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Flame Spraying of Titania and Magnetite

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Abstract

The effect of process conditions on flame spraying of titania (TiO_2) and magnetite (Fe_3O_4) was investigated. Designed experiments were conducted to determine spraying conditions, specifically total combustible gas flow, stand off distance, and oxygen/acetylene ratio that produce high deposition efficiency (DE) and dense coatings. Along with DE, particle temperature and velocity were determined and correlated with process conditions. Results indicate that for both titania and magnetite, hot and high velocity molten particles result in higher DE and lower porosity coatings. Micrographs of coating cross-sections and surfaces were taken with both field emission scanning electron microscope (FESEM) and optical microscope. X-ray diffraction analysis shows that the titania coating retained its rutile structure while the magnetite coating had small amounts of maghemite (γ-Fe_2O_3) in addition to magnetite.

Introduction

Flame sprayed ceramics with melting points below 1900ºC have not been well characterized. To deposit these types of materials and prevent vaporization, a lower temperature process such as flame spraying is used. Plasma and HVOF are relatively expensive processes that produce high temperature and high velocity particles, limiting the choice of substrates [1]. Powder flame spraying on the other hand is simple to operate, costs less, produces lower velocity particles, and is lower in temperature. Relatively little work as been published on particle diagnostics and operating space characterization [2]. This study extends quantitative characterization of ceramic powder flame spray with a specific examination of magnetite which has a melting point of 1597ºC and titania with an 1855ºC melting point.

Experimental Procedure

A Sulzer-Metco 6P flame spray torch (Sulzer-Metco, Winterthur, Switzerland) was used to deposit magnetite (F. J. Brodmann & Co. L.L.C., Harvey, LA) and titania (Bay State Surface Technologies, Westborough, MA) for these experiments. The particle size distribution for these two powders was performed on a Beckman Coulter Model LS100 particle size analyzer (Beckman Coulter, Fullerton CA) at Sandia National Laboratory, Albuquerque, NM. The titania powder had a mean particle size of 16.1 ± 10.2 µm and magnetite had a mean particle size of 23.1 ± 17.2 µm. Steel substrates approximately 50 mm square and 3 mm thick were grit blasted then washed in acetone and methanol prior to drying with compressed air. Thermal spraying was conducted at the Thermal Spray Research Lab, Sandia National Laboratory. The torch configuration used for spraying both materials has a gun cooling air cap and a D nozzle. An AccuraSpray G3 (Tecnar Inc., Montreal Canada) was used to measure particle temperature and velocity for each spraying condition. The 6P flame spray torch was placed on a Staubli RX-60 robot (Staubli Unimation, Faverges, France) at Sandia National Labs, Albuquerque, NM, which was controlled using a using a custom gas control system which provides mass flow control of all the process gasses and is driven by custom LabVIEW™ 7 software (National Instruments Inc., Austin, TX). The custom software package communicates with the gas controllers, robot, and other sensors such as the AccuraSpray G3. A raster pattern (step size of 3 mm and linear speed of 152.4 mm/sec) was used for depositing the ceramic coatings. Samples were coated using three patterns with a powder feed rate set at approximately 10 g/min.

Designed experiments were used to examine the effect of spraying conditions on particle temperature, particle velocity, and DE on a plain carbon steel substrate. The experiments were setup as a 2^3 factorial design with three center points

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using MINITAB®14 software (Minitab Inc., State College, PA). This results in eleven runs being conducted for each experiment with the factors of stand off distance, total flow of combustible gas, and oxy-fuel ratio. The responses for these experiments were the scientific deposition efficiency, particle temperature and particle velocity. Scientific deposition efficiency is calculated as the percentage of powder adhering to the substrate divided by powder sprayed on the part.

X-ray diffraction patterns of as received and flame sprayed materials were obtained using an X-ray diffractometer (SIEMENS D500, Munich, Germany) with Cu Kα (λ=1.54059Å) at New Mexico Institute of Mining & Technology, Socorro, NM. Scan step size of 0.05° and a dwell time of 1 second were used for each sample. Cross sections of the flame sprayed coatings were examined with a Hitachi S800 FESEM (Hitachi High Technologies America, Electron Microscope Division, Pleasanton, CA). Samples were also examined using a Cameca SX-100 electron microprobe (Cameca Instruments Inc., Trumbull, CT).

