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A Highly Strain and Damage Tolerant Thermal Barrier Coating Fabricated by Electro-sprayed Zirconia Hollow Spheres

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Abstract

An approach to make air plasma sprayed (APS) thermal barrier coatings (TBCs) with the enhanced strain and damage tolerance was reported, using a novel hollow spheres produced by electro-spraying (ESP) technique. Compared with agglomerated & sintered (A&S) and hollow spherical (HOSP) yttria-stabilized zirconia (YSZ) powders, the ESP powder showed a unique network microstructure and the TBCs exhibited a 2-3 times longer thermal cycling lifetime. The splat morphology and the top coats microstructure were investigated. Some semi-melted ESP particles were observed in the as-sprayed top coat. The indentation coupled with the Raman mapping technique was employed to evaluate the strain and damage tolerance of the TBCs. The coatings deposited by the ESP powder show a lower in-plane stiffness determined by three-point bending tests. It is proposed that the superior performance is attributed to the lower amount of the short microcracks (0.5–4 μm) with low angle ($< 45^\circ$) and the semi-melted ESP particles remained in the YSZ top coat.

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Keywords

Thermal barrier coatings; Air plasma spray; Strain tolerance; Electro-spraying; Yttria stabilized zirconia.

I. Introduction

The most important factor for the thermal barrier coatings (TBCs) used in aero-engine or industrial gas turbines is the lifetime. Failure of the air plasma sprayed (APS) TBCs is usually associated with the cracks nucleated from the interface, which is driven by the strain energy in the ceramic coatings.¹⁻³ The durability of the TBCs is largely controlled by the strain and damage tolerance. Currently, there are two primary approaches to increase the strain tolerance of the APS TBCs. One is the introduction of segmentation cracks with length of at least half of the coating thickness.^{4,5} However, segmentation cracks are usually formed in the thick thermal barrier coatings ($>500\text{ }\mu\text{m}$).⁶ The increased thickness of the TBCs could cause greater thermal gradients during the high temperature service and consequently higher thermal stresses will generate in top coats. In addition, the thickness increase of the coating will increase the elastic strain energy stored and hence increase energy release rate for a crack.⁷ Another approach to enhance the strain tolerance of the APS TBCs is to optimize the coating porosity.⁸ While a high amount of porosity around the interface could weaken the interfacial bonding.⁹ Previous literature also showed TBCs are more susceptible to erosion than fully dense ceramics because the coating microstructures contain many crack-like features, so the TBCs with lower porosity can improve the impact and erosion resistance. Therefore, to increase the strain/damage tolerance but maintain a certain porosity level is of practical importance for the TBCs applications. The orientated inter- and intra-splat cracks is beneficial to lower the in-plane stiffness of the TBCs, then reducing the driving force of spallation.^{7, 10-12} Researchers have been devoted to stiffness modification of APS TBCs by controlling the coating porosity. These work focused on the plasma spraying parameters¹³⁻²⁰, feedstock materials (e.g., morphology and size distribution).²¹⁻²⁴ Lima et al.²⁵⁻²⁸ developed a bimodal structured in top coats to

enhance the TBCs durability, using nano-structured YSZ powder prepared by spray drying.

Previous works have shown that the powder morphology can affect the coating porosity.^{29,}
³⁰ The commercial yttria stabilized zirconia (YSZ) powders for the APS TBCs falls into three categories: fused and crushed (F&C), agglomerated & sintered (A&S) and hollow spherical (HOSP). The TBCs sprayed by the porous powders, e.g., A&S and HOSP powder, showed higher porosity than these by the dense powder (e.g., F&C).^{14, 15} Present powder manufacturing techniques include spray drying, fusing & crushing, spheroidization and Sol-Gel. These techniques have been focused on the flowability of the powder. Novel techniques producing ceramic powder with a unique porous structure could provide an alternative approach to modifying the coating microstructure, hence improve the TBCs strain tolerance.

This work developed an electro-spraying (ESP) technology to produce the YSZ powder, then investigated the strain and damage tolerance of TBCs. One home-made and two commercial YSZ powders, with the same particle size distribution, were used for the top coat deposition. The thermal cycling life of the TBCs was investigated. The splat morphology, coating microstructure and indentation mechanical properties were also compared. In addition, a method to characterize the strain and damage tolerance of the TBCs was developed, which utilized the indentation technique combined with the Raman mapping. The in-plane stiffness of the TBCs was also measured by three-point bending test. Finally, the relationship between the strain tolerance, the coating microstructure and the powder morphology was discussed.

