UPSCALING OF PULSE ELECTRODEPOSITION PROCESS FOR THE PRODUCTION OF Ni-P/SiC NANOCOMPOSITE PROTECTIVE COATINGS

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ABSTRACT

Wear and corrosion of materials causes GDP losses of 3-4% and billions of Euros are spent annually on capital replacement and control methods for wear and corrosion infrastructure. In the protective coatings sector two main techniques dominate: hard chromium plating (HC) and thermal spray (TS), though both methods face serious environmental, authorization and hazard issues. Thus, alternatives to hard Cr have been extensively studied at lab scale from various scientific group [1,2,3,4]. In the framework of EU's Horizon 2020 research and innovation programme "PROCETS"[5], Creative Nano's electroplating pilot line has been employed for the successful upscaling (120 L) of direct and pulse current plating processes, towards the development of low P Ni-P/SiC composite coatings with improved hardness and corrosion resistance. One of the test cases of the project involves the production of coated cylindrical steel rods. Before every plating experiment, the rods were subjected to a pre-treatment process including alkaline degreasing, anodic electro-cleaning and acidic etching in order to properly clean and activate the substrate surface. During plating the electrolyte was circulated by utilizing a pump and an adjustable nozzles system placed at the bottom of the tank, to enhance the suspension of the particles, reduce their sedimentation and constantly replenish the cathodes with particles. Additionally, a specially designed rotation mechanism was employed for the rotation of the rods during the plating process, thus ensuring the homogeneous incorporation of SiC nanoparticles across the surface of the rods. The electrolyte contained 10 g/L 100 nm sized SiC nanoparticles and the applied current density varied from 0.5 to 2 A/dm^2. The coated parts were subjected to various characterization methods in order to evaluate their performance in terms of surface morphology, nanoparticle incorporation, microhardness, corrosion and wear resistance. SEM-EDS analysis revealed that the composite coatings exhibit stable P content at 4-6 % wt, while the corresponding SiC incorporation ranges from 4 to 9 % wt. Moreover, the samples showed hardness values about 900 HV, which increased up to 1200 HV after heat treatment at 300 °C for 1 h. Finally, the produced rods were subjected to real environment testing, exhibiting promising results.

INTRODUCTION

For several years hard chromium coatings have been employed by the industry due to the outstanding mechanical properties they possess. Unfortunately, the fabrication process of this coating contains the hexavalent Cr^{+6} ion which is a carcinogenic substance along with its wetting agent (PFOS) which is harmful to the environment. Thus, the EC restricted the Cr^{+6} processes since September 2017[6]. Hence, alternatives to hard chromium have been tested from various research groups[7,8,9]. Ni-P coating has drawn attention due to its promising mechanical and tribological characteristics. Additionally, the incorporation of nano or submicron particles in the Ni-P metal alloy matrix enhances the favourable properties of the coating, depending on the application that is going to be evaluated. Despite the promising results of the composite coatings, minor efforts have been made to the upscaling of the electrodeposition process[10]. In the framework of the PROCETS [5] project, pulse plated Ni-P/SiC (100nm) low Phosphorous composite coatings were fabricated in pilot scale (120L).

EXPERIMENTAL PART

The electroplating bath formulation and the operating parameters are presented below in Table 1.

Table 1. *Chemical formulation of the electrolyte* *Operating parameters*

Chemical	Concentration (g/L)	*Parameter*	*Value*
$NiSO_4 \cdot 6H_2O$	100-300	pH	2
$NiCl_2 \cdot 6H_2O$	10-50	T	50 °C
H_3PO_3	10-50	Current density	0.5-2 A/dm^2
H_3PO_4	10-50		
Additive 1	1-5		
Additive 2	0.5-2		
SiC (100nm)	10		

