Testing Results of Plasma Spraying Ceramics Coatings by Pulse Plasma Modulation Technology

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Abstract: The work below was done mainly in the USSR (Tajikistan) and partly continued in Israel. This technology provides substantially better coating performance compared with the respective individual processes (plasma, Cold Spraying, arc or oxy-fuel, etc.). The coatings of large areas can be accomplished at much higher quality and deposition rates than conventional plasma, arc or flame spray techniques and at a far lower cost. These benefits have been accomplished through a specially designed torch head and power supply modulation unit. The system does not require expensive argon-helium based plasma of hydrogen, nitrogen or helium mixtures but rather uses air plasma alone or in combination with hydrocarbon fuel. The plasma chemical technology overcomes a previously fundamental limitation of air plasma systems - oxidation of the coating. In addition, the proprietary design of the torch head and supply modulation unit produces both superior coating and substantially reduces the erosion rate of expensive torch electrodes thereby significantly increasing the resource of operating time of a plasma generator. Detailed design specifications and process validation experiments have been of successfully completed, and the design, technology and market of a pre-production prototype has passed through an evaluation by potential strategic partners with the impressive estimation.

Keywords: Pulse Plasma Spraying, DC Torch Shock Wave Spraying Technology, DC Arc Pulse Modulation, Pulse Modulation

1. Introduction

Testing of pulse plasma spraying technology [1-13] (-“subtractive”, + “addition” pulse modulation) by SULZER METCO AG Company/Praxair were shown in the report below and was “strictly confidential” for a long time.

The results of the first phase of collaboration between Plasma Model Ltd (Dr. B. Gutman project) and SULZER METCO were presented in the report 97PE149A composed by Dr. G. Barbezat.

During the meeting, the execution of a second series of test was decided and samples were delivered to Sulzer's Metco laboratory in city Wohlen of Switzerland.

THE PRESENT REPORT SHOW THE IMPRESSIVE POTENTIAL OF THE TECHNOLOGY OF SDr. B. GUTMAN.

2. Material Used

All ceramics were sprayed using bond coat M450 NS (NiAl5). The following powder materials were used:

AMDRY 6060 Al₂O₃

AMDRY 6420 Cr₂O₃

AMDRY 6254 Al₂O₃ 40%TiO₂

3. Results of the Investigations

The results of the investigations are summarized in the figure 1. All the investigated samples shows a good quality of coating.

Some samples of Al₂O₃ and Cr₂O₃ can be considered as excellent.

All samples are characterized by low porosity level, relative high hardness and reasonable bond strength, especially the samples PM41 (Cr₂O₃), PM46 (Al₂O₃) and PM42 (Al₂O₃ 40% TiO₂).

The influence of the spray distance on the micro hardness and the bond strength is shown in the figure 2.

The process show only a low sensitivity to the spray distance regarding the coating properties. However the deposition efficiency is significantly affected by the spray distance.

DE versus spray distance for A6060		
Spray distance [mm]	DE [%]	Appreciation
200	79	Excellent
250	62	Medium
300	34	Low

Test No	Material	Porosity [%]	Quality level	Microhardness HV _{0.05}	Bond strength [MPa]
98-2013 / PM40	M450 + A6060 (NiAl5 + Al ₂ O ₃)	2	High	1068	>60
98-2014 / PM41	M450 + A6420 (NiAl5 + Cr ₂ O ₃)	2	High	1547	40
98-2015 / PM42	M450 + A6254 (NiAl5 + Al ₂ O ₃ TiO ₂)	1	High	1048	57
98-2016 / PM43	M450 + A6060	2	Good	918	>65
98-2017 / PM44	M450 + A6060	2	High	1059	>60
98-2018 / PM45	M450 + A6060	3	Medium	936	>55
98-2019 / PM46	M450 + A6060	2.5	High	1131	>55
98-2020 / PM47	M450 + A6060	2	High	1121	>55
98-2021 / PM48	M450 + A6060	2.5	Medium	941	45
98-2022 / PM49	M450 + A6420	2.5	High	1420	43
98-2023 / PM50	M450 + A6254	1	High	1001	48
98-2024 / PM51	M450 + A6060	2.5	Good	1004	33
98-2025 / PM52	M450 + A6420	3	Medium	1357	>60
98-2026 / PM53	M450 + A6254	1	High	999	34

Figure 1. Summary of the test results of ceramics layers.

