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Low Cost, Net Shape Fabrication of Rhenium and High Temperature Materials for Rocket Engine Components

Timothy N. McKechnie, Robert R. Hickman, Arvind Agarwal
Plasma Processes, Inc.
www.plasmapros.com
(email: tim.mck@plasmapros.com)
Huntsville Alabama 35811

Abstract
Vacuum Plasma Spray techniques (VPS) have been developed to reduce the cost and fabrication time of metal and ceramic rocket engine components. Refractory metals and ceramics such as Re, Hf, W, W/Re, HfC, and HfN are being used for their high melting temperatures and chemical stability. However, the difficulty of forming these materials into complex shapes has limited their application in the past. The VPS technique involves spraying material onto a mandrel of the desired shape and subsequently removing the mandrel. A primary advantage of VPS forming over other powder metallurgy techniques is that near-net-shape spray forming of components significantly simplifies and reduces the cost of fabrication due to the high material utilization and reduction of laborious machining. Rocket nozzles have been fabricated and successfully tested in advanced applications with zero erosion. Standard metallurgical techniques have been used to characterize the effect of processing parameters on the microstructure of spray formed deposits. The deposited materials have high density with fine grain microstructures.

Introduction
VPS forming techniques have been demonstrated by PPI as a method for fabricating combustion chambers, non-eroding nozzles, inserts, and liners. This technique involves spraying material onto a mandrel of the desired shape and subsequently removing the mandrel. The plasma is formed by passing gases such as argon and hydrogen through an electric arc between a tungsten cathode and a water-cooled copper anode. The gas passing through the arc is ionized and results in temperatures on the order of 16,650°C (30,000°F). Powder, which is injected into the hot plasma by an argon carrier gas, is melted and accelerated toward the surface of a part at speeds up to Mach 2-3. Deposition rates can be as high as 9 kg/hr (20 lb/hr). Spraying is performed in a large vacuum chamber that has been evacuated and back-filled with a partial pressure of argon to prevent oxidation of oxygen sensitive materials.

Specialized VPS techniques have been developed to deposit the components to near net shape. The technique involves spraying material onto a mandrel of the desired shape and subsequently removing the mandrel. Figure 1a shows a thin walled nozzle liner fabricated by VPS-forming tungsten on a low cost, reusable graphite mandrel. This specialized process has also been used to fabricate W, HfC/Hf, and Re rocket nozzle inserts (i.e. throats). Figure 1b shows a picture of the VPS-formed Re and W nozzles. Note that two (2) net shape inserts were deposited on each mandrel. The process results in very efficient use of precursor materials since there is minimal waste and the inserts require little final machining. In contrast, traditional fabrication techniques require that each part be machined from a large billet, which produces higher waste and significantly increases fabrication time. Also, the use of expensive machining processes such as

EDM and diamond grinding are required since refractory materials are brittle at room temperature and very difficult to machine.

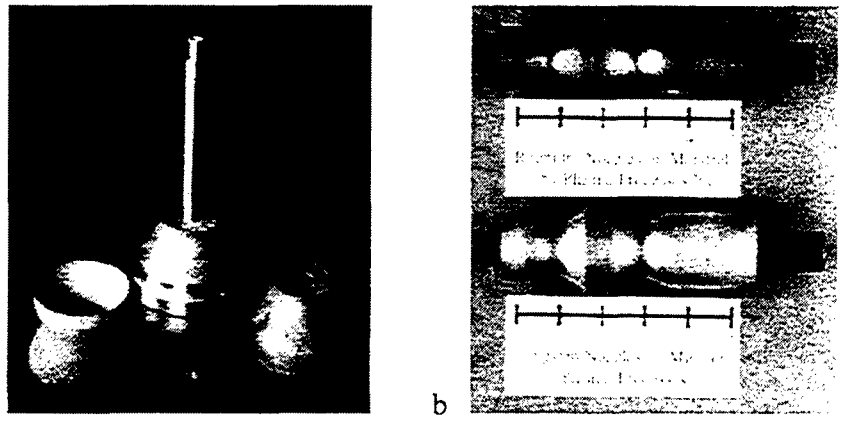


Figure 1: a) VPS-formed tungsten thin wall nozzle liner removed from reusable mandrel. b) W and Re rocket, nozzle inserts (2 inserts per mandrel) for Air Force.