II. Experimental procedures

(1) Fabrication of spherical YSZ powder by the ESP technique

The ESP technique was used to prepare the YSZ powder, as the schematic shown in Fig.

1. Firstly, the slurry was prepared by mixing the fine YSZ powder (particle size ~200 nm),

polyethersulfone (PES) and N-methyl-2-pyrrolidone (NMP) by mechanical stirring. Secondly, the degassed slurry was injected into the syringe needle (0.5 mm in internal diameter). The electric potential difference between the needle and collecting tank is ~ 20 kV. Due to the electrostatic forces, the slurry was subsequently disintegrated into numerous micro-droplets, as shown in Fig. 1a. Once the micro-droplets immersed into the coagulant (water), they would be transformed into solid precursor spheres through a phase inversion mechanism,³¹ because the NMP is soluble in water but the PES is not. Fig. 1b is the schematics of the cross-sectional microstructure of the ESP droplets before and after phase inversion. The submicron YSZ particles were dispersed in the organic solvent (PES/NMP) as the ‘sphere A’. Then a dense skin layer and a porous core formed due to diffusion rates of the PES into water is different from surface to core, as the solid ‘sphere B’. The submicron YSZ particles were connected by the PES (solid phase). Detailed mechanism of the phase inversion can be found elsewhere.³² After 2 hours annealing at 1100 °C, the organic (predominantly PES) was burned out. Only the YSZ was left in ‘sphere C’ (Fig. 1b). These annealed particles can be sieved for coating spraying.

(2) Sample preparation and testing

A supersonic atmospheric plasma spray (SAPS) system (Model: HEPJ-II; National Key Laboratory for Remanufacturing, Beijing, China) was used for coating deposition. The key advantage of this system was the novel gun fixed with a laval nozzle. The feedstock powder was radially injected into the plasma jet by an internal injection port with an inlet diameter of 2 mm inside the nozzle. The characteristics of the in-flight particles can refer to somewhere.²⁷ Different carrier gas (Ar) flow rate was used to ensure a good injection of feedstock powder into the plasma jet. The plasma spraying parameters were summarized in Table I.

Both bond coats and top coats were sprayed by APS. Prior to deposition of the YSZ top coats, NiCoCrAlY (AMDRY 365-2; Oerlikon Metco, Westbury, NY) bond coats were sprayed on grit blasted Hastelloy-X alloy (Shanghai Niesheng Alloy Materials Co., Ltd., Shanghai, China). Then different top coats were sprayed using the ESP powder and two commercial products, i.e., A&S (233C; Oerlikon Metco, Westbury, NY) and HOSP (204B-NS; Oerlikon Metco, Westbury, NY). All YSZ powders were 7-8 wt.% YSZ and sieved to the same particle size distribution (45-75 μm). The thicknesses of the bond coats and the top coats were $\sim 150\ \mu\text{m}$ and $\sim 250\ \mu\text{m}$, respectively.

The thermal cycling lifetime of TBCs was tested using a laboratory furnace, which consists of a 10-min heating up to 1150 $^{\circ}\text{C}$, 23.5-h dwell at 1150 $^{\circ}\text{C}$ and then followed by a 20-min air cooling. The test conditions employed in this study are severe for the bond coat oxidation. The choice of the test conditions is to accelerate the coating degradation process. The TBCs failure was defined as approximate 10 % visible delamination. At least 20 samples were evaluated for each type of TBCs with the size in $15\times 15\ \text{mm}^2$ cut from the plate specimens.

The YSZ splats were collected on the polished surface of steel plates to investigate the splat morphologies of different powders. The surface of the steel plates were polished to Ra 0.1 μm , and there is no preheat treatment prior to the splats collection.

(3) Sample characterization

The microstructure of the YSZ powder and coatings was observed using a scanning electron microscope (SEM, FEI Quanta 200; Eindhoven, Netherlands). The coatings were mounted using a high fluidity epoxy at a low pressure. The porosity orientation of the top coats was evaluated by image analysis. All images were taken in backscattered electron (BSE) mode, and 10 images for each sample were used, covered area up to $1.95 \times 10^5\ \mu\text{m}^2$.