Results and Discussion

After checking the required normality criteria for the data, main effects plots were generated for magnetite which can be seen in Figure 1. The only factor that significantly influences deposition efficiency in this experiment was the SD. While TF was not statistically significant within 95% confidence, it was close to significance. The significant factors for particle temperature are the OFR and SD. For the particle velocity all three factors influence the results significantly. Conditions that produce higher deposition rates are an OFR of 2, TF of 44.8 SLPM and a SD of 114.3mm.

When examining all three responses, it becomes clear that SD has a great influence in the spraying process. Another important factor is the OFR value, which affects the particle temperature. TF primarily affects the particle velocity. So to efficiently produce a dense coating, a short SD and a high TF should be used. The role of OFR on DE is less clear. At SD= 114.3 mm, the DE is over 70% for all OFR and TF. Deposition efficiency is the largest at 2.5 OFR, 44.8 SLPM TF and 114.3mm SD as shown in Figure 2. The DE is slightly lower at 1.5 OFR which is attributed to magnetite vaporizing. This suggests that a different hardware set which has a lower flame temperature and/or injects powder into a cooler portion of the flame should be used with magnetite[2].

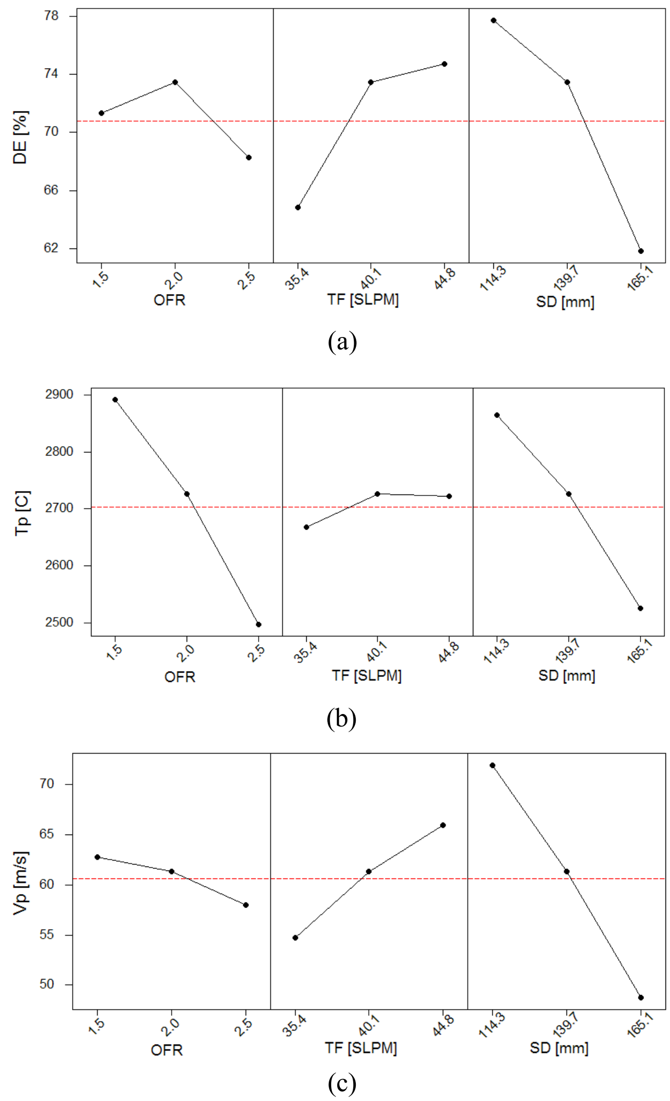


Figure 1: Main Effects plots for magnetite: (a) mean deposition efficiency, (b) mean particle temperature and (c) mean particle velocity

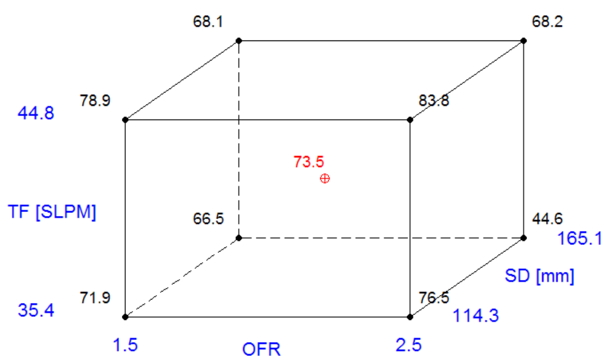


Figure 2: Deposition efficiency of magnetite as a function of OFR, TF and SD.