SULZER METCO

200 μm

50 μm

$$f_m = 0$$

		1. Layer	2. Layer
Coating Material	[name, Lot]	Metco 450 NS	Amdry 6060
Deposition Efficiency	[%]	n.d.	n.d.
Coating Thickness	[μm]	40	210
Surface Roughness	[μm]	Ra = n.d. Rz = n.d.	Ra = n.d. Rz = n.d.
Bond Strength	[MPa]	$\bar{x} > 60$	
Porosity	[%]	n.d.	~2
Microhardness		n.d.	1066 HV0.3 s=96.89
Macrohardness		n.d.	n.d.
Test No.	98-2013 / PM40		Comments:
Process (principle, gun)	Plasma Model		
Substrate	n.d.		9

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Spraying without DC arc modulation

Spray Distance [mm]	AMDRY 6060 Al ₂ O ₃		AMDRY 6420 Cr ₂ O ₃		AMDRY 6254 Al ₂ O ₃ :40TiO ₂	
	HV _{0.3}	Bond strength [MPa]	HV _{0.3}	Bond strength [MPa]	HV _{0.3}	Bond strength [MPa]
Short 200	1066	>60	1547	40	1046	57
Medium 250	941	45	1420	43	1001	48
Long 300	1004	33	1357	60	999	34

Figure 2. Influence of the spray distance on the micro hardness and the bond strength.

Sprayed with modulation frequency ~-25.6 kHz

Sprayed with modulation frequency ~ 9.6 kHz.

SULZER METCO 200 μm 50 μm

$$f_m = -3,2 \text{ kHz}$$

		1. Layer	2. Layer
Coating Material	[name, Lot]	Metco 450 NS	Amdry 6060 (Al_2O_3)
Deposition Efficiency	[%]	n.d.	n.d.
Coating Thickness	[μm]	70	100
Surface Roughness	[μm]	Ra = n.d. Rz = n.d.	Ra = n.d. Rz = n.d.
Bond Strength	[MPa]	$\bar{x} > 55$	
Porosity	[%]	n.d.	~3
Microhardness		n.d.	936 HV0.3 s=134.65
Macrohardness		n.d.	n.d.
Test No.		98-2018 / PM45	Comments:
Process (principle, gun)		Plasma Model	
Substrate		n.d.	14

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Sprayed with modulation frequency ~3.2 kHz.

Sprayed with modulation frequency $\sim +4.4\text{kHz}$.

Sprayed with modulation frequency $\sim + 2.24 \text{ kHz}$.

The sample having received without DC Arc modulation

Figure 3. Bond strength test characterization.

During my communications with the leadership of a plasma spraying company, it was revealed that their experiments with pulse Arc spraying did not provide them

their wishful results, because their experiments have been being done not correctly.

Our experiments carried out by plasma forming gas Air +

hydrocarbon admixture with the smallest arc time constant-in contrary with plasma forming gas Argon where this constant is relatively high (Figure 4). As is very well known, the process of shock waves creation, by pulse current with gradient around 10^7 - 10^8 A/s, corresponds to the smallest time constant and creates a highly effective shock wave [11, 13] also to deepest disintegration.

TENSILE BOND STRENGTH AND POROSITY DATA MADE BY PRAXAIR INC.

Tensile bond strength between ceramic coatings and stainless steel substrate are within 10, 000 – 12, 000 psi without any sub- layer (see Praxair's data below).

Figure 4. Time μ s constant of plasma forming gases vs. plasma operation current.