The hardness and Young's modulus of the top coats were measured using a micro-indenter (MHT; Anton Parr, Graz, Austria). The indentation measurements were carried out on the cross-sections, with a constant loading rate of 0.05 N/s and a holding time of 10 s. At least 20 indentations were made per sample. The maximum load on the indenter was 1.5 N, and the imprint size is approximately 15 μm . The Poisson's ratio of the TBC is 0.2. The Young's modulus was determined from the unloading curve using Oliver-Pharr method.³³

The Raman mapping coupled with indentation technique was developed to characterize the strain tolerance of the TBCs. The indenter was applied on the polished cross-sections of the coatings, then indentation fields were evaluated by a Raman spectroscopy coupled with a 532 nm laser (LabRAM HR Evolution; Horiba, France). The laser beam was focused through a 50 $\times$ (NA=0.75) objective lens, and the step size is 5 μm both in the x and y axial direction. All the spectra were fitted by a mixed Lorentzian-Gaussian function using a Labspec 6 software to obtain the peak position. The Raman band at 465 cm^{-1} was selected for analysis of peak shift.³⁴ Free-standing YSZ coatings were used as the reference sample.

Three-point bending test of free-standing top coats was carried out using a bend fixture with adjustable spans. The rectangular bar specimens ($\sim 2 \times 15 \text{ mm}^2$) were cut from the as-sprayed plate using a SiC abrasive cutting blade in a precision cut-off machine (Accutom-10; Struers, Rodovre, Denmark). Then the cross-sections of the sliced beams were polished to 1 μm finish using diamond paste. Freestanding YSZ beams ($\sim 15 \times 2 \times 0.25 \text{ mm}^3$) were prepared by soaking the bars in aqua regia. A support span of 10 mm was used to maintain a sufficiently large span to avoid fracture by shear stresses. The loading nose was aligned across the central of the TBC beams and the three-point bending tests were conducted with a constant crosshead speed of 0.1 mm/min. The recorded load-displacement curve was linearly fitted. The flexural

modulus, E_{beam} , for three-point bending within the range of elastic deformation is determined by:

$$E_{beam} = \frac{PL^3}{4bh^3} \times \frac{1}{w}$$

where L is support span; P is the applied load; w is the deflection at the centre of the beam; b is the width of the rectangular beam and h is thickness.

III. Results

(1) Microstructure of the powders

The morphology of the ESP powder (before sieving) was shown in Fig. 2a. All the particles are in spherical shape, which can ensure a good flowability. Submicron-sized particles were observed on the ESP particle surface (Fig. 2b). The size of these submicron-sized particles is on the same level with the original powder used in the ESP process. The ESP particle shows a finger-liked porous structure packed with a spongy shell, as the dot line marked in Fig. 2c. The porosity of the spongy shell is less than 10 %, and the total porosity of the ESP powder is approximately 35-45 %.

For comparison, two types of commercial YSZ powder were also used. Although these particles are all in spherical shape, there are significant differences in cross-sectional microstructure (insets in Fig. 3). The powders made by the A&S technique involves spray drying and subsequent high temperature sintering, showing a rough-textured microstructure. The A&S particle consists of several micron-sized particle clusters, and several large pores exist among these clusters. The HOSP process, involving spray drying and plasma densification, produces spheres with a hollow core and a dense shell.

(2) The microstructure of splats and YSZ top coats

It is well known that the different powder morphology can cause differences in the coating microstructure, which is fundamentally affected by the splat morphology. Therefore the coating microstructure and the splat morphology produced by three powders were compared. Fig. 4 shows the splat morphologies of the HOSP and the ESP powder. All splats of the HOSP powder present a well-melted state and splashed shapes, as shown in Fig. 4a. The splat morphology of the A&S powder was very similar to the HOSP powder, and it is not shown in Fig. 4. While the ESP powder shows different molten states and various splat morphologies. The splats of the ESP powder were disk-shaped. Different types of mud cracking were observed, e.g., crack size and spacing among cracks (Fig. 4b-c). In addition, the semi-melted ESP particles were observed (Fig. 4d). The difference in the splash extent and the melted-state among the three powders should be associated with particle microstructure, which should affect the powder injection and heat conductivity between the powder and plasma jet.