The X-ray diffraction data for magnetite are shown in Figure 3. The major phase in both the as-received powder and the coating sprayed at center point conditions (OFR=2, TF=40.1 SLPM, SD=139.7 mm) is magnetite (Fe_3O_4). The thermal sprayed sample does appear to contain some amount of maghemite (γ-Fe_2O_3).

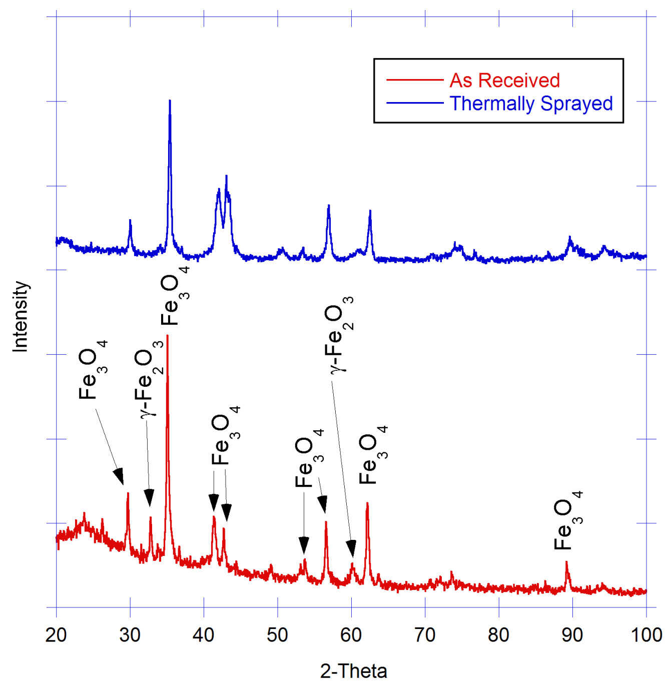


Figure 3: XRD pattern of magnetite as received and sprayed at center point conditions.

Cross-section and surface micrographs were taken of magnetite with an electron microprobe in backscattered (BSE) and SEM modes. The BSE images (Figure 4) show changes in composition with the lighter regions having higher molecular weights. The lighter regions are most likely magnetite and the darker, which have a lower molecular weight, are possibly maghemite. This is consistent with the XRD results. The sample imaged was sprayed using center point conditions, OFR=2, TF=40.1 SLPM and SD=139.7mm.

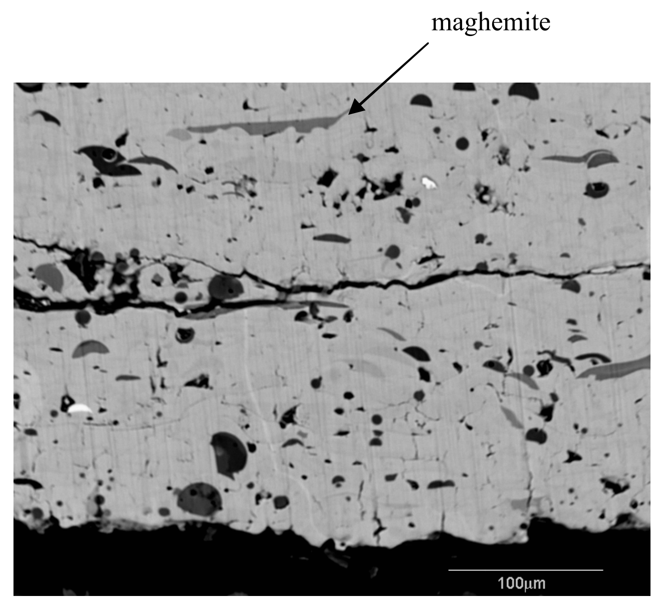


Figure 4: BSE image of cross-section for magnetite at center point conditions.

Images taken of the coating surface can be used to show the droplet structure upon impact. This structure is an indication of the quality of the coating being sprayed. As can be seen in Figure 5, the platelets are round in shape after impact with the substrate which is indicative of complete particle melting. In addition, the droplets have fused together producing a high quality coating.