Rhenium

PPI fabricated rhenium using a 140 KW plasma spray system modified with high efficiency nozzles (U.S. patent 5,573,682). Experiments were carried out to optimize the process parameters such as primary arc gas, secondary arc gas, volts, amps, powder carrier gas, stand off, and preheat temperature to produce dense, uniform deposits. The rhenium powder was deposited to a target thickness of 0.065-0.080" onto 1" and 0.75" diameter graphite mandrels. The cylinders were EDM into 0.25" wide sample rings for metallurgical and residual stress analyses. Flat samples were fabricated by depositing Re onto graphite plates. The bulk deposits were 0.150" thick, 2" wide, and 6" long. Figure 2 shows the Re material property samples.

Three heat treatments of the Re deposits were performed to evaluate further consolidation and microstructural refinement. Samples were sintered in H_2 and some samples were HIPed. Multiple samples were sectioned from the cylindrical and flat deposits. The samples were mounted and polished using standard metallurgical techniques. Figure 3 shows typical optical micrographs of the VPS Re in the as sprayed, sintered, and sintered/HIP conditions. The deposits are dense and fine grained. Notice the elimination of the splat microstructure for the heat-treated samples. Optical and digital image analysis techniques were used to measure the grain size and porosity content. Additionally, density was measured by water immersion methods. Table 1 lists the test results.

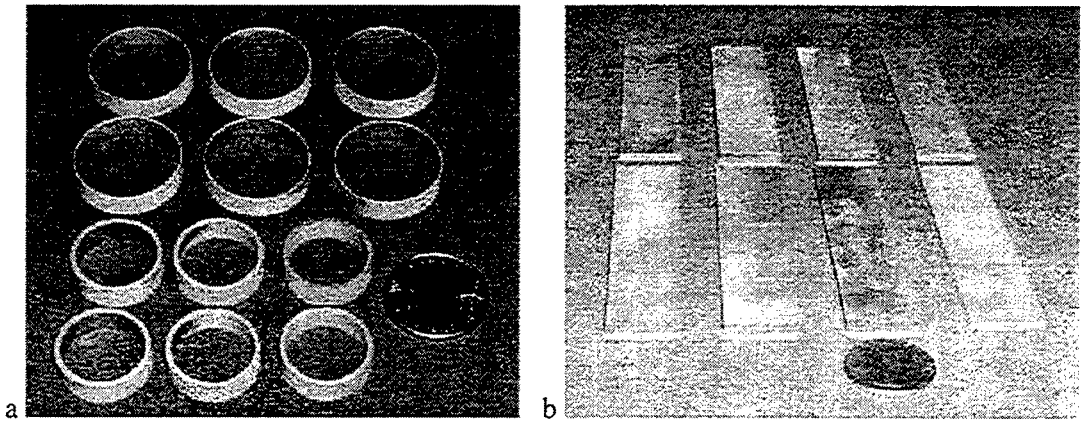
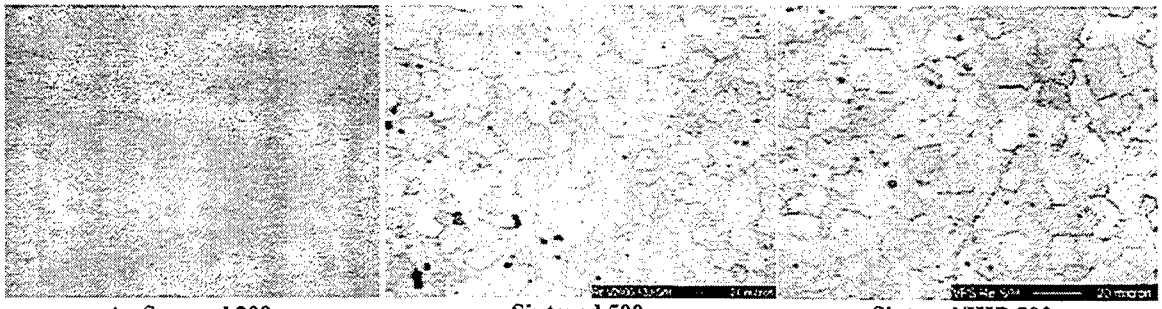


Figure 2: a) VPS Re ring samples. b) VPS Re flat tensile blanks.



