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A Comparative Study of High Velocity Oxygen Fuel, Vacuum Plasma Spray, and Axial Plasma Spray for the Deposition of CoNiCrAlY Bond Coat Alloy

A. Scrivani, U. Bardi, L. Carrafiello, A. Lavacchi, F. Niccolai, and G. Rizzi

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In the aerospace field as well as in the stationary gas turbine field, thermally sprayed coatings are used to improve the surface properties of nickel-super-alloys materials. Coatings are commonly used as bond coat and antioxidation materials (mainly MCrAlY alloys) and as thermal barrier coatings (mainly yttria partially stabilized zirconia). The purpose of the current study was to assess the properties of thermally sprayed bond coat CoNiCrAlY alloys comparing the performance of three different techniques: vacuum plasma spray (VPS), high velocity oxygen fuel (HVOF), and axial plasma spray (AxPS). The quality of the deposited films has been assessed and compared from the point of view of microstructural (porosity, oxide concentration, unmelted particles presence) and mechanical (hardness) characteristics. The surface composition and morphology of the coatings were also determined. Specific efficiency tests were performed for the three examined technologies. The highest quality coatings are obtained by VPS, but also high velocity oxygen fuel and AxPS sprayed films have interesting properties, which can make their use interesting for some applications.

Keywords axial plasma spray, CoNiCrAlY, high velocity oxygen fuel (HVOF), MCrAlY, VPS

1. Introduction

Coating technology is progressing at a steady rate with continuous significant improvements in the performance of coatings. In general, however, performance alone is not sufficient to determine the success of a new technology, and it must be balanced against cost and environmental impact. In this sense, the use of different methods for depositing the same coatings may lead to very different results in terms of quality to cost ratio.

In the aerospace field, as well as in the stationary gas turbine field, thermal spray coatings are becoming more and more important. Thermal spray coatings are commonly used as oxidation resistant materials (mainly MCrAlY alloys where M stands for Co, Ni, or CoNi) and as thermal barrier coatings (mainly yttria partially stabilized zirconia, YSZ).

Usually, the specifications of the main OEMs (original equipment manufacturers) call for the deposition of MCrAlY alloys by vacuum plasma spray (VPS). Other methods such as air plasma spray (APS) and high velocity oxygen fuel (HVOF) may also be required for their lower cost, even though it is commonly held that the quality of MCrAlY coatings deposited by HVOF or APS is lower due to the partial oxidation that the materials undergoes while being sprayed.[1] This "lower quality" is, however, rarely quantified on the basis of experimental data. The aim of the current study is to obtain such data and to compare the performance of VPS coatings with coatings sprayed in the presence of air at atmospheric pressure, i.e., axial plasma spray (AxPS) and HVOF.

The quality of the deposited films has been determined and compared in terms of structural properties (porosity, oxide concentration, unmelted particles presence) and mechanical characteristics (hardness). We observed that—as expected—the highest quality films are obtained by VPS; but that also HVOF and AxPS sprayed films have interesting properties, which can make their use interesting for some applications in view of their lower cost.

2. Experimental

2.1 Spraying Equipment

For HVOF and VPS deposition we used, respectively, a TAFA JP 5000 equipment and an EPI - Sulzer Metco torch. For axial plasma spray, we examined the technologies existing on the market. Three different types of axial torch technologies can be found.[2,3] These technologies differ in the set-up of the electrodes. The three cases are: three electrode cylindrical; single cathode-anode + plasma splitting; and a single cathode-anode without plasma splitting.

For the current work we used an axial plasma torch manufactured by Mettech (Axial III Trielectrode Model 600; Richmond, BC, Canada) with a three electrode cylindrical system in which the powder is injected along the longitudinal axis. Traditional

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A. Scrivani, Department of Industrial Engineering, University of Parma, Parma, Italy; and **U. Bardi, L. Carrafiello, A. Lavacchi**, and **F. Niccolai**, Dipartimento di Chimica, Università di Firenze, Via della Lastruccia n.3, 50019, Sesto Fiorentino, Firenze, Italy; and **G. Rizzi**, Turbocoating SpA, Via Volta 3, Rubbiano di Solignano, Parma, Italy. Contact e-mail: bardi@unifi.it.

plasma torches inject powder through the side of the plasma stream.[2] Side injection induces powder classification as the larger particles pass through the plasma and the smaller particle tends to bounce off or vaporize. Only those particles within the optimum particle range are fully entrained in the plasma and deposited on to the target resulting in high loss of materials. In the axial plasma spray technology, the powder is injected axially, directly into the center of the plasma jet with little or no segregation of the feedstock. After the powder is injected, the plasma can be compressed, accelerated, or decelerated to achieve the optimum residence time and particle velocity. The two main expected advantages of this new technology are higher spraying rate and a higher spraying efficiency.