The microstructure of the coatings deposited using different YSZ powders was investigated, as the polished and fractured cross-sections shown in Fig. 5. Top coats deposited by the A&S and the HOSP powders show the typical columnar structure. All the A&S and HOSP particles were well melted, as the columnar grains in each splat (Fig. 5g and 5h). The porosity was composed of globular pores, inter-splat cracks. Although the typical columnar grains occurred in the coatings deposited by the ESP powder, some semi-melted particles were also observed. Some even retained their original shape, as the black arrows marked in Fig. 5f. The area fraction of semi-melted ESP particles is up to 20 % estimated by image analysis. The boundaries (gaps) were occurred between the melted and semi-melted particles (white arrows marked in Fig. 5f). The fracture morphology of semi-melted ESP particles packed by the splats with columnar structure is shown in Fig. 5i. The semi-melted particle consists of numerous

submicron-sized particles, which could lead to a higher porosity than the fully-melted splats. Overall, the TBCs deposited by the ESP particles showed a bimodal structure, consisting of melted splats with the columnar structure and semi-melted particles with agglomerated submicron-sized powder.

Difference in splat morphologies and cross-sectional microstructure of the YSZ coatings should cause differences in porosity. For a typical APS TBC, it consists of the large pores (called ‘globular pores’, 3-10 μm), fine pores (around 0.1 μm) and micro cracks (>0.5 μm in length). Fig. 6 compared the porosity for the three types of the TBCs by image analysis. The top coats deposited by the ESP powder show a relatively higher level in the total porosity than the conventional (A&S and HOSP) coatings. The coatings deposited by the A&S powder have the highest level in the globular pore. While the microcracks and the fine pores show the highest level in the coating sprayed by the ESP powder.

(3) Failure of the TBCs

Fig. 7 shows the thermal cycling lifetime of the TBCs prepared by different powders. The lifetime of the A&S and the HOSP TBCs is on the same level (8-12 cycles at 1150 $^{\circ}\text{C}$), while the lifetime of TBCs made by the ESP powder exhibited a 2-3 times longer. Fig. 8 shows the failure position of three types of the TBCs. All the TBCs failed at the top coat/thermally grown oxides (TGO) interface. Since all the top coats were deposited on the same bond coat, the only possibility for the different lifetime can be attributed to the differences in the microstructure of the top coats. The presence of semi-melted ESP particles is the biggest difference, which should contribute to the enhanced thermal cycling lifetime.

(4) Evaluation of the strain/damage tolerance of the coating

The indentation technique is a simple way to detect the effect of defects on the coating

mechanical properties. The hardness and the Young's modulus of the three TBCs by micro-indentation were plotted in Fig. 9. Both the hardness and the Young's modulus of the top coats deposited by the ESP powder are slightly lower than those deposited by the A&S and the HOSP powder. It is due to some indenter were applied on (or close to) semi-melted ESP particles, then resulted in low values of the hardness and the Young's modulus. Therefore the top coats deposited by the ESP powder can be considered as a composite consisting of soft inclusions (semi-melted particles) and hard matrix (melted particles).

The longer thermal cycling lifetime may be associated with the higher strain tolerance of the coatings deposited by the ESP powder. To verify this idea, indentation test was conducted on the cross-section of the TBCs. An indentation load 3 N was chosen in order to avoid the stress relaxation by radial cracks. As shown in Fig. 10, no apparent radial crack was generated. Fig. 10c and d show the Raman mapping of the peak shift for the top coats deposited by the HOSP and the ESP powder, respectively. Since the peak shift is proportional to the strain, the stress field can be easily visualized by the mapping. Both TBCs exhibit positive peak shifts around the imprints, indicating of a compressive stress field. For the TBCs deposited by the ESP powder, the indentation-induced residual stress region is far smaller than that deposited by the HOSP powder. This implied that the strain was confined within the indented field and could not propagate too far. Fig. 10e plots the Raman peak shift as a function of the distance from the imprint center. The maximum peak shifts at the imprint center are almost the same. Compared with the top coat deposited by the HOSP powder, the strain in the coating by the ESP powder can only extend to a shorter distance. This means the TBCs deposited by the ESP powder are more strain tolerant.