As-Sprayed 200x Sintered 500x Sintered/HIP 500x

Figure 3: Micrographs of the VPS rhenium

Table 1: Density, porosity, and grain size data for VPS Re

Sample ID	Heat Treatment	Density (Water Immersion)	Theoretical Density %	Porosity %	Grain Size (microns)
V2000-93A	HIP	18.7	89.2	10	4
V2000-93D	HIP	19.4	92.2	8	5
V2000-93E	HIP	17.5	83.1	17	5
V2000-93G	HIP	18.4	87.7	5	7
V2000-93C	Sintered/HIP	20.7	98.7	-	-
V2000-93Fa	Sintered/HIP	17.9	85.3	9	9
V2000-93Fb	Sintered/HIP	18.2	86.8	16	8
V2000-93J	Sintered/HIP	18.9	90.1	10	9

As shown in Table 1, the bulk density values taken by water immersion techniques were 83-99% of the theoretical density of Re. The inconsistent densities were traced to powder feedstock problems. The Re powder used for the effort has a dendritic, "snowflake" morphology, which causes fluctuations and inconsistencies in powder flow characteristics. These fluctuations can cause injected particles to escape, re-solidify, and become trapped in the deposit causing voids. Figure 4a shows a micrograph of the Re powder. In contrast, Figure 4b shows a micrograph of spherical molybdenum (Mo) powder that was used as a low cost material used to verify programming. The spherical powder allows optimization of the VPS process to provide consistent, uniform dense deposits. Figure 5a shows a micrograph of the as-sprayed VPS Mo that

was deposited during the effort. Note the elimination of the industry typical splat structure without any additional heat treatment. Also, Figure 5b shows a micrograph of as-sprayed W VPS material, which was fabricated using free-flowing powder. PPI is currently developing better flowing Re powder to provide increased deposition efficiency, better process control, and higher as-sprayed density, strength, and ductility.

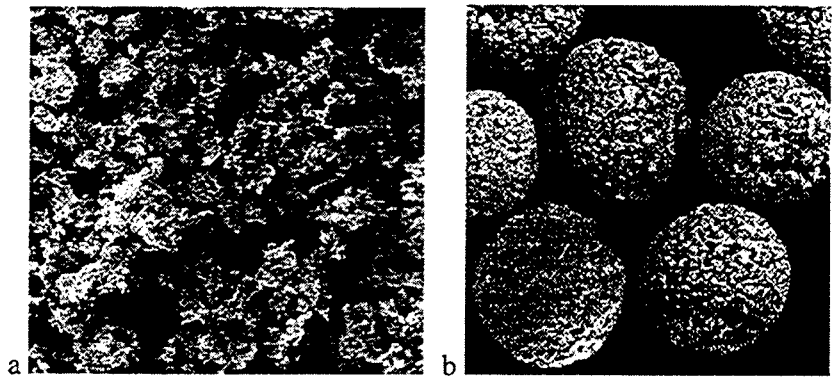


Figure 4: a) Micrograph of Re powder used for the effort. b) Micrograph of spherical Mo powder used as a low cost setup material.

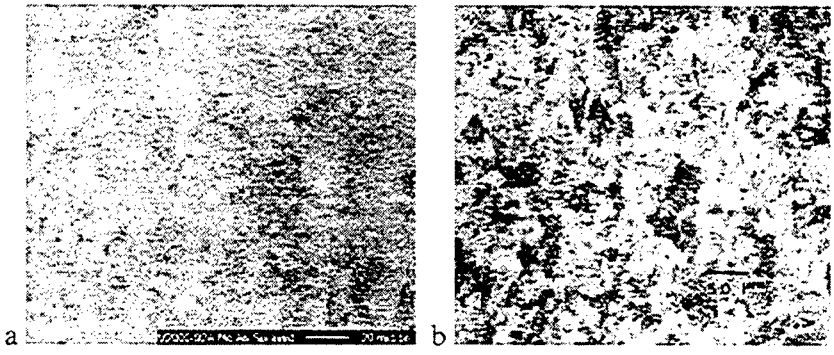
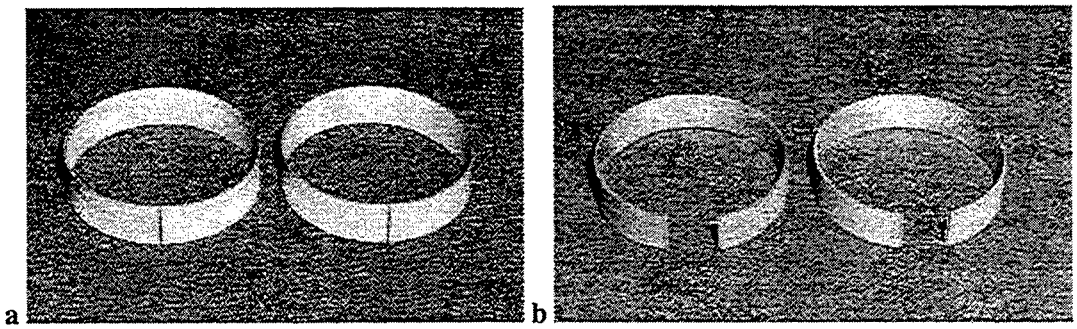


