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WC-Co COATINGS FOR HIGH TEMPERATURE ROCKET NOZZLE APPLICATIONS: AN APPLICATIONS NOTE

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ABSTRACT
High velocity oxy-fuel (HVOF) sprayed tungsten carbide – cobalt (WC-Co) coatings exhibit attributes that allow them to be a candidate material for high temperature applications; such as temperature insulators for rocket nozzles. This application note investigates the effect of surface preparation, in this case the grit blasting process, on the characteristics of the so-formed coating.
The WC-Co coatings exhibited high hardness and low porosity. The composition of WC-Co coating varied in different regions, but on average was close to the composition of the initial feedstock, implying that there was no preferential loss of the material during the spray process. Microanalysis indicated diffusion of tungsten to the interface between the coating and the substrate and partly explains the high bonding strength of the coating. These physical characteristics suggest that the HVOF sprayed WC-Co is an appropriate coating technology for rocket nozzles.

Keywords: Adhesion strength; Grit blasting; HVOF thermal spray; Roughness; WC-Co

1. INTRODUCTION
Technology for ballistic rockets has been being developed in Indonesia since the early 1960's. The first rocket, named Kartika I, was launched in 1962 with a weight of 220 Kg. Since then, various ballistic rockets, all with solid propellant, have been launched. However, a major problem remains with their development; that of weight optimization. The ideal weight proportion for a rocket is: 3% for the structure, 91% for the fuel, and 6% for the payload (Rycroft, 1990). There is much discussion on the design of launch vehicles (Miele et al., 2005) with the focus being on what is termed as "the structural factor"; i.e., "ε", which is the "ratio of the structural mass to the sum of the structural mass and the propellant mass". The aim of recent research has been to maximize the structural factor so that the maximum payload can be delivered. In general, the weight proportion of rockets developed in Indonesia is far from the ideal proportion, with a relatively large proportion being contributed by the structural weight.

At the other extreme of rocket research is the development, design and fabrication of microrockets (Rossi et al., 2002). These microscale thrusters deliver a force of several mN and have dimensions of about 1 mm in length and 0.2 mm in diameter. Their intended application is as microscale thrusters for the control of very small satellites.

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Such rockets are of relevance to the macroscopic work described herein because similar materials and manufacturing processes can be employed. The rocket nozzle contributes the most to the structural weight; therefore, this research focuses on the weight reduction of this critical component.

The literature is rich with materials science and engineering approaches that are intended to manufacture efficient rocket nozzles. Several main approaches have been taken since the 1960's. Initial work was oriented towards using massive carbon structures within the nozzle region in order to insulate the superstructure of the nozzle. The majority of rockets use massive solid carbon as a temperature insulator for the nozzle. The C-C composite (Windhorst & Blount, 1997; Lacoste et al., 2002, Ellis & Berdoyes, 2002) and ceramic matrix (Schmidt et al., 2004) materials can resist temperatures to about 2,500^{o}C and retain high specific mechanical properties. A long-standing concern has been that of erosion of the nozzle under high heat flux and supersonic gas discharge (Neilson & Gilchrist, 1968) and it can be remarked that early work (Ault, 1959; Ault & Miligan, 1959) in the flame spray addressed such materials issues by the flame spraying of alumina radomes.

Work in the area of thermal spray processing has approached rocket nozzle manufacture from several approaches; (i) via use of thermal spray technology to create near net shapes of nanostructured (Agarwal et al., 2003) or nanocomposite (Hong et al., 2005) materials that are known to exhibit good high temperature characteristics, and (ii) by forming spray formed components consisting of refractory metals and ceramics for aerospace hardware needs (Burns et al., 1990; Liaw et al., 1993). This work on materials that have been processed by thermal spray technology has evolved confidence that materials that exhibit good mechanical properties at high temperatures can be formed into applications for the aerospace market.

The patent literature on the use of thermal spray processes for rocket nozzle applications is summarized in Table 1.

The patents on this topic are focused on several specific topics; (i) employing the near-net shape attributes of thermal spray technology to form ceramic and intermetallic materials (Holmes & McKechnie, 2001; Van ierland et al., 2003); (ii) creating new functional surfaces from complex materials (Terner et al., 1980; Terner et al., 1981); (iii) re-designing existing engines to take advantage of inserts (Canfield & Shigley, 2004) in those regions of the components that need additional, enhanced properties; (iv) enhancing corrosion resistance (McKechnie et al., 1998); and enhancing erosion resistance (Chiang & Yang, 1996; Singer & Carr, 2001). The upshot of this literature review is that thermal spray technology of certain materials has an established benefit for the rocket nozzle and aero-engine application.