To evaluate the damage tolerance of the coatings, a larger indentation load of 5 N was

used to induce cracks in the coatings. Under this load, both the coatings deposited by A&S and HOSP powder showed the radial cracks around the imprint corner, but no apparent cracks occurred in coatings deposited by the ESP powder (Fig. 11), suggesting that the latter is more resistant to the cracks (i.e., damage tolerance).³⁵ This is because the bimodal structured TBCs deposited by the ESP powder could absorb more energy induced by the indentation deformation. Higher damage tolerance means the crack nucleation around the imperfection sites at the interface can be largely suppressed. The APS TBCs usually fails in the top coats (several micrometers above the TGO)^{1,2}, therefore the TBCs deposited by the ESP powder should show a longer thermal cycling life.

Although the indentation technique is being increasingly applied to porous materials,³⁶⁻³⁹ the granularity of the porous structure may cause the non-conservation of volume during deformation (crushing, collapse and densification)³⁸. Therefore the indentation-induced stress field is too local to represent the strain tolerance of the bulk coating. The in-plane Young's modulus measured by three-point bending tests was compared in Fig. 12. The top coat deposited by the ESP powder showed the lowest in-plane Young's modulus and the difference can interpret the thermal cycling lifetime, i.e., $ESP > A\&S > HOSP$.

IV. Discussion

In this work, the coatings were deposited with the same plasma gun power and most of the ESP particles were fully melted in the plasma jet. Therefore the powder injection should be the key factor affecting the melting state of the feedstocks.⁴⁰ The ESP particles could be fully melted in the plasma jet by an optimal the carrier gas flow rate for a feedstock with a narrow size distribution or increase gun power.²⁷ In addition, the difference in powder microstructure may affect the particle-plasma interaction, e.g., heat transfer.⁴¹ The relatively dense shell and a

porous skeleton of the ESP powder could reduce the heat transfer in the particle. While there are open pores in the A&S powder, heat transfer in particle through convection is more effective. For the HOSP powder, it is easy to be melted due to the hollow structure.^{15, 40}

Previous research suggested that the porosity in the coating could lead to large scattered data of the hardness and the Young's modulus by indentation test.⁴² The imperfection-induced displacements could change the measured elastic constant and hardness through their contributions to the recorded load-depth curve, due to the irrecoverable (non-penetration) displacement.^{42, 43} The work by Lima et al.²⁵ demonstrated a two slopes in the Weibull distribution of indentation mechanical properties for the APS TBCs with a bimodal structure. A high slope (high Weibull modulus) represented non-molten/semi-molten feedstock particles and a low slope (low Weibull modulus) for fully molten particles.²⁵ The indentation data of the coating deposited by the ESP powder shows a larger scatter (Fig. 9). The semi-melted ESP particles act as a soft phase in the YSZ coating, as proved by the smaller residual stress field induced by indentation. The large indentation stress field indicates the less stress relief effect for the imperfections (pores and microcracks) in the conventional APS TBCs deposited by the HOSP powder. No radial indentation cracks and lower in-plane Young's modulus determined by three-point bending test also proved the higher strain and damage tolerance of the coatings deposited by the ESP powder.

The results presented above indicate a higher strain and damage tolerance of the TBCs deposited by the ESP powder, which is consistent with the longer lifetime. While all the improvements are directly related to the unique microstructure, especially the orientated inter- and intra-splat cracks.¹¹ Previous research indicated that the total porosity (in a range 15-20 %) plays a minor role,⁴⁴ which is in consistent with the results in this work (a similar total porosity

but different durability). As shown in Fig. 6, the top coat deposited by the ESP powder shows a higher proportion of microcracks and fine pores. As well known, the horizontal microcracks can facilitate the crack propagation along the interface and lead to a short TBCs lifetime, and the vertical microcracks can improve the strain tolerance, which lower the driving force for coating delamination.¹⁷ Therefore the crack orientation distributions were analyzed statistically in different crack length intervals (Fig. 13). The 0° represents the microcracks parallel to the top coat/bond coat interface. Fig. 13a shows the orientation distribution of all the cracks with length $\geq 0.5 \mu\text{m}$, and there is no apparent difference in the three types of YSZ coatings. While both the area fractions of low angle ($< 45^\circ$) cracks with length in $0.5\text{-}2 \mu\text{m}$ and $2\text{-}4 \mu\text{m}$ are the lowest in the coatings deposited by the ESP powder (Fig. 13b and c), especially the later follows $\text{ESP} < \text{A\&S} < \text{HOSP}$. It could interpret the lifetime results ($\text{ESP} > \text{A\&S} > \text{HOSP}$), due to the lower crack angle the lower crack propagation resistance. In addition, the coatings deposited by the ESP powder have the highest amount of long cracks ($> 4 \mu\text{m}$), especially orientated in $45\text{-}90^\circ$ (Fig. 13d). This is attributed to the presence of the semi-melted particles, which generated boundaries between the melts and semi-melts due to poor contact. In a word, the lower amount of the short cracks ($0.5\text{-}4 \mu\text{m}$) with low angle ($< 45^\circ$) and the porous semi-melted particles contribute to the longer lifetime of the TBCs deposited by the ESP powder.

