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A Design of Experiment Study of Plasma Sprayed Alumina–Titania Coatings

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ABSTRACT

An experimental study of the plasma spraying of alumina–titania powder is presented in this paper. This powder system is being used to fabricate heater tubes that emulate nuclear fuel tubes for use in thermal–hydraulic testing. Coating experiments were conducted using a Taguchi fractional–factorial design parametric study. Operating parameters were varied around the typical spray parameters in a systematic design of experiments in order to display the range of plasma processing conditions and their effect on the resultant coating. The coatings were characterized by hardness and electrical tests, image analysis, and optical metallography. Coating qualities are discussed with respect to dielectric strength, hardness, porosity, surface roughness, deposition efficiency, and microstructure. The attributes of the coatings are correlated with the changes in operating parameters.

PLASMA SPRAYING IS COMMONLY USED TO FORM CERAMIC COATINGS.[1] The plasma spray guns typically use a nontransferred dc plasma torch configuration with powers up to 100 kW. The more common coating functions include wear resistance, heat and oxidation resistance, corrosion resistance, electrical or thermal conductivity or resistivity, restoration of dimension, and clearance control. The scientific research lags behind the technical applications, and spraying has developed to a large extent by empirical means, with relatively little scientific understanding of the mechanisms involved in coating formation and of the factors controlling the structure and properties of the coatings.[2,3] As coating property requirements become more sophisticated, a better knowledge of the underlying principles is necessary for improved process control and coating quality. This work attempts to further the scientific understanding of the physical mechanisms involved in the formation of ceramic coatings by determining which processing parameters affect the structure and properties of the coatings. Former work in this area centered on the use of super–fine ceramic powders.[4]

Thermal spray technology is being used to fabricate heater tubes for use in thermal–hydraulic experiments.[5] These heater tubes are heated with a high–amperage dc power source to simulate nuclear fuel tubes. The heaters are fabricated using a multilayered coating system (metal bond coat, ceramic insulator, metal conductor, ceramic insulator, aluminum skin). Plasma spraying is used to fabricate the bond coat, conductor, and two insulator layers, while a twin–wire electric arc system is used to fabricate the heater skin. For this application, the capability of thermal spray processes to apply very thin layers of insulating materials well bonded to an aluminum base tube, metallic conductor, and aluminum skin is crucial to the success of the heater tubes.

Plasma–sprayed alumina–titania coatings have also been used for varied applications in the automotive, transportation, aerospace, and aircraft industries because of their refractory nature. The coatings produced are extremely wear resistant, heat resistant, resistant to most acids and alkalis, and have high dielectric strength. In addition, bond strength is high, interparticle strength is high, and finish is very smooth. The coatings exhibit little evidence of through porosity.

The alumina–titania coating used for this application must survive thermal cycling from thermal–hydraulic testing, which induces the tendency for spalling and destruction of the insulator coating. The coating must be thin enough to match the prototypical heat storage and transfer of a nuclear fuel tube. The coating must also have sufficient dielectric strength to insulate the electrical conductor from the aluminum skin. If the electrical resistance at any point in the insulator layer is very low or zero (electrical short), either the insulator layer was damaged during spraying (i.e., by cracking) or an insulator coating was too thin, allowing tendrils of molten or vaporized metal to follow the interconnected porosity and thus short through the insulator layer.

For this application, porosity, electrical resistance, and cracking of the ceramic insulator are the most important microstructural features that must be controlled for the construction of durable heaters.

Experimental Procedure

Taguchi experiments were utilized to optimize the selected powder systems for the layers of the heater tubes. Figure 1 illustrates a typical fabricated heater tube. A Metco plasma spray system and commercially available thermal spray powder (Metco 130 alumina–titania) was used for this study.

A Taguchi–style,[6] fractional factorial L8 design of experiment was employed to evaluate the effect of seven plasma processing variables on the quantitatively measured responses. The quantitative Taguchi evaluation of the plasma spray process is ideal because it displays the range of measured coating characteristics attainable, and it statistically delineates the impact of each factor on the measured coating characteristics across all combinations of other factors. This information is useful in examining the physical science involved in plasma spray coatings, establishing realistic coating specifications, and developing new equipment. The Taguchi analysis was accomplished with personal–computer–based software[7] on the measured responses.