2.2 Materials

CoNiCrAlY commercial powder (Sulzer Metco Amdry955) has been used for the coating test, with the orientative composition shown in Table 1.

Inconel 738 metal strips were used as substrates. The coating thickness for all tests reported here is 1000 ± 50 μm. After coating, the samples were heat treated in vacuum at 1100 °C for 2 h to obtain a metallurgical bonding between the base material and the coating.

2.3 Testing

For metallographic examination and for hardness measurements, the samples were infiltrated and mounted with epoxy resin and subsequently polished. Porosity and thickness were measured by metallographic microscopy using gray contrast image analysis. Hardness measurements were carried out on the cross section by a Shimadzu Microhardness Tester with a Vickers type head with a load of 300 *g* applied for 15 s.

Table 1 Orientative composition of the CoNiCrAlY Powders Used for Deposition Tests

wt.%	Cr	Ni	Al	Y	Co
Matrix	21.0	32.0	8.0	0.5	Bal.

Specific tests were carried out to compare the efficiency of the three examined technologies by spraying a rotating cylinder and measuring the ratio between the amount of sprayed powder (intended as powder injected in the flame) and material sprayed on the surface (determined by weighting the cylinder before and after spraying).

2.4 X-Ray Photoelectron Spectroscopy Analysis

X-ray photoelectron spectroscopy (XPS) measurements were performed using a standard UHV XPS spectrometer and a conventional Al K_α x-ray source.

Quantification was carried out using the atomic sensitivity factors (ASF) reported by Briggs and Seah[4] and the binding energies scale was calibrated with respect to the carbon 1s peak assumed to be at 284.8 (eV). Before XPS measurements all the samples were sputtered by a 3 KeV Ar^+ beam (current density of about 1 $\mu A/cm^2$) to eliminate contaminants such as water or carbon.

3. Results and Discussion

We focused our study on the following parameters: microstructure (porosity, oxide concentration, unmelted particles presence); mechanical properties (hardness); efficiency of deposition (ratio of powder fed to powder actually forming the coating); and chemical composition of the coating surface, to evaluate the overall amount of oxide.

3.1 Microstructure

The different coating methods used result in significant variations in the coating microstructure. Figure 1, 2, and 3 show the microstructure of the considered coatings before thermal treatment. Axial plasma sprayed coatings show higher amounts of unmelted particles with respect to other traditional technolo-

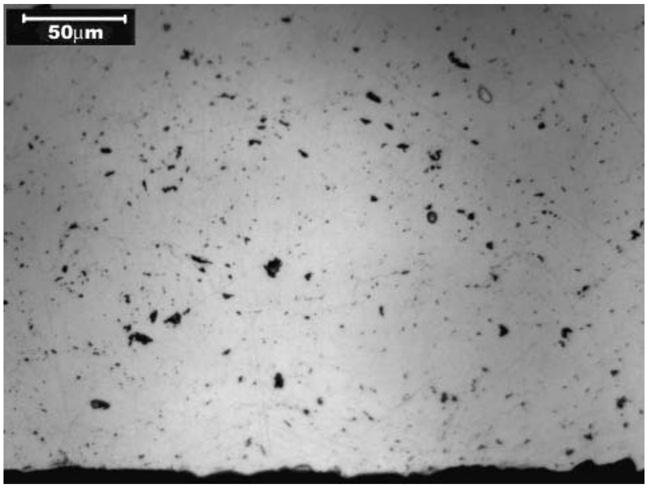

Fig. 1 HVOF sprayed CoNiCrAlY coating

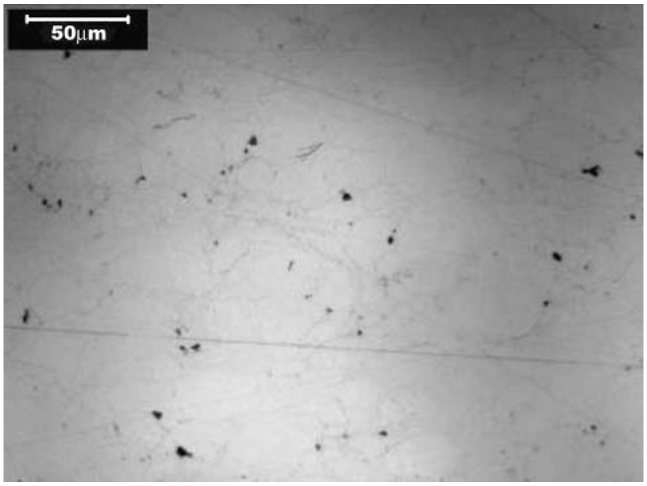

Fig. 2 VPS sprayed CoNiCrAlY coating

gies. HVOF coating shows some unmelted particles and this could be expected because the HVOF flame is colder than the plasma jet. Unmelted particles could not be observed in the coatings produced by VPS.