V. Summary

The APS TBCs produced by the ESP powder exhibited a much longer lifetime (2-3 times) than the TBCs deposited using the commercial powders, which can be attributed to its enhanced strain and damage tolerance. The strain and damage tolerance of the TBCs deposited by the ESP powder comes from the higher amount of short microcracks (e.g., $0.5\text{-}4 \mu\text{m}$) with low angle ($< 45^\circ$) and porous semi-melted particles retained in the coating. The smaller residual

stress fields induced by indentation is consistent with the lower in-plane Young's modulus determined by the three-point bending tests of the TBCs deposited by the ESP powder.

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Figure captions

Fig. 1 Schematics of (a) electro-spraying and (b) phase inversion of the electro-sprayed droplets.

Fig. 2 SEM images the ESP YSZ powder before sieving: (a) morphology under low magnification, (b) surface and (c) cross-sectional microstructure.

Fig. 3 Morphology of the commercial YSZ powders: (a) A&S, (b) HOSP.

Fig. 4 Splat morphologies of (a) the HOSP and (b-d) the ESP particles.

Fig. 5 Microstructure of the as-sprayed YSZ top coats deposited by different powders: (a-c) low magnification and (d-f) high magnification of polished cross-sections, (g-i) fractured cross-sections; (a/d/g) A&S, (b/e/h) HOSP, (c/f/i) ESP.

Fig. 6 The porosity of the as-sprayed YSZ top coats deposited by different powders.

Fig. 7 The lifetime of the TBCs deposited by different powders.

Fig. 8 The delamination of the TBCs deposited by different powders: (a) A&S, (b) HOSP, (c) ESP.

Fig. 9 (a) Hardness and (b) Young's modulus measured by micro-indentation of the as-sprayed TBCs deposited by different powders.

Fig. 10 The imprints under 300 g load on the cross-sections of as-sprayed YSZ top coats deposited by (a) HOSP and (b) ESP powder; (c/d) is the corresponding Raman peak shift ($\sim 465\text{ cm}^{-1}$) mapping; (e) the dependence of the Raman peak shift on the distance from the imprints center.

Fig. 11 The SEM images of indentation cracks under 500 g load on the cross-sections of the as-sprayed TBCs deposited by (a) A&S, (b) HOSP and (c) ESP powder.

Fig. 12 The in-plane Young's modulus determined by three-point bending tests of the as-sprayed TBCs deposited by different powders.

Fig. 13 Cracks orientation distributions of the as-sprayed top coat in different intervals of crack length: a) $> 0.5 \mu\text{m}$, b) $0.5\text{-}2 \mu\text{m}$, c) $2\text{-}4 \mu\text{m}$, d) $> 4 \mu\text{m}$. The 0° of the microcrack angle means the microcracks parallel to the TBC/bond coat interface. Area Fraction was normalized to total microcrack porosity.

Table I Summarized spraying parameters for the APS coatings

Spraying parameters	Top coats			Bond coats
	A&S	HOSP	ESP	
Primary gas Ar (SLPM*)	110	110	110	90
Secondary gas H ₂ (SLPM)	19	19	19	15
Carrier gas Ar (SLPM)	7	7	10	5
Current (A)	420	420	420	380
Voltage (V)	140	140	140	130
Spray distance (mm)	90	90	90	100
Gun traverse speed (mm/s)	500	500	500	500

*SLPM---Standard liter per minute.

Fig. 1

Fig. 2

Fig. 3

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Fig. 9

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Fig. 13