Experiments ATN01 through ATN08 represent the eight runs evaluated with the Taguchi L8 approach. The experiments are detailed in Table 1. Each variable has two levels selected to band around the nominal settings (i.e., experiment ATN09) in order to demonstrate the plasma processing capabilities at a variety of stable plasma conditions. The parameters varied were current, primary gas flow, secondary gas flow, powder feed rate, spray distance, traverse

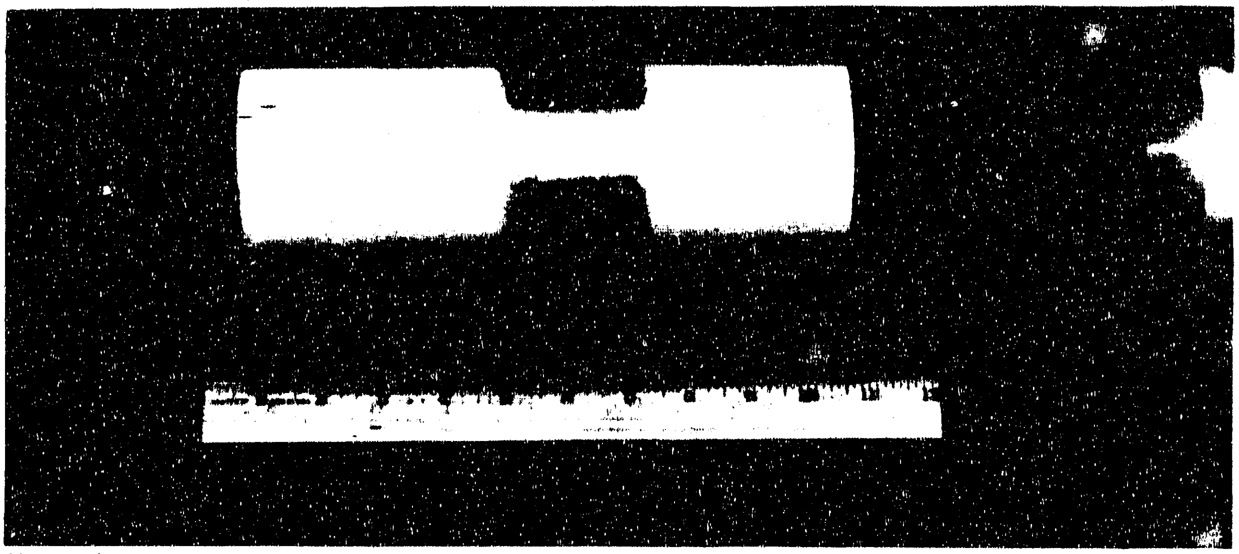


Fig. 1 – Heater tube.

Table 1. $Al_2O_3Ti_2$ Metco 130 Thermal Spray Experiments ATN01 through ATN09.

Experiment number	Current (A)	Primary flow (scfh)	Primary flow (scmh)	Secondary flow (scfh)	Secondary flow (scmh)	Feed rate (lb/h)	Feed rate (kg/h)	Distance (in.)	Distance (mm)	Traverse rate (in./s)	Traverse rate (mm/s)	Cooling (yes/no)
ATN01	450	65	1.84	10	0.28	3.0	1.36	3.5	88.9	18	457.2	N
ATN02	450	65	1.84	10	0.28	5.0	2.27	4.5	114.3	26	660.4	Y
ATN03	450	85	2.41	15	0.43	3.0	1.36	3.5	88.9	26	660.4	Y
ATN04	450	85	2.41	15	0.43	5.0	2.27	4.5	114.3	18	457.2	N
ATN05	500	65	1.84	15	0.43	3.0	1.36	4.5	114.3	18	457.2	Y
ATN06	500	65	1.84	15	0.43	5.0	2.27	3.5	88.9	26	660.4	N
ATN07	500	85	2.41	10	0.28	3.0	1.36	4.5	114.3	26	660.4	N
ATN08	500	85	2.41	10	0.28	5.0	2.27	3.5	88.9	18	457.2	Y
ATN09	500	75	2.13	10	0.28	5.0	2.27	4.5	114.3	18	457.2	Y

rate, and substrate cooling. The resulting responses evaluated were thickness through optical microscopy, superficial hardness with a Rockwell 15T test, microhardness with a Vickers test, porosity with image analysis, dielectric strength, coating roughness with image analysis, coating electrical resistance, and deposition efficiency.