Figure 5: a) Micrograph of as-sprayed Mo. b) Micrograph of as-sprayed W routinely deposited by PPI for high temperature applications.

VPS Re has been characterized as having a fine, equiaxed microstructure. The digital image analysis data shows that the VPS Re has an average grain size of 5 microns for sintered material and 9 microns for the sintered/HIP material. Grain size is important for strength and fatigue/crack resistance. Re components produced by CVD processes for other rocket applications have failed due to de-cohesion of large grains. CVD Re has been characterized as having a grain size of >65 microns, which is a 13x increase in grain size as compared to the VPS Re material.

Plasma Processes measured the residual stress of the Re deposits in the as sprayed, sintered, sintered/HIP and HIP conditions. The measurements were taken by electro discharge machining (EDM) an axial 0.0127" cut in the 0.25" wide ring samples. After making the cut, the kerf width closed or opened indicating the direction (compressive or tensile) of the residual stress. The magnitude of the residual stress was then calculated using the following equation *Stress (ksi)* =

(1.05x10^6 x Thickness x Gap)/ID^2. Figure 6 shows VPS Re rings made for residual stress measurements after the 0.0127" axial cut. Table 3 lists the residual stress data. The as-sprayed samples had a tensile residual stress as indicated by the opening of the kerfs. The measurements for the heat-treated materials indicate a neutral or very small compressive residual stress. This is important because residual stresses can affect fatigue and crack behavior. Crack initiation and propagation are greatly reduced when neutral or slightly compressive residual stress values are present. In contrast, tensile residual stresses allow cracks to propagate quickly, especially in refractory metal and ceramic materials, which exhibit brittle behavior.



Sintered **As-Sprayed**

Figure 6: VPS Re rings made for residual stress measurements after a 0.0127" axial cut.

Table 3: Residual Stress Data for As-Sprayed and Heat Treated VPS Rhenium

Sample ID	Post Heat Treatment	*Residual Stress (psi)
V2000-38B	HIP	-187
V2000-38B	HIP	-209
V2000-38B	Sintered/HIP	-231
V2000-38B	Sintered/HIP	-275
V2000-95A	Sintered	-99
V2000-95A	Sintered	-42
V2000-95A	As-Sprayed	6294
V2000-95A	As-Sprayed	5601

*A negative number indicates a compressive stress

Hot Fire Testing

Plasma Processes fabricated non-eroding Re throats for hot fire testing at Thiokol Propulsion. The throats were fabricated to net shape on low cost mandrels. Figure 7 shows the Re non-eroding throats before and after hot fire testing. The hot fire test is used by Thiokol to screen for thermal shock and erosion resistance. It has been used extensively for various boost and tactical missile applications. The propellant grain is 5 inches in diameter and is center perforated (CP). An advanced reduced smoke propellant, which has been used in Thiokol studies of low erosion throat materials, was used to test the throats. The conditions in the nozzle are very representative of those expected for advanced rocket motors.