The present applied R&D investigates replacement of the massive solid carbon with a relatively thin (less than 1 mm) thermal spray coating that is intended to reduce the overall nozzle weight. The coating material is WC-Co powder, which has high hardness, high temperature resistance and high erosion resistance (Pawlowski, 1995; Stoke & Looney, 2000) and this is applied via a conventional HVOF process. The literature indicates that the HVOF process is produces high-quality carbide-metal, cermet coatings that exhibit high density, high hardness, and superior bond strength compared to thermal spray methods (Wang & Shui, 2002; Li & Li, 2002; Qiao et al., 2003) such as plasma and flame spray.

Table 1 Summary of the patent literature on the thermal spray processing and forming of rocket nozzle components

Patent Number	Date of award	Inventors	Title of patent
4,226,911	October 7, 1980	L.L. Terner, D. Moskowitz, R.L. Van Alsten	Novel spraying composition, method of applying the same and article produced thereby.
4,288,495	September 8, 1981	L.L. Terner, R.L. Van Alsten, D. Moskowitz	Article coated with beta silicon carbide and silicon
5,557,927	September 24, 1996	K-T.K. Chiang, S. Yang	Blanching resistance coating for copper alloy rocket main chamber lining
5,773,104	June 30, 1998	T.N. McKechnie, R.R. Holmes, F.R. Zimmerman, C.A. Power	High temperature and highly corrosive resistant sample containment cartridge
6,209,312	April 3, 2001	V. Singer, C.E. Carr Jr.	Rocket motor nozzle assemblies with erosion-resistant liners
6,314,720	November 13, 2001	R.R. Holmes, T.N. McKechnie	Rocket combustion chamber coating
6,666,646	December 23, 2003	A. Van ierland, A. Verbeek, I. Danielse, J. Beeren, O. Alexandrov	Drag reduction for gas turbine engine components
6,711,901	March 30, 2004	A.R. Canfield, J.K. Shigley	Rocket motor nozzle assemblies having vacuum plasma-sprayed refractory metal shell throat inserts, methods of making, and rocket motors including same

A key ingredient to the quality of the HVOF coating is the surface preparation of the substrate. Thus, this work focuses on this prime variable concerning coatings on rocket nozzles

2. EXPERIMENTAL METHODS

The HVOF coating was sprayed onto coupons representative of the rocket nozzle material; i.e., S45C steel of composition 0.423 C, 0.639 Mn, 0.0045 P, 0.01 S, 0.05 Cr, 0.072 Cu, 0.191 Si, 0.045 Ni, and balance Fe. A Sulzer-Metco HVOF torch (Sulzer-Metco, Inc., Westbury, NY-USA) using 50 mesh WC-12 wt%Co powder from Deloro Stellite GmbH (Koblenz Germany)., with the composition specifications of 82.71 W, 5.49 C and 11.8 Co (in wt.%). The HVOF process used a carrier gas pressure of 45 psi at 31.5^{o}C.

The sample surfaces were machined and grit blasted prior to spraying by using 24 mesh - Al_2O_3 grit at an air pressure of 0.1, 0.3, 0.4 and 0.5 MPa. The sample roughness was measured with a Surfcom 120A surface roughness tester (Tokyo Seimitsu Co. Ltd., Tokyo, Japan) The qualitative results indicate that the higher the grit blasting pressure, the rougher the surface of the substrate. Coating thickness was measured by means of a mechanical micrometer with an average of 14 measurements. These measurements were confirmed by optical microscopy on cross sections of witness coupons. The surface roughness and topography affects the bonding strength of the coating, although quantitative results were not obtained in this study.

Cylindrical samples were made in accordance to ASTM C633-01 (Anonym) with a diameter of 25 mm and a height of 35 mm, which incorporated a blind threaded hole to allow coupling to a tensile testing device. A Devco Epoxy adhesive was used to assemble the tensile adhesion test (TAT) samples. The adhesive was manually applied and cured at room temperature. The TATs were tested in a Shimadzu EHF-EB20 servopulser machine (Shimadzu Corp., Kyoto, Japan) with 20000 kg maximum load.