A Metco MBN plasma spray system was utilized with a 9MB gun for this study. The primary gas was nitrogen. The secondary gas was hydrogen. The powder carrier gas was nitrogen, flowing typically at 1.416 scmh (50 scfh) (console flow) for all nine experiments. The powder injection was external to the torch and directed perpendicular to the flow. An x–y manipulator ensured the standoff distance and repeatability in the experiments. A y-step of 0.0032 m (0.125 in.) was used. Four passes were used to fabricate each of the coatings.

The powder was plasma sprayed onto 6061 aluminum plates (51 × 63 × 3 mm) cooled by air jets on the back side. One side of each steel coupon was grit blasted with No. 30 alumina grit before spraying. The substrates were coated with a nickel–aluminum bond coat of approximately 75 µm (3 mils), which was plasma sprayed at the manufacturer's recommended process parameters).

Materials Characterization Results

Table 2 lists the coating characterization results for this study. The coating attributes evaluated were ceramic thickness, superficial hardness, microhardness, porosity, dielectric strength, deposition efficiency, electrical resistance, and roughness.

The coating thicknesses, as revealed by optical metallographic observations at 300X magnification, are listed in Table 2. Average thicknesses from 12 measurements of the alumina–titania layers ranged from 102 to 219 µm (4.0 to 8.6 mils) reflecting the influence of the various spraying parameters.

Porosity for the coatings, as revealed by image analysis, are listed in Table 2. A Dapple Image Analyzer with a Nikon Epiphot metallograph was used for the metallurgical mounts. Image analysis procedures were first tested for sensitivity to parameter variance. The average porosity of the ceramic coatings ranged from 1.41 to 5.51%.

Superficial Rockwell hardness and Vickers microhardness measurements were taken on the coatings. The superficial Rockwell hardness measurement was taken normal to the deposit using the 15N method. Vickers microhardness measurements were taken perpendicular to the body of the coating. Ten measurements were taken and averaged. The superficial Rockwell hardness ranged from 47.0 to 68.2, while the microhardness measurements ranged from 917 to 1091.

Dielectric strength was determined using an Associated Research AC Hypot Model 4030. The test was conducted by applying an increasing voltage across the coating surface to the aluminum substrate using a 1-mm–diameter probe. Average values from three measurements ranged from 10.6 to 15.1 V/µm (268 to 383 V/mil).

Deposition efficiency for the 10 experiments was determined with conventional techniques by measuring the amount of sprayed ceramic deposited for an allotted time. The deposition efficiencies ranged from 74.1 to 93.6%.

Surface roughness was determined with image analysis. The data from each image was mathematically treated according to ANSI Standard B46.1 which indicates that roughness is calculated as the average departure y from the mean height in a given region. The average departure y was determined for 20 frames, and the 20 frames were averaged to yield the final measured roughness.

Table 2. Coating characterization results for Experiments ATN01 through ATN09.

Experiment Number	Thickness (µm)	Thickness (mils)	Hardness*	Hardness**	Porosity (%)	Dielectric Strength (V/µm)	Dielectric Strength (V/mil)	Deposition Efficiency (%)	Roughness (µm)	Tube (kΩ)	Plate (kΩ)
ATN01	152	6.0	55.4	997	2.14	11.9	302	74.1	1.98	75	260
ATN02	152	6.0	61.0	933	1.57	15.1	383	93.6	1.56	145	980
ATN03	102	4.0	54.7	967	5.06	11.8	300	93.3	1.98	54	230
ATN04	211	8.3	63.0	1091	3.44	10.6	268	85.6	1.88	130	890
ATN05	140	5.5	57.0	1062	3.28	10.9	277	80.6	1.84	150	590
ATN06	160	6.3	47.0	917	5.51	11.3	287	90.1	1.83	48	350
ATN07	102	4.0	55.4	1017	4.16	13.9	354	91.9	2.17	135	780
ATN08	219	8.6	58.0	1005	1.41	12.0	306	84.5	2.13	55	360
ATN09	193	7.6	68.2	1071	1.87	12.8	326	83.1	1.54	155	1080

*Superficial Rockwell 15N hardness measurement
**Vickers microhardness values (300–g load)

The coating roughnesses ranged from 1.54 to 2.17 µms (higher values are rougher).

The electrical resistance of the insulator coating was determined by spraying the first three heater coatings on 6061 aluminum tubes (diameters representative of the actual fuel tubes) and coupons, and then measuring the electrical resistance from the conductor to the base metal. The bond coat thickness was 76.2 µm (3 mils), the insulator thickness was 127 µm (5 mils), and the conductor thickness was 356 µm (14 mils). The tube insulator resistances ranged from 48 to 155 kΩ. The plate insulator resistances ranged from 260 to 1080 kΩ.