It is possible to note that VPS produces coatings that are quite completely oxide free, due to the absence of oxygen from the spraying atmosphere (Fig.1). The HVOF deposited coatings show some oxide, in lower amounts than for axial plasma spray. Although in the HVOF flame the oxygen is still present, the flame is colder than the plasma jet, allowing less formation of metallic oxides (Fig. 2, 3).

Another examined parameter was the porosity. As expected, porosity was lowest in the VPS coatings and highest in axial plasma spray coating. This could be explained because, due to the reduced air resistance, the plasma jet in vacuum equipment is very fast and the kinetic energy coupled with the enthalpy of the plasma gives the best compromise that results in very dense coatings. Also, HVOF coating shows good porosity level due to the velocity of the particles in the flame.

Axial plasma spray gives the highest porosity due to the velocity of the flame and which, although higher than for traditional air plasma spray, it is still lower than VPS and HVOF.

Vickers microhardness tests with a load of 300 *g* were performed on the cross sections of coatings (Table 2). In general, the hardness of the coatings was observed to be of the same order of magnitude for all the examined methods.

From the point of view of the adhesion, the diffusion heat treatment results in metallurgical bonding of the coating to the substrate and for this reason it makes no sense to perform conventional adhesion test.[5]

Table 2 Overall Microhardness Average Values, M, of Considered Coatings

Spray Process	M [$HV_{0,0300/15}$]
VPS	398 ± 37
Axial plasma	391 ± 40
HVOF	410 ± 35

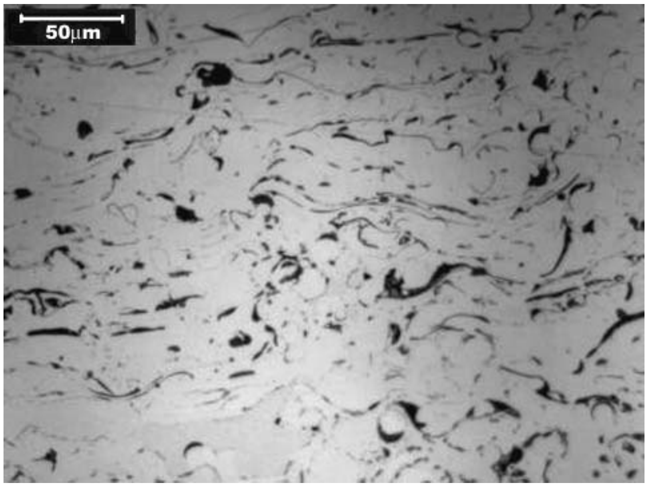

Fig. 3 Axial plasma spray CoNiCrAlY coating

3.2 XPS Measurements

XPS measurements have been carried out to determine the composition changes occurring to the coating surface during the spraying process. The samples were analyzed before and after heat treating, to study also the effect of thermal treatment. Figure 4 shows a typical XPS spectrum.

The results reported in Table 3, 4 and 5 show that all the examined surfaces have a large amount of oxygen, and oxygen binding energies correspond to the values attributable to oxygen in metal oxides.

As expected, VPS is the method that gives surfaces with the lower amount of oxides. Conversely, HVOF produces the surfaces with the larger oxides concentration. From reported atomic percentages it is evident, and confirmed by the binding energies analysis, that in the case of AxPS and VPS there is the formation of oxides like NiO, CoO, and Cr_2O_3, while in the case of HVOF only aluminum oxide, Al_2O_3, is present. This result confirms what was reported by Toma et al.[1]

After heat treatment, the atomic percentage of aluminum and oxygen increases, while the other elements, and especially chromium, decreases. This is due to the formation of aluminum oxide, and we attribute this oxide growth to the presence of residual oxygen in the treatment furnace, but it is interesting to note that in the case of VPS coatings also the atomic percentage of yttrium increases during the heat treatment. We think this can be due to the formation of mixed oxides like $Al_xY_yO_z$, but more analysis is needed to verify this hypothesis.

3.3 Efficiency

The efficiency, defined as the ratio of powder remaining on the sample to the total sprayed, was measured by spraying a rotating cylinder. Table 6 shows the quantitative results: axial plasma spraying performs significantly better than the other technologies examined, with value of about 60% versus the usual 30-40%.

In the case of VPS and HVOF, low values of deposition efficiency can be due to the high kinetic energy of the particles, which may lead to losses out of the flame or bouncing out of the surface of relatively cold particles.