Fracture surfaces were visually observed as well as assessed via optical and scanning electron microscopy (SEM) equipped with energy dispersive x-ray spectroscopy (EDXS). The samples were ground, polished and then etched by an etchant composed of $K_3Fe(CN)_6$: NaOH = 1:1.

3. RESULTS AND DISCUSSION

3.1. Surface roughness

The grit blasting pressure shows a proportional effect on the surface roughness Figure 1. The surface roughness due to machining process is 4.25 μm. After grit blasting at 0.1 MPa, the surface becomes smooth since the grit is relatively fine in size. However, with the increase in the pressure, the impact energy of the grit blasting media is higher, so that the deformation of the sample surface is more severe. Therefore there are more asperities on the sample surface which directly increase roughness.

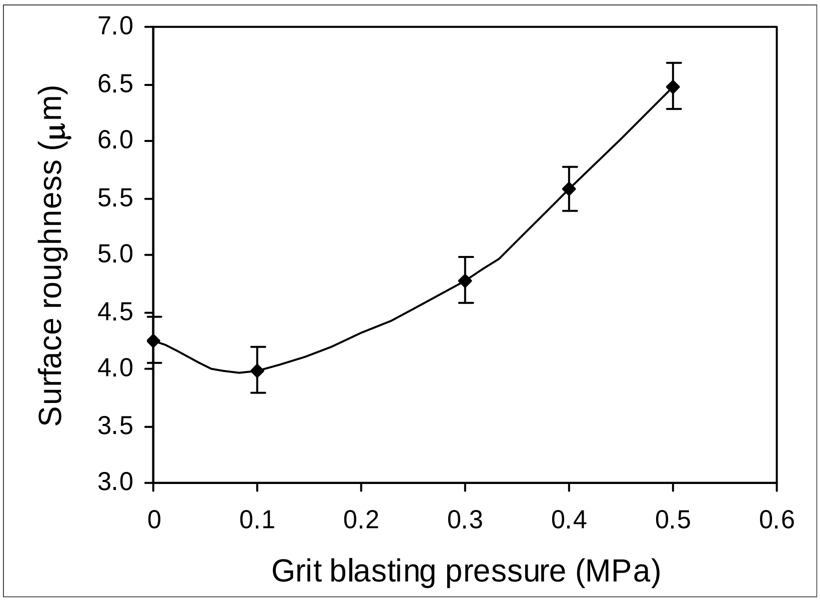

Figure 1 Effects of grit blasting pressure on the surface roughness

3.2. Coating Thickness

The target thickness of the WC-Co coating was ~ 400 μm. However, since the size of the samples is much smaller than the size of the HVOF torch, it was difficult to control the thickness of the coating. As shown in Figure 2, the thickness of the coating varies from 346.6 μm to 492.9 μm that is with a deviation of ~ 18 % of the target thickness. Previous results also showed that the deviation in the target thickness of HVOF coating is 15-40 %6. In application, the HVOF coating is usually machined to level the surface. However, this was not done since the focus of the research is on the surface preparation of the samples.

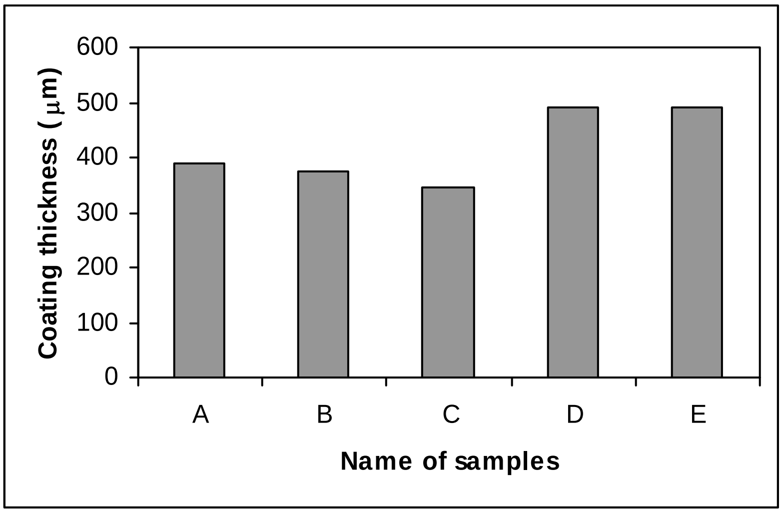

Figure 2 Variety of WC-Co coating thickness on samples with different surface roughness. Sample A: without grit blasting, and other samples with grit blasting with the pressure of: B: 0.1 MPa, C: 0.3 MPa, D: 0.4 MPa and E: 0.5 MPa