Image analysis revealed variances in the microstructures (i.e., porosity, cracking, unmelted particles) for the experiments. Figures 2a, 2b, 2c, and 2d illustrate microstructures for coatings ATN02, ATN05, ATN06, and ATN08. Coatings ATN02 and ATN05, shown in Figures 2a and 2b, were produced with a primary nitrogen gas flow of 1.84 scmh (65 scfh) and a spray distance of 114.3 mm (4.5 in.). The coatings were relatively thin with high insulating qualities (i.e., resistance, dielectric strength) and possessed low values of porosity and roughness. They are considered the best coatings produced in this test series. Coating ATN08 shown in Figure 2d had the lowest porosity value for the series but the resistance values for the coating were low. Coating ATN06 shown in Figure 2c exhibited the worst attributes for the application of this study including low hardness, high porosity, low resistance, and low dielectric strength.

Discussion of Taguchi Fractional Factorial Experiment Design

Taguchi–type fractional–factorial testing is an efficient means of determining broad–based factor effects on measured attributes. This methodology statistically delineates the impact of each variable on the measured coating characteristics across all combinations of other factors.

The spray tests were conducted and evaluated once, and all data points were considered in the analysis of variance (ANOVA) calculations. The rho percent (ρ%) calculation indicates the influence of a factor or parameter on the measured response, with a larger number indicating more influence. The ANOVA calculations guide further experimentation by indicating which parameters are the most influential on coating attributes. This information is extremely useful in developing new coating specifications.

The optimum coating for this application (as shown in Table 3 in order of priority) would have high insulator resistance, low porosity, high dielectric strength, low thickness, rough surface finish, high hardness, and a high deposition efficiency. Table 3 illustrates the results of the Taguchi analysis.

The Taguchi evaluation indicated that spray distance was the most dominant contributor to tube resistance at a 95.3 ρ%, with longer standoff [114.3 mm (4.5 in.)] resulting in higher resistance.

Spray distance was also the most significant contributor to plate resistance at 84.3 ρ%, with longer standoff [114.3 mm (4.5 in.)] resulting in higher resistance. Another contributor was powder feed rate at a 10.5 ρ% with the higher feed rate [2.27 kg/h (5 lb/h)] resulting in higher resistance.

Secondary hydrogen flow was the most significant contributor to lowering porosity at 48.2 ρ%, with lower flow [1.84 scmh (10 scfh)] resulting in lower porosity. Other contributors were traverse rate at 27.3 ρ%, with the low rate [457.2 mm/s (18 in./s)] resulting in lower porosity; and substrate cooling at 11.6 ρ%, with cooling resulting in a lower porosity.

Dielectric strength was also most influenced by hydrogen flow at 52.4 ρ%, with lower flow resulting in higher dielectric strength. Other contributors were traverse rate at 33.8 ρ%, with the higher rate [660.4 mm/s (26 in./s)] resulting in higher dielectric strength; and spray distance at 8.7 ρ%, with a longer spray distance resulting in a higher dielectric strength.

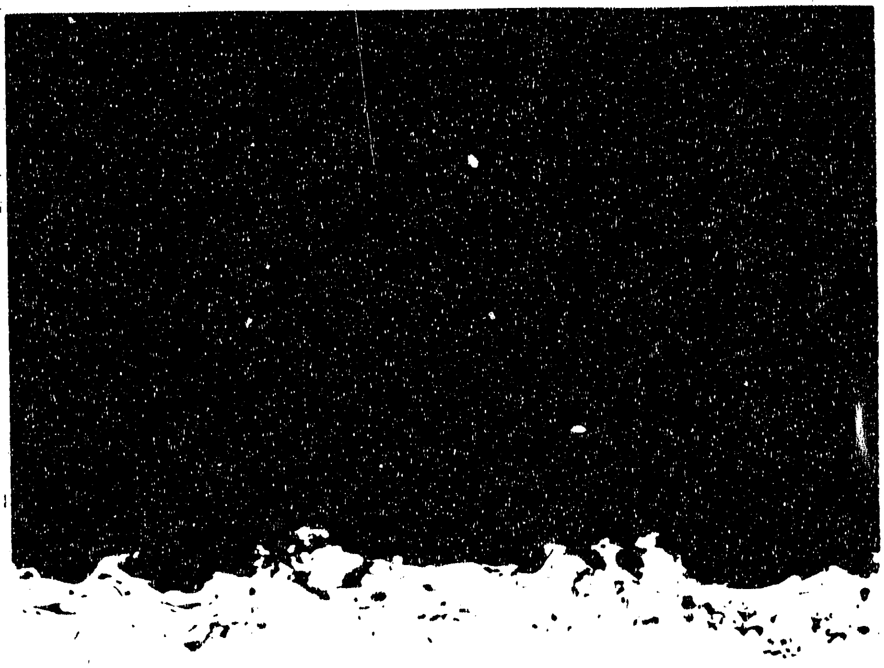
Coating thickness buildup is dominated by powder feed rate (i.e., 57.9 ρ%) and traverse rate (40.3 ρ%). Decreasing the powder feed rate and increasing the traverse rate will limit the thickness of the coating to acceptable requirements for the heater design.