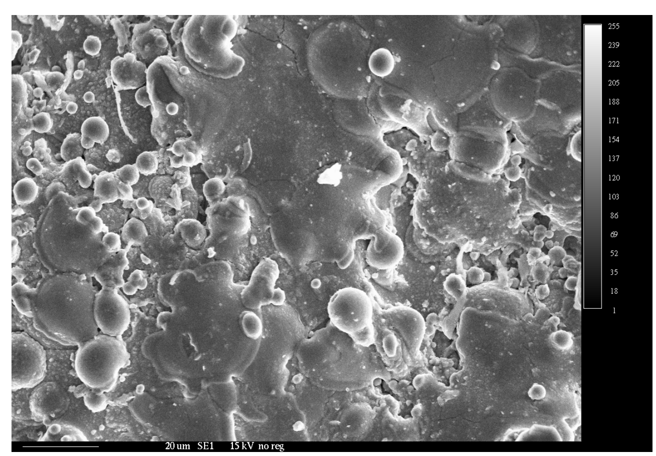
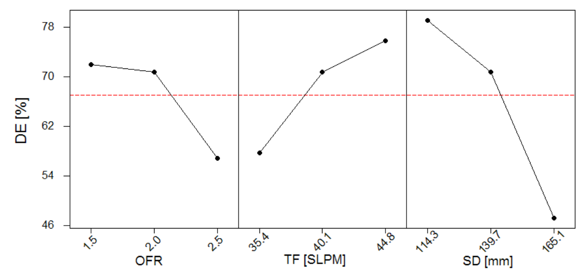
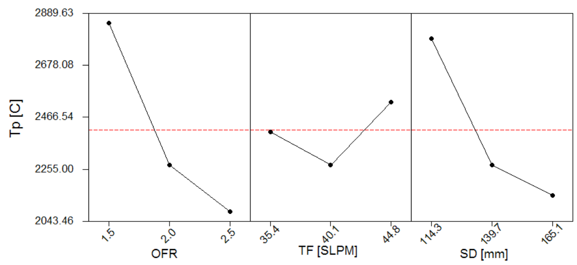


Figure 5: SEM image of magnetite coating surface, sprayed at center point conditions.

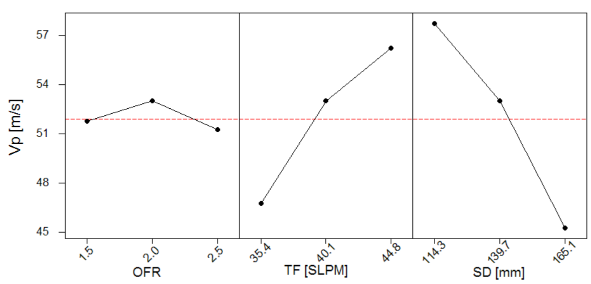
The DE results for titania show that hot, fast particles produce the highest DE. Particle temperature is relatively independent of TF and particle velocity is unaffected by OFR as expected. Main effect plots are provided in Figure 6.



(a)



(b)



(c)

Figure 6: Main Effects plots for titania: (a) mean deposition efficiency, (b) mean particle temperature and (c) mean particle velocity

XRD patterns were taken of the raw powder and the coating that was sprayed at center point conditions. As can be seen in Figure 7, the major phase in the starting powder and the sprayed coating is rutile.

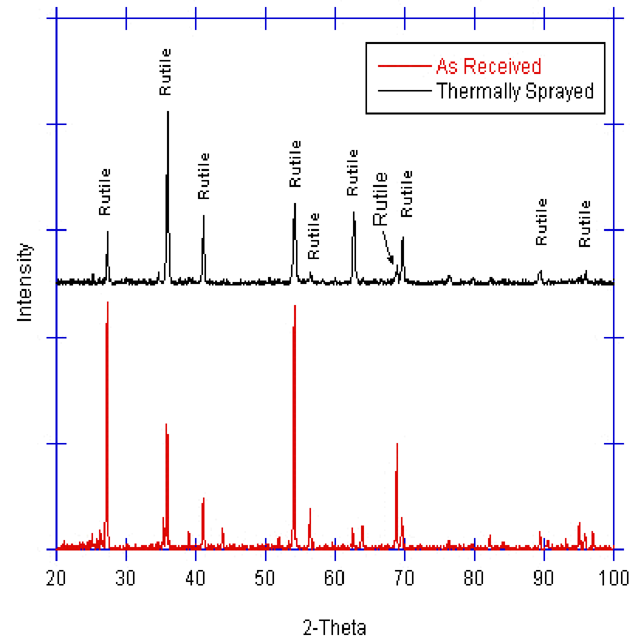


Figure 7: XRD pattern of As Received and titania sprayed at center point conditions.

An electron microprobe was used to make both BSE and SEM images of the titania coatings. These images indicate that the majority of the coating surface is of a single phase and has low porosity. The BSE image in Figure 8 shows the majority of the surface to be single phase rutile as indicated by XRD results. The SEM image in Figure 9 shows droplets in pancake-like shapes with little space between platelets. A cross-section of this sample was also imaged using a light microscope. This image (Figure 10) shows relatively low porosity and fully melted particles consistent with the surface morphology.