3.3. Adhesion Strength

Samples that were grit blasted demonstrated a high WC-Co bond strength that could exceed the strength of the epoxy adhesive (~ 40 MPa) as evidenced by epoxy failures. Figure 3 presents the fracture surfaces of the grit blasted samples. The dark surface is the fracture that occurs within the epoxy layer, while the light surface represents fracture between the epoxy and the WC-Co coating. No quantitative results on the adhesion strength were obtained because the fracture mode was not within the WC-Co coating.

(a)
(b)
(c)
(d)

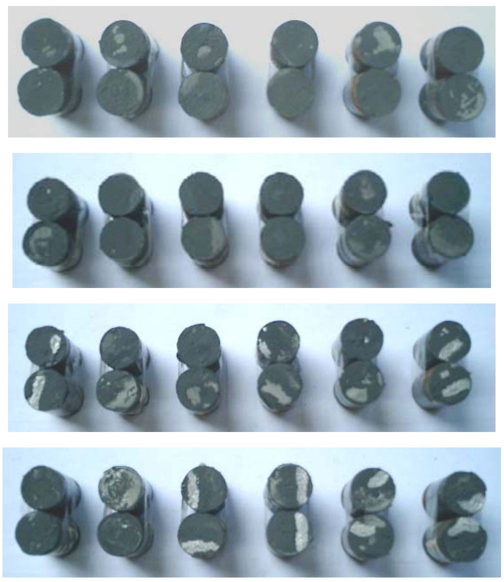

Figure 3 Fracture surfaces of adhesion test samples with grit blasting pressure of (a) 0.1 MPa, (b) 0.3 MPa, (c) 0.4 MPa and (d) 0.5 MPa. The dark surface is the fracture occurs within the epoxy layer, while the light surface is the fracture occurs between the epoxy and the WC-Co coating

The coating adhesion on unprepared surfaces is low; i.e., the coating peeled off easily from the substrate on adhesion strength testing; despite the fact that the coating exhibited a rough texture. Thus, the coating roughness is not indicative of coating adhesion. The presence of dirt on the substrate surface, including oil residues and a humid environment, prevents any substantial bonding (Windhorst & Blount, 1997). Voids between the coating and the substrate are evident from micrographic cross section, Figure 4.