Surface finish is most influenced by the primary nitrogen flow rate (i.e., 43.5 ρ%), current (15.7 ρ%), and powder feed rate (15.7 ρ%). Using the higher nitrogen flow rate [2.41 scmh (85 scfh)] and current (500 A) and the lower powder feed rate [1.36 kg/h (3 lb/h)] will result in a rougher coating which is desired for better bonding in the multilayered coating heater design.

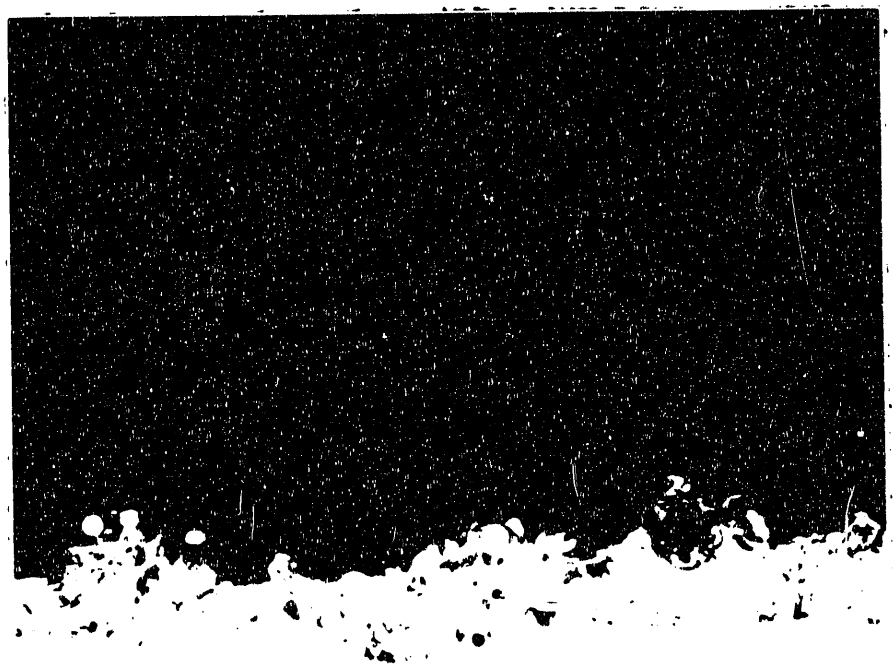
Superficial hardness increase (i.e., Rockwell) was influenced by a shorter spray distance [88.9 mm (3.5 in.), 35.3 ρ%], higher current (500 A, 21.7 ρ%), and faster traverse rate [660.4 mm/s (26 in./s), 18.2 ρ%]. Microhardness increase (i.e.. Vickers) was most influenced by a faster traverse rate [660.4 mm/s (26 in./s), 51.7 ρ%], shorter spray distance [88.9 mm (3.5 in.), 23.6 ρ%], and higher nitrogen flow [2.41 scmh (85 scfh), 14.7 ρ%].

Deposition efficiency was most influenced by a high traverse rate (i.e., 73.3 ρ%) and secondarily by a high hydrogen flow rate (i.e., 10.8 ρ%).