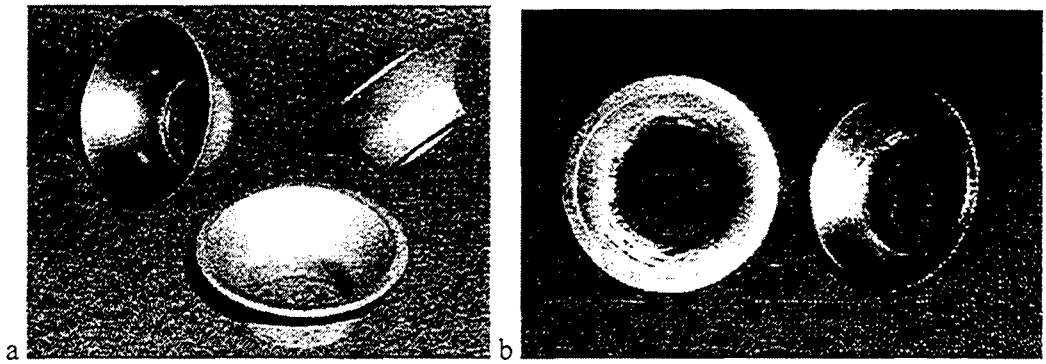


Figure 7: VPS Re non-eroding throats before (a) and after (b) hot fire testing.

The VPS Re throats performed extremely well during the hot fire testing. Motor burn time was 2.26 seconds with an average pressure of 2375 psi. Flame temp was about 2815°C (5100°F) with the temperature at the throat about 2704°C (4900°F). Figure 8 shows the pressure trace data from the 5 inch CP test. Table 3 lists the pre-fire and post-fire measurements of the test specimens. Post test evaluations revealed no cracks or erosion with only minor grooving on the aft end. Instead of eroding, the Re throat actually constricted 0- 0.015".

Table 3: Pre fire and Post-fire Measurements of VPS Re Blast Tube Test Specimens

	Pre-Fire ID, inches			Post-Fire ID, inches			Delta ID, inches			Weight, grams		
Location / Material	Forward	Middle	Aft	Forward	Middle	Aft	Forward	Middle	Aft	Pre-Fire	Post-Fire	Delta, gms
THROAT:												
TUNGSTEN	0.5830	0.5000	0.7490	0.5340	0.4940	0.7490	-0.0490	-0.0060	0.0000	545.80	544.50	1.30
MX-2600 Spacer	0.5870	0.5875	0.5870	0.6370		0.7090	0.0500		0.1220			
VPS Rhenium, S/N V2000-94a	1.0690	0.6125	0.5800	1.0540	0.6085	0.5660	-0.0150	-0.0040	-0.0140	21.70	21.50	0.20
MX-2600 Spacer	0.5880	0.5870	0.5875	0.6110	0.6580	0.6620	0.0230	0.0710	0.0745			
VPS Rhenium, S/N V2000-94c	1.0730	0.6100	0.5800	1.0660	0.6100	0.5660	-0.0070	0.0000	-0.0140	26.50	26.10	0.40
MX-2600 Spacer	0.5870	0.5870	0.5870	0.6800	0.6510	0.6468	0.0930	0.0640	0.0598			
NOTES: Burn Time = 2.26 seconds, Max Pressure = 2889 psig, Average Pressure = 2375 psig.												
New Propellant Formulation, DL-N246												
Leak through bond gap between Tungsten and last SiPH spacer due to too large of a bond gap (20 mils) in the RTV												