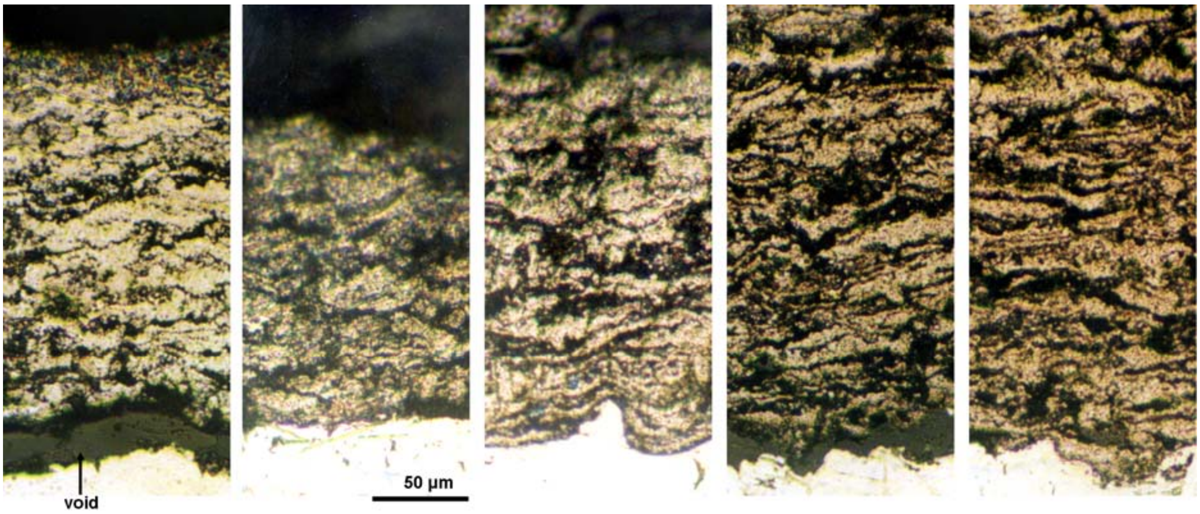

Figure 4 Micrographs of WC-Co coating on samples with grit blasting pressure of
(a) 0 MPa (without grit blasting), (b) 0.1 MPa, (c) 0.3 MPa, (d) 0.4 MPa and (e) 0.5 MPa

3.4. WC-Co Coating Microstructure

Microstructures of WC-Co coating applied on substrates of different surface roughness are presented in Figure 4. The WC-Co coating shows a high density with minimum porosity; a prime advantage of the HVOF thermal spray method (Rossi et al., 2002; Windhorst & Blount, 1997; Lacoste et al., 2002, Ellis & Berdoyes, 2002; Schmidt et al., 2004). The unique wavy lamellae of the thermal spray coating are consistent with the nature of WC-Co droplets deposition. The interlamellae spacing of ~0.01 – 0.1 μm with different morphology and this is consistent with previous results (Wang & Shui, 2002; Qiao et al., 2003). The morphology differences were depicted in term of lamellae that consisted of different gray levels. Differences in surface roughness cannot be detected in these micrographs since the area analysed by the optical microscope is small. However, the WC-Co coating completely covers the surface of the grit blasted samples (Figure 4 b-e), while there is a void between the coating and the surface that was not grit blasted (Figure 4a). The mechanical interlocking between the WC-Co coating and the substrate contributes to the high coating adherence.

Detailed SEM observation on the coating microstructure, Figure 5, and microanalysis in 6 locations, was conducted, Table 1. Note that Table 1 does not represent the exact wt.% composition because EDXS is not accurate in identifying light elements such as carbon and oxygen. However, the data still can be used for comparison purposes. The SEM micrograph not only depicts the typical lamellae structure of a thermal spray coating but also the distinct boundaries between lamellae. As well, no porosity was detected, thereby confirming the high density of the WC-Co coating produced by HVOF process that would be most suitable for the rocket nozzle application.