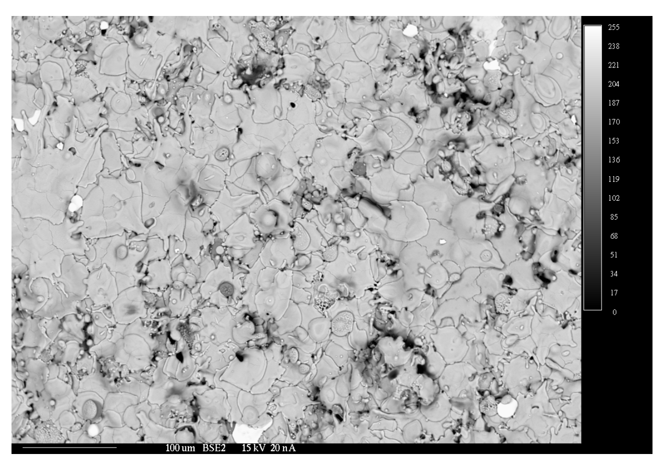


Figure 8: BSE image of titania surface sprayed under center point conditions

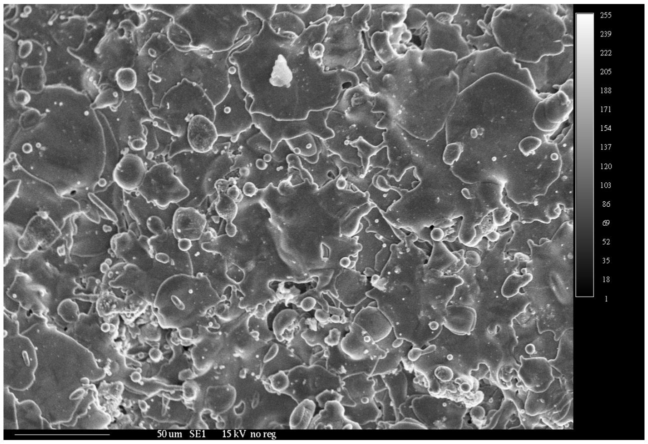


Figure 9: SEM image of titania surface sprayed at center point conditions

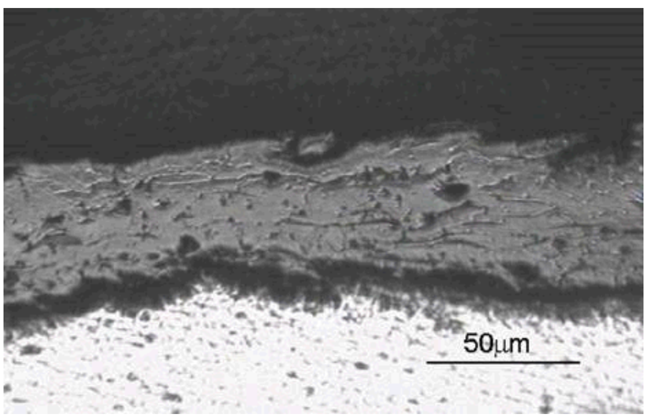


Figure 10: Light microscope image of titania cross-section sprayed under center point conditions

Conclusions

The powder flame spray operating space of titania and magnetite ceramics have been described in terms of oxy-acetylene fuel ratio, total flow of combustible gases, and standoff distance. Results indicate that deposition efficiencies >70% can be achieved when particles are powder flame sprayed hot and fast. With high particle velocity and temperatures, the droplets adhere to the substrate better and form splats which yield denser coatings. If the flame temperature is too high and the powder has a relatively low melting point, there is evidence that smaller particles may vaporize lowering the DE.

1. Friedrich, C., R. Gedow, and T. Schirmer, Lanthanum Hexaaluminate-a New Material for Atmospheric Plasma Spraying of Advanced Thermal Barrier Coatings, *J. Therm. Spray. Technol*, Vol 10, 2001, p. 592-598
2. A.C. Hall, D.A. Hirschfeld, A.J. Mayer, J.W. Cates, T.J. Roemer, D.E. Beatty, D.A. Urrea, D.J. Cook, R.A. Neiser, and M.F. Smith, Effect of Torch Hardware on Powder Flame Spray Torch Performance and Operating Space, *J. Therm. Spray. Technol.,* Submitted for Publication.