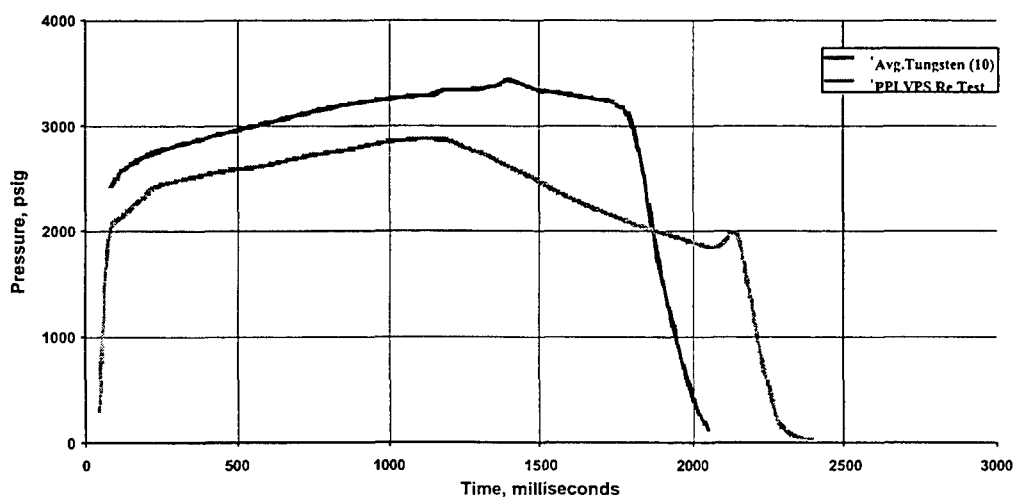


Figure 8: Pressure trace data for the VPS Re 5 inch CP test

Figure 9a shows a 2" throat diameter nozzle, which was successfully hot fire tested with zero erosion or damage evident after motor firings. The motor had a flame temperature of 3121°C (5650°F) and an average pressure of 725.4 psig. Figures 9b and 9c show the throat during the net shape VPS fabrication and just after spraying. The images show the high temperatures employed during the VPS process to produce dense refractory metal components.

The results of the 2" diameter throat effort demonstrate the ability to rapidly fabricate refractory metal components using low cost VPS processes. The throat was fabricated at PPI, composite wrapped, and successfully tested in less than one (1) month. Table 5 compares the fabrication time for the VPS nozzles with equivalent carbon/carbon composite (C/C) and forged tungsten materials.

Table 5: Comparison of fabrication time for high temperature nozzle throat materials

Material	Fabrication Time	Comments
VPS+low cost wrap	< 1 Month (includes composite wrap)	Up to 40" diameter parts
C/C	4-9 months (bulk fabrication only)	Requires final machining
Forged W	Months	Laborious machining per part

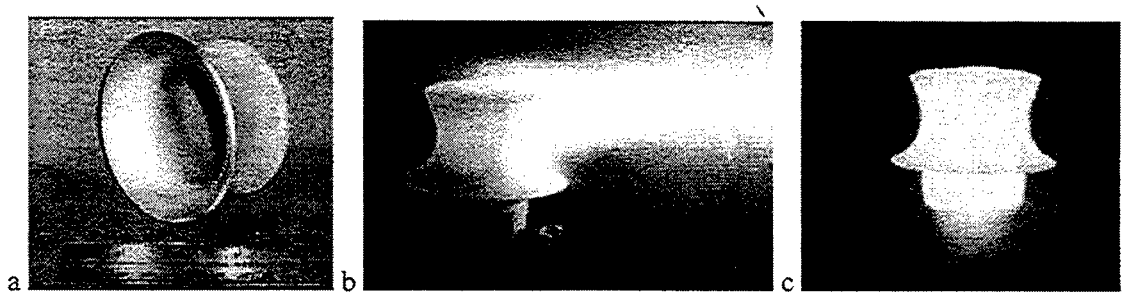


Figure 9: a). Non-eroding throat nozzles VPS fabricated at PPI. b) VPS fabrication to net shape. c) Same throat after nozzle material deposition.

Hafnium

PPI has also developed VPS parameters to deposit pure Hf material. The Hf was deposited to a target thickness of 0.065-0.080" onto a 0.5" diameter graphite mandrel. Samples were sectioned and mounted for metallurgical analysis. Figure 10 shows microstructure of the VPS Hf. The hafnium is 99% dense with totally recrystallized grains in the as-sprayed condition. Density was also measured by water immersion techniques. A density of 13.1 g/cc was observed, which is 99% of the theoretical density of 13.3 g/cc. Digital image analysis measured an average grain size of 45 microns.

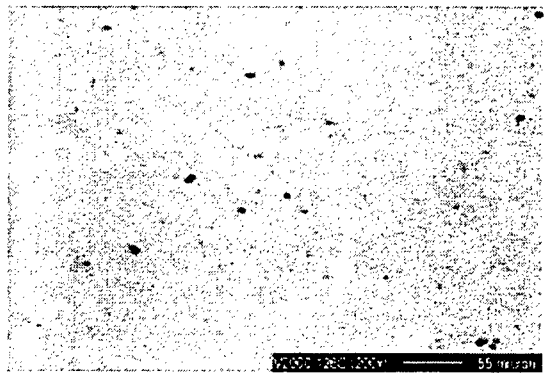


Figure 10: Micrograph of as-sprayed Hf showing a 99% dense microstructure.

