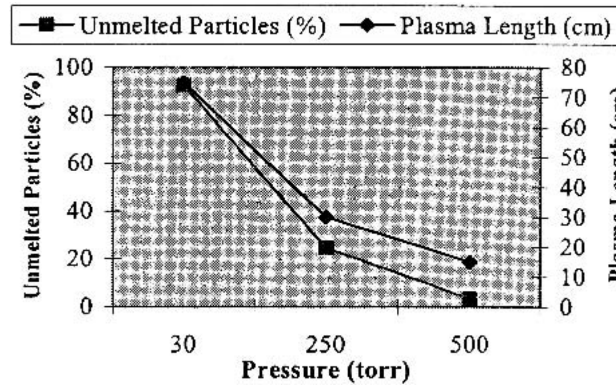

Fig. 17 Plot showing the percentage of unmelted particles as a function of processing pressure; also shown is the plasma length as a function of processing pressure. Note as processing pressure increases, the plasma length decreases resulting in a higher intensity plasma. This higher intensity plasma significantly alloys and spheroidizes more particles leaving fewer unmelted or partially melted particles.

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