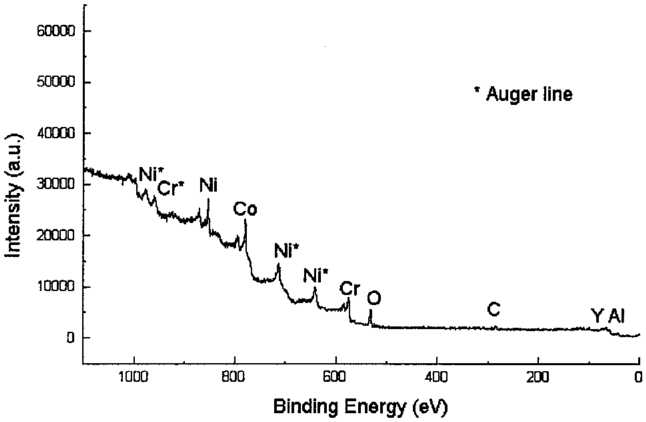

Fig. 4 Typical XPS spectrum of examined bond coat layer

Table 3 Atomic Percentage Obtained by XPS Spectra Quantification

	AxPS: at.%		VPS: at.%		HVOF: at.%	
XPS Peak	As Coated	Thermally Treated	As Coated	Thermally Treated	As Coated	Thermally Treated
Ni 2p 3/2	8.0	1.9	14.9	16.9	0.6	0.9
Co 2p 3/2	13.2	1.5	18.2	13.5	0.5	0.7
Cr 2p 3/2	13.7	1.9	21.1	11.2	0.7	1.1
O 1s	52.8	63.8	39.0	43.4	68.6	69.4
Y 3d	1.1	0.7	Traces	1.2	1.2	0.7
Al 2p 3/2	11.2	30.2	6.9	13.8	28.4	27.2

Table 4 VPS: Binding Energies and Atomic Percentage Obtained by XPS Spectra Quantification

XPS Peak	B.E., eV	at.%
Ni	852.6	14.9
Co	777.6	18.2
Cr	573.6	21.1
O	531.1	42.0
Y	158	Traces
Al	74.1	6.9

Table 5 HVOF: Binding Energies and Atomic Percentage Obtained by XPS Quantification

XPS Peak	B.E.	at.%
Ni	852.3	0.6
Co	777.7	0.5
Cr	575.4	0.7
O	531	68.6
Y	158.2	1.2
Al	74.3	28.4

Table 6 Efficiency Data: Ratio Between the Weight of Sprayed Powder and the Weight of the Coatings

Spray Process	Axial Plasma	VPS	HVOF
Efficiency	60%	35%	40%

4. Conclusions

VPS technologies currently remain the state of the art for the production of MCrAlY alloys coatings to be used as oxidation resistant material and bond coat in TBC systems. We found that the quality of the coatings obtained by VPS is higher than that obtained by means of AxPS and HVOF. Due to the absence of air resistance, the VPS plasma jet is very fast and the kinetic energy coupled with the enthalpy of the plasma give the best compromise for very dense and oxide free coatings. Axial plasma spray shows a considerably better efficiency than the other methods in terms of fraction of powder used. Against this evident advantage, the quality of the coatings deposited by AxPS is lower: we observed higher porosity, larger amounts of unmelted particles, and a higher degree of oxidation. HVOF coating shows good porosity level due to the velocity of its flame, but the oxide content is still high with respect to VPS.

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References

1. D. Toma, W. Brandl, and U. Köster: "Studies on the Transient Stage of Oxidation of VPS and HVOF Sprayed MCrAlY Coatings," *Surf. Coat. Technol.*, 1999, *120-121*, pp. 8-15.
2. R.B. Heinmann: *Plasma Spray Coating*, VCH, Weinheim, 1996.
3. A. Scrivani, R. Groppetti, S. Ianelli, U. Bardi, G. Ballerini, S. Bertini: "A Comparative Study of the Deposition of Chromium Carbide Based Metal Matrix Composites by Axial Plasma Spray, Air Plasma Spray and High Velocity Oxygen Fuel," *New Surfaces for a New Millenium,* Proceedings of the International Thermal Spray Conference 2001, ASM International, Materials Park, OH, 2001, pp. 301-05.
4. D. Briggs and M.P. Seah: *Practical Surface Analysis*, John Wiley & Sons, New York, NY, 1983.
5. M. Okazaki, M. Okamoto, and Y. Harada: "Evaluation of Adhesive Strength of Coating Film on Ni-Base Superalloy for Gas Turbine" in *Surface Engineering via Applied Research,* Proceedings of the International Thermal Spray Conference 2000, ASM International, Materials Park, OH, 2000, pp. 635-41. *Proceedings of 1st ITSC* 2000, pp. 635-41.