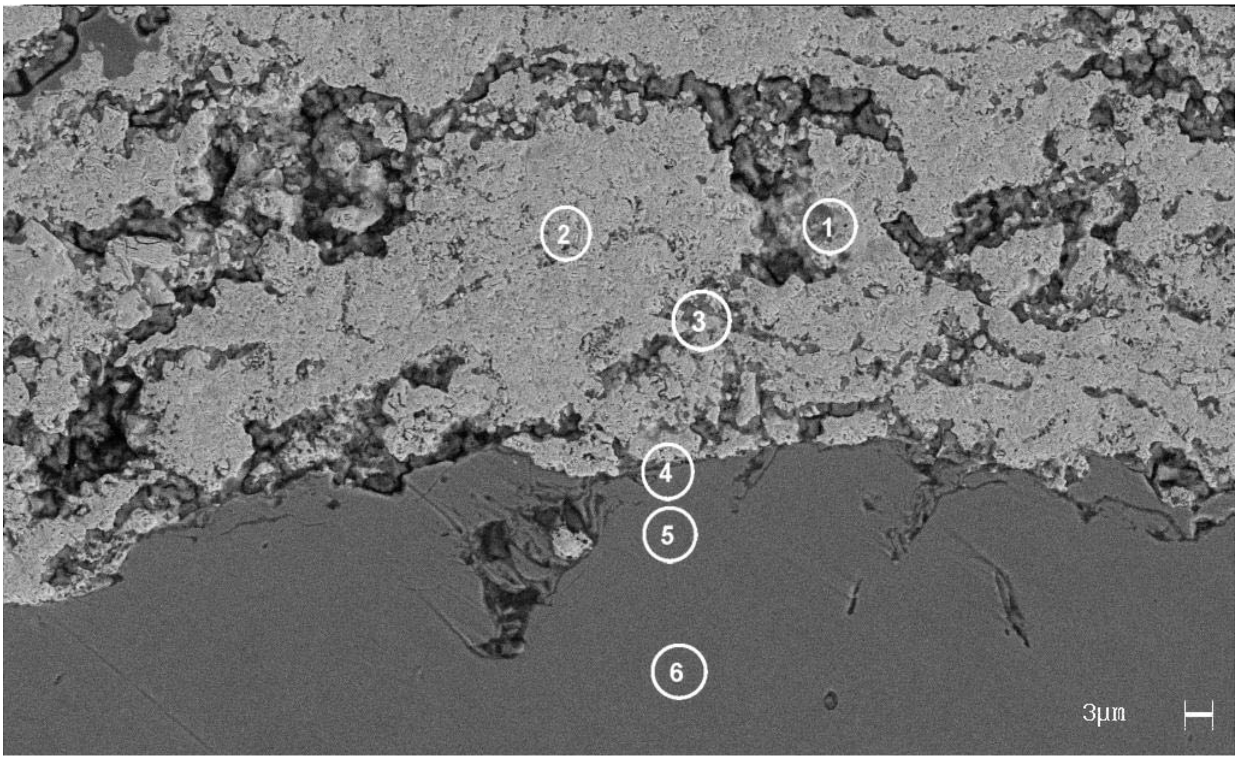

Figure 5 SEM micrograph of the coating - substrate interface region

Table 2 EDXS analysis results on positions 1-6, as shown in Figure 5.

Potition	C (wt. %)	O (wt. %)	Fe (wt. %)	Co (wt. %)	W (wt. %)
1	1.4	8.3	0	16.4	73.3
2	2.7	0.3	0	5.0	92.0
3	1.3	6.9	0	18.5	72.6
4	2.9	0	94.3	0	2.8
5	2.0	0	98.0	0	0
6	1.9	0	98.1	0	0

The composition of the coating varies from area to area (Table 2), but on average it is close to the composition of the initial feedstock; implying that there was no preferential material loss during spraying. Areas with a light colour (position 2) are rich in W and C, while gray areas (positions 1 and 3) tend to be rich in Co. This artifact arises from the melting and atomization of the powder before it impacts the surface. The melting points of WC and Co are significantly different (T_m Cobalt = 1493°C, T_m WC = 2780°C) (4), so segregation of elements during the melting and atomization of the powder is probable.

Oxygen was detected within the coating (positions 1 and 3), which may be interpreted to arise from oxidation of the feedstock particles during their transport from the HVOF gun to the surface of the substrate. The microstructures on the coating – substrate interface are indicative of superior bonding since there is no porosity or voids present. It is noteworthy that a small amount of tungsten (~2.8 wt.%) was detected at the interface (point 4). This may indicate that there was either (i) diffusion of tungsten from the coating into the substrate, or (ii) there was some carryover of the coating into the substrate during the polishing process. The likelihood of such contamination from the polishing process is slight; however, there may be a slight inaccuracy in the physical location of the tungsten due to the finite spot size of the EDX probe analysis. Any diffusion of tungsten would contribute to the high bonding strength of the WC-Co coating that was experimentally observed.

The upshot of the metallographic examination is that HVOF WC-Co is appropriate to be applied as a hard wear-resistant coating on rocket nozzles. On going work is necessary to further investigate the erosion resistance and thermal barrier properties of these materials so that the full benefit of thermal spraying can be realized.

4. CONCLUDING COMMENTS

This applied R&D presents a relatively straightforward application where WC-Co has been sprayed directly onto rocket nozzles in order to create a weight saving for rocket nozzles. The prime benefits of the thermal spray process include its ability to coat complex geometries with functional materials that are of dissimilar chemistry.

The major conclusions of this work are listed below.

1. The higher the grit blasting pressure, the rougher the surface of the substrate. The increase in grit blasting pressure from 0.1 to 0.5 MPa, increases the surface roughness from 3.99 to 6.48 μm.
2. The adhesion strength of the HVOF WC-Co coating is more than 40 MPa. The high strength is primarily due to mechanical interlocking between the coating and substrate. Diffusion of tungsten on the coating – substrate interface may also occur.
3. The microstructure of WC-Co HVOF coating is dense with minimum porosity and layered lamellae, material attributes that are advantageous for this particular rocket nozzle application.

5. ACKNOWLEDGEMENT

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