The pilot line of Creative Nano consists of 18 tanks. The dimensions of the tanks are W 30cm x L 40 cm x H 70 cm with effective volume of 120 L. The tanks are made from PP and the maximum size of the plating component can be up to 12 dm^2. The tanks that U/S is imposed are made from stainless steel that allows the wave to propagate without being absorbed. The anodes and the racks that hold the substrates to be plated are held from copper alloy bus bars that allow the current to flow. Two different rectifiers for the pre-treatment and the plating process are employed. The deposition process was performed under galvanostatic conditions by imposition of Direct and Pulse current (DC and PC). For the pilot scale pulse plating experiments a Munk rectifier is employed. The current densities applied varied from 0.5 A/dm^2-2 A/dm^2. The DC power generator has a capacity of 10-200 A and the PC one from 150 - 300 A with pulse time ranging from 100 to 56000 msec. A crane has been installed above the pilot line to transfer the racks from tank to tank. The solution level is controlled by floaters, the temperature (where needed) is regulated by heaters, which along with the pumps are connected to a PLC system that allows the operators to monitor and adjust the temperature. The tanks that emit fumes due to electrolysis or evaporate due to heating, are connected with a ventilation system. Aspirators are placed on top of the tanks in order to protect the operators from potential hazardous inhaling. Additionally, a piping system is linked in the rear side of the tanks that ends up in a collection tank outside of the building to safely neutralize and dispose the produced chemical wastes. The electrolyte was agitated constantly by utilization of a pump at 100 L/min, connected with a custom-made closed loop nozzle system in order to circulate the particle suspension during the plating process and replenish the cathodes constantly. The geometry of the cathodes was cylindrical, and the substrates were medium carbon steel. The anodes used, were pure Ni plates in parallel configuration. Before every plating experiment, the substrates were pre-treated according to the following process. Firstly, the substrates (appropriately mounted to a custom-made rack) were degreased in alkaline solution under ultrasonication. Triple rinse in water followed and the rods were subsequently anodically electro-cleaned in 1.25 M NaOH solution for 1 minute at 5 A/dm^2. Rinsing in three tanks was again performed and then the substrate surface was activated in 2.5M H_2SO_4 for 1 minute. A final triple rinsing was made and after that the substrates were immersed in the electrolyte for the formation of the composite coating. After the composites production the coated substrates were rinsed in ultrasonication tank in order to remove any residues present in the surface of the components. After production, the coated articles were heat treated at 300 ^{0}C for 60 minutes. The as plated and heat-treated components as well as their cross sections, were characterized by SEM-EDS to identify the microstructure and evaluate the composition of the coating. The microhardness measurements were performed on the surface of the coated articles by utilizing a Shimadzu Vickers microhardness meter under 50 gf load and a dwell time of 15 sec.

PILOT SCALE PLATING

Figure 1. *(a) View of the rear of the line (b) View of the pilot line*

As previously stated, one of the challenges in composite plating is the handling of nano-powders and their behaviour within the electrolyte. A suitable pumping system is of upmost importance in order to maintain the particle suspension circulating in the entire volume of the tank. In this way, the particles are continuously replenishing the cathode during plating and the sedimentation of the particles due to gravity is minimized. At the bottom of the tank a custom designed closed loop nozzle system connected with the pump was installed. This system allows the operator to control the angles of the nozzles thus ensuring the necessary flow and allowing control of the hydrodynamics. Special attention should be given to the intensity of the circulation since too vigorous agitation of the electrolyte deteriorates the particle incorporation in the coating. Moreover, beyond the physicochemical reactions between the electrolytic ions and the particles, the agglomeration effect is also reduced. Finally, the contamination of the electrolyte from pollutants should be prevented as much as possible, since filtration is not an option because of the presence of nanoparticles in the electrolytic solution.

RESULTS AND DISCUSSION

MICROSTRUCTURE-COMPOSITION

The microstructure of the produced coatings under different plating parameters (DC plating at 1 A/dm^2 and PC plating at 0.5, 0.75 and 1 A/dm^2) has been determined by utilizing SEM measurements from both the surface and the cross sections of the plated components. The homogeneity of the plated rods is of crucial importance; thus, the characterization was performed in three areas around the circumference of the rod. The morphology of the surface is typical of the Ni-P alloy, exhibiting fine grained, crack free and compact coatings. From the EDS measurements the P content in the coatings varies from 3.7 – 5.1 wt% on the surface and between 4 – 5.4 wt% on the cross section as presented in Figure 2. On the other hand, the EDS analysis showed that the SiC varied from 3.7 wt% to 9.4 wt% on the surface and 3 wt% to 8.9 wt% on the cross sections. Finally, the SEM images were analysed with ImageJ [11] an open source image processing program, in order to identify the particle size of the co-deposited SiC particles within the Ni-P matrix. The values of the particle sizes ranged from 1.9 to 3.8 μm, suggesting the presence of agglomeration. The distribution of the particles was