Selection of the optimum levels of the design factors can produce an optimum coating for this particular application. This coating would have high insulator resistance, low porosity, high dielectric strength, low thickness, high hardness, rough surface finish, and high deposition efficiency. This coating can be obtained by using a current of 500 A, a primary nitrogen gas flow of 1.84 scmh (65 scfh),



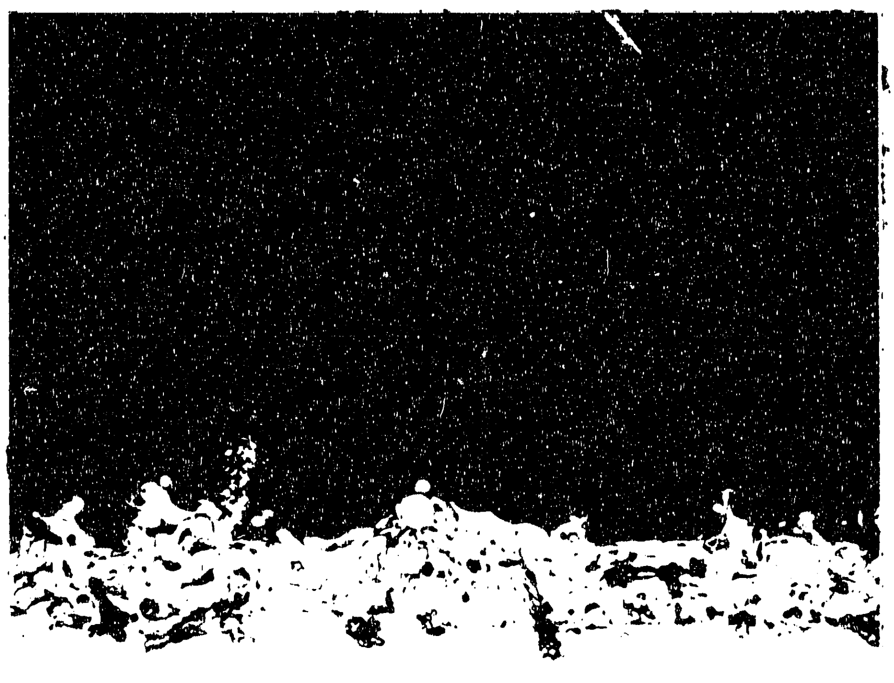
(2a) ATNO2



(2b) ATNO5

Fig. 2 – Optical photomicrograph of as–sprayed coatings ATN02, ATN05, ATN06, ATN08.

(2c) ATN06



(2d) ATN08

Fig. 2 – (continued).

Table 3. Results of the Taguchi Analysis.

Desired Attribute	Current (ρ%/A)	N_2 flow (ρ%/scfh)	H_2 flow (ρ%/scfh)	Feed rate (ρ%/lb/h)	Spray distance (ρ%/in.)	Traverse rate (ρ%/in./s)	Cooling (yes/no)
	Processing Factors						
1 **High** Tube Resistance	0.2/450	1.7/65	0.70/10	1.20/3	95.3/4.5	0.70/18	0.20/Y
2 **High** Plate Resistance	1.6/450	0.1/85	2.07/10	10.5/5	84.3/4.5	1.17/26	0.29/N
3 **Low** Porosity	3.5/450	1.9/65	48.2/10	5.50/5	2.1/4.5	27.3/18	11.6/Y
4 **High** Dielectric Strength	1.0/450	0.5/65	52.4/10	0.14/5	8.7/4.5	33.8/26	3.50/Y
5 **Low** Thickness	0.0/450	0.7/65	0.15/15	57.9/3	0.7/4.5	40.3/26	0.15/Y
6 **High** Surface Finish	15.7/500	43.5/85	4.6/10	15.7/3	10.6/3.5	4.1/18	5.9/N
7 **High** Hardness (Rockwell)	21.7/500	8.9/65	5.1/15	3.3/3	35.3/3.5	18.2/26	7.6/N
8 **High** Microhardness	0.0/500	14.7/85	3.6/15	4.7/3	23.6/3.5	51.7/26	1.5/Y
9 **High** Deposition Efficiency	0.0/500	10.8/85	1.14/15	7.3/5	3.5/4.5	73.3/26	4.0/Y

a secondary hydrogen flow of 0.28 scmh (10 scfh), a powder feed rate of 1.36 kg/h (3.0 lb/h), a spray distance of 114.3 mm (4.5 in.), a traverse rate of 457.2 mm/s (18 in./s), and no cooling of the substrate.

The Taguchi evaluation employed in this study is significant in that it directs further experimentation considering the most important process or coating attributes and the process parameters that affect these attributes. The most important attributes may differ for the same material in different applications, and the baseline data generated in this study can be used to develop specific confirmation runs that approach the desired application attributes.