Vacuum Plasma Sprayed Hafnium Based Ceramics

Group IV hafnium based ultra high temperature ceramics (UHTC) are potential coating/structural materials with high ablation and erosion resistance due to their resistance and stability against complex gaseous and thermal environments. They possess excellent properties of high erosion and wear resistance and oxidation resistance These materials also exhibit exceptional configuration stability at temperatures of 1650-2800^{0}C in the presence of high velocity dissociated air. In addition, hafnium and zirconium based ceramic composites are prime candidate materials for thermal protection systems on the exterior surfaces of the spacecraft reentering the atmosphere and other aggressive environments containing hot oxidizing gases. Table 6 lists the salient physical properties of these refractory ceramics.

Table 6. Physical Properties of Hafnium Based Ultra High Temperature Ceramics

Material	Melting Point (K)	Density (gm/cc)	Thermal Conductivity (W/m.K)	CTE (10^{-6}/K)
HfB_2	3250	10.0	50-60	6.3 - 6.8
HfC	4223	12.6	16-37	6.8 - 7.2
HfN	3660	13.9	5-20	6.9

However, fabrication of these ultra high temperature ceramics (UHTCs) into useful bulk shapes is a complex problem as they are intrinsically brittle and susceptible to thermal stresses and cracking. In the present study, vacuum plasma spray (VPS) technique has been employed to spray form UHTCs into near net shape structures.

Figure 11 shows some of the near net shape parts of Hf-based ultrahigh temperature ceramics fabricated by vacuum plasma spraying. These components are thin walled (thickness varying from 0.5-1.0 mm) in nature and of varying diameter. Such thin walled components can be used as inserts/liners in several high temperature and hot gas applications for minimal erosion and oxidation. Figure 11(c) shows a spray formed HfN nozzle liner/insert for next generation aerospace applications.

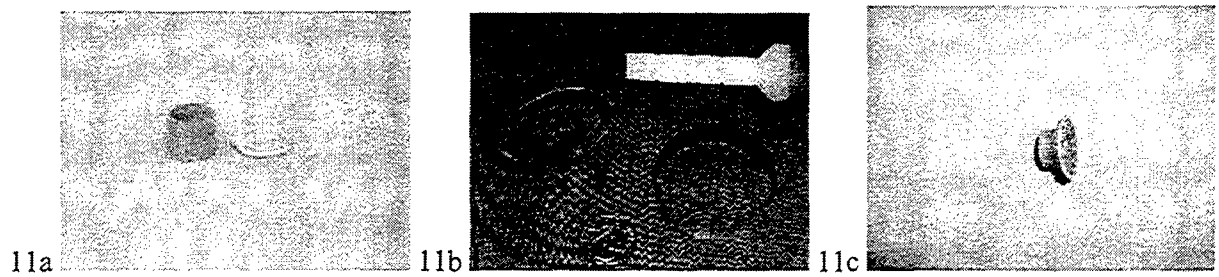


Figure 11. Vacuum Plasma spray formed (a) HfB_2 ring: 12 mm in diameter and 0.8 mm wall thickness (b) HfC rings on graphite mandrel: 12 mm and 50 mm diameter, thickness of the ring varies from 0.5-1.0 mm. and (c) Spray formed HfN nozzle liner on a graphite mandrel: 1.5 mm wall thickness.