also evaluated, with the highest amount of area being 19.3% corresponding to 1.9 μm particle size.

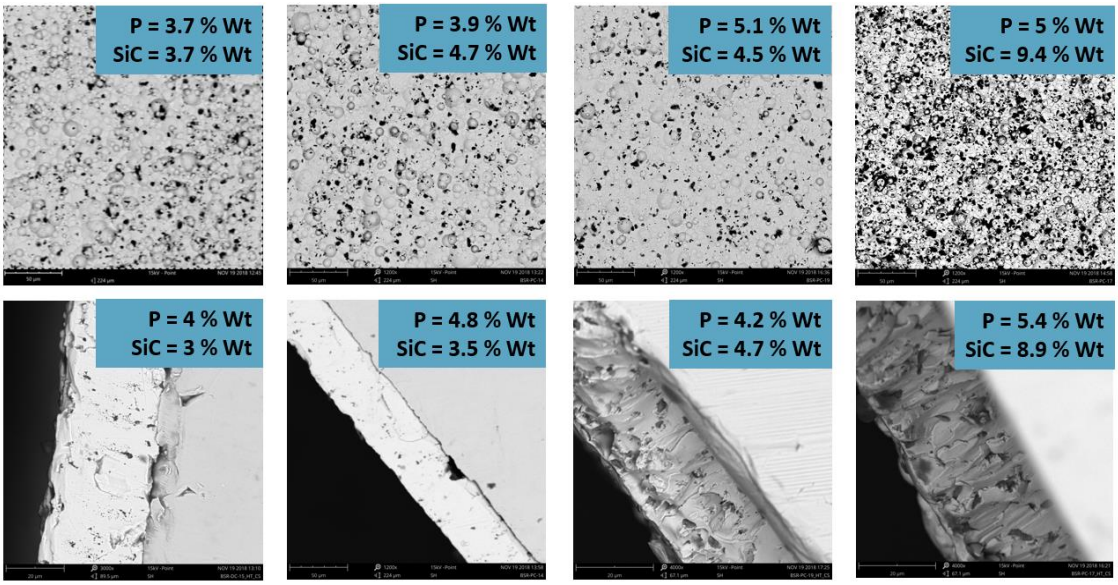

Figure 2. *(1st row): Surface microstructure (2nd row): Cross section microstructure*

MICROHARDNESS

The microhardness measurements were performed on the surface at 10 different positions along the length and around the circumference of the component. The values varied from 788 ± 28 HV to 967 ± 40 HV. The coated components that were heat treated for 1 h in 300 ^{0}C exhibited an increase of 10-37%.

FIELD TESTING

The evaluation of the tribological properties of the coated components was performed in order to compare them with the hard chrome coatings. The main concern was to assess the wear damage on the coatings and to identify the low friction of the coated components. The tests were performed under lubricated conditions. The duration of the tribological characterization procedure was kept for 20h. The equipment employed for the evaluation of the tribological properties is depicted in Figure 3. The reference used for the analysis was Cr plated rods and the Coefficient of Friction (COF) evolution during the time of the testing is presented in Figure 5.

Figure 3. *Wear tester*

In Figure 4 the COF evolution of the as plated composite coated rods is presented. As it can be seen the behaviour of the pulse plated components exhibits similar behaviour with the reference Cr plated rods after 20h of testing presented in Figure 5. These tests have been developed and optimized to represent the wear mechanism in the real applications as closely as possible. Similar geometry, materials and lubrication regime, as well as load and speed conditions allow a simplified and accelerated evaluation of the coatings.