PRAXAIR DATA

Data Book No.	POWDER	FEEDRATE	METALLURGICAL SAMPLE				OTHER COATING PROPERTIES				
			WIRELESS		POROSITY		THICKNESS	COARSE	POSSIBLE	FAILURE	PRETTING
			IN/T	OUT/T	100 420/10	%		%	STRENGTH	TYPE	WAX/100
Praxair Model 130		REPORTED							PSI 1 Cap type	nd (physical data)	
4002 7.1	ALCO-100	"							HOLD		
4002 7.2	ALCO-100	"							HOLD		
4002 7.3	ALCO-100	"							HOLD		
4002 7.4	ALCO-100	"				1.2	0017	1			
4002 7.5	ALCO-100	"									
4002 7.6	ALCO-100	"							4,076	II	
4002 7.7	ALCO-100	"							4,331	II	
4002 7.8	ALCO-100	"							5,705	II	
4002 7.9	ALCO-100	"				3	0100	2			
4002 7.10	ALCO-100	"				7	010	2			
4002 7.11	ALCO-100	"							10,025	II	
4002 7.12	ALCO-100	"							11,000	II	
4002 7.13	ALCO-100	"							9,248	M	
4002 7.14	ALCO-100	"				4	0005	2			
4002 7.15	CRG-172	"							HOLD		
4002 7.16	CRG-172	"							HOLD		
4002 7.17	CRG-172	"							HOLD		
4002 7.18	CRG-172	"				4.1	0000	1			
4002 7.19	CRG-172	"							10,573	II	
4002 7.20	CRG-172	"							10,945	II	
4002 7.21	CRG-172	"							11,763	II	
4002 7.22	CRG-172	"									
4002 7.23	CRG-172	"				1.5	0017	2			
4002 7.24	CRG-172	"							9,248	II	
4002 7.25	CRG-172	"							10,002	II	
4002 7.26	CRG-172	"							10,506	II	
4002 7.27	CRG-172	"				2	0026	2			
4002 7.28	ZIRCO	"									
4002 7.29	ZIRCO	"				3	0025	2			
4002 7.30	ZIRCO	"							10,500	II	
4002 7.31	ZIRCO	"							10,000	II	
4002 7.32	ZIRCO	"							10,102	II	
4002 7.33	ZIRCO	"									
4002 7.34	ZIRCO	"				3	0026	2			
4002 7.35	ZIRCO	"							10,100	II	
4002 7.36	ZIRCO	"							11,201	II	
4002 7.37	ZIRCO	"							8,804	II	
4002 7.38	ZIRCO	"							11,230	II	
4002 7.39	ZIRCO	"							10,955	II	
4002 7.40	ZIRCO	"							10,229	II	
4002 7.41	ZIRCO	"									
4002 7.42	ZIRCO	"				7	0023	2			

Figure 5. PRAXAIR's data of tensile Bond strength.

4. Conclusion

Thus, pulse plasma-spraying technology (Figure 6) is demonstrating compelling arguments about significant advantages in comparison with any traditional plasma-spraying one, including production of Nano particles in the modulated Plasma jet:

- 7) Lowest coating porosity
- 8) Comparatively low torch noise level
- 9) Control of the coating porosity, micro hardness, bond strength and density by arc modulation during spraying process

Figure 6. Sizes of sprayed particles nm- μ m (absciss axes) vs. modulation parameters.

This system is a 75 kW power DC plasma spray system that provides superior quality of ceramics coatings on surfaces of any size. That is achieved by using pulse's core technology[•], is the result of almost 30 years of extensive R&D.

The core technology is based on a high enthalpy plasma-chemical reaction involving a modulated plasma Arc within a specially designed torch head. Highest parameters are achieved through a proprietary Arc current modulation scheme and the specially designed torch head. This technology allows controlling the size of spray particles on their way to a target surface.

5. Deliverables

- 1) Unique system allowing to control spray particles' size before they reach target surface
- 2) Ceramic and other coating cost is 3-10 times less than for leading competitors' products
- 3) Excellent coating results
- 4) Highest bond strength of over 80 mega Pa (without sub layer)
- 5) Highest deposition rate
- 6) Highest deposition efficiency

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