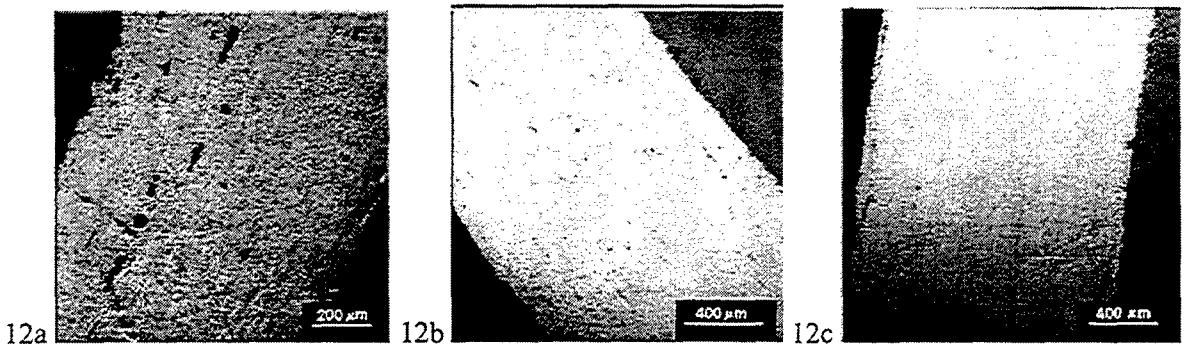


Figure 12. SEM micrographs of as-sprayed (a) HfB_2, (b) HfC and (c) HfN.

Figure 12 shows the low magnification SEM micrographs of the cross section of spray formed HfB_2, HfC and HfN samples in as-sprayed condition. Porosity level in the as-sprayed HfB_2 (Figure 12a) was ~ 8 vol.%. Such high porosity is attributed to the coarse pores in the deposits, which are present due to the inconsistent flow of HfB_2 powder. The porosity was found to be less than 2 vol. % in as-sprayed HfC deposit (Figure 12b). Moreover, these pores are very fine (< 4 µm) and closed in nature. Such high-density deposit of HfC could be attributed to the uniform powder size distribution. The porosity level in as sprayed HfN was measured to be 6 vol.% (Figure 12c). Moreover, the structure is layered with a higher concentration of pores at the junction of each layer. Hf-HfN cermet powder of stoichiometry $HfN_{0.7}$ was also sprayed. The two-phase structure in as-sprayed condition was revealed after etching (Figure 13a). Hf appears to be distributed as very fine rounded structure surrounding the HfN splats. The porosity level in the as-sprayed HfN cermet was found to be 4 vol.%. It was envisaged that hot isostatic pressing (HIP) would result in a significantly dense structure. Figure 13b shows optical micrograph of the as sprayed Hf-HfN sample hipped at 2000^0C at 25 ksi for 2 hours. The hipped microstructure is highly dense (> 99 vol.%). There is no more splat structure suggesting complete transformation of plasma sprayed structure. Grain growth has also occurred.

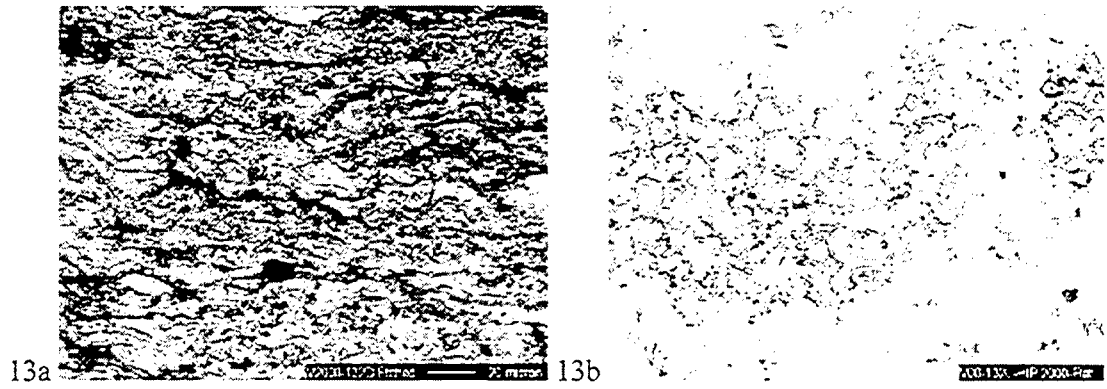


Figure 13. Optical micrographs of Hf-HfN cermet (a) in as-sprayed condition and after being hipped at 2000^0C for 2 hr at 25 ksi under N_2 environment.

Conclusions

Dense, net shape, Re, Hf, W, W/Re and Hf-based ultra high temperature, ceramic components can be fabricated using the VPS process. Rhenium, tungsten, molybdenum, hafnium, Hf/HfN can be formed into near net or net shapes at 99% densities. However, the as-sprayed properties and process control can be greatly enhanced by improving flow characteristics. Residual stress of net shape rhenium components is less than a 1 ksi after heat treatment. Near net shape formed rhenium components have been tested successfully in the stringent thermal and mechanical requirements of hot gas systems.