Summary and Conclusions

An experimental study of the plasma spraying of alumina-titania powder has been presented. Experiments employed a Taguchi fractional-factorial approach with typical process parameters. The coatings were characterized by hardness tests, electrical tests, surface roughness, image analysis, and optical metallography. Coating qualities were determined with respect to insulator resistance, dielectric strength, hardness, porosity, deposition efficiency, and microstructure.

The alumina-titania coating thicknesses, reflecting influences of spraying parameters, ranged from 102 to 219 µm (4.0 to 8.6 mils). Insulator tube resistance ranged from 48 to 155 kΩ. Insulator plate resistance ranged from 260 to 1080 kΩ. Porosity for the coatings, as revealed by image analysis, ranged from 1.41 to 5.51%. The superficial Rockwell hardness ranged from 47.0 to 68.2, while the microhardness measurements ranged from 917 to 1091. Dielectric strength measured for the coatings ranged from 268 to 383 V/mil. Deposition efficiencies ranged from 74.1 to 93.6%. Surface roughness ranged from 1.54 to 2.17 µm.

The Taguchi evaluation indicated that hydrogen flow and traverse rate were the most significant contributors to porosity. Spray distance dominated the insulator plate and tube resistance. Surface finish was most influenced by primary nitrogen flow. Deposition efficiency was most influenced by traverse rate. Dielectric strength was most influenced by hydrogen flow. Rockwell hardness was equally influenced by spray distance, amperage, and traverse rate. Vickers hardness was influenced by traverse rate and spray distance. An optimum coating for this particular application can be obtained by using a current of 500 A, a primary nitrogen gas flow of 1.84 scmh (65 scfh), a secondary hydrogen flow of 0.28 scmh (10 scfh), a powder feed rate of 1.36 kg/h (3.0 lb/h), a spray distance of 114.3 mm (4.5 in.), a traverse rate of 457.2 mm/s (18 in./s), and no cooling of the substrate.

The objective of this and future work is to optimize alumina-titania coatings. After baseline data are generated on factors that influence coating characteristics, other important characteristics must be quantitatively evaluated using a similar design of experiment approach. Then the design engineer wishing to utilize an alumina-titania coating can review the ranges of coating characteristics generated through the plasma spray process. Coatings of known structure can be applications-tested to prioritize which coating characteristics impact the coating performance in that specific application. From this methodology, processing parameters can be adjusted, optimized, and confirmed. A realistic specification can be made for the coating as sprayed, and ultimately, the specification will be transferred back to the control parameters only.

The procedure described in this paper will assist in selecting and optimizing operational parameters for future alumina-titania plasma spray processing experiments and applications. Future work is needed in analytical modeling to obtain a better understanding of the process.

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References

1. Kubel, E. D., *Advanced Materials and Processes, 132*, 6, December 1987, pp. 69–80.
2. Pfender, E., "Fundamental Studies Associated With the Plasma Spray Process," *Proceedings of the National Thermal Spray Conference, Orlando, Florida September 14–17, 1987.*
3. Fauchais, P., "State of the Art for the Understanding of the Physical Phenomena Involved in Plasma Spraying at Atmospheric Pressure," *Proceedings of the National Thermal Spray Conference, Orlando, Florida, September 14–17, 1987.*
4. T. J. Steeper, D. J. Varacalle, Jr., G. C. Wilson, A. J. Rotolico, J. E. Nerz, W. L. Riggs, "A Taguchi Experimental Design Study of Plasma-Sprayed Alumina-Titania Coatings," published in symposium volume *Thermal Spray Coatings: Properties, Processes, and Applications," American Society of Metals National Thermal Spray Conference, Pittsburgh, Pennsylvania, May 1991.*
5. Steeper, T. J., D. J. Varacalle, Jr., G. C. Wilson, V. T. Berta, "Use of Thermal Spray Processes to Fabricate Heater Tubes for Use in Thermal-Hydraulic Experiments," published in symposium volume *Thermal Spray Coatings: Properties, Processes, and Applications," American Society of Metals National Thermal Spray Conference, Pittsburgh, Pennsylvania, May 1991.*
6. Taguchi, G., and S. Konishi, *Taguchi Methods: Orthogonal Arrays and Linear Graphs*, ASI Press, 1987.
7. Culp, R. F., *SADIE*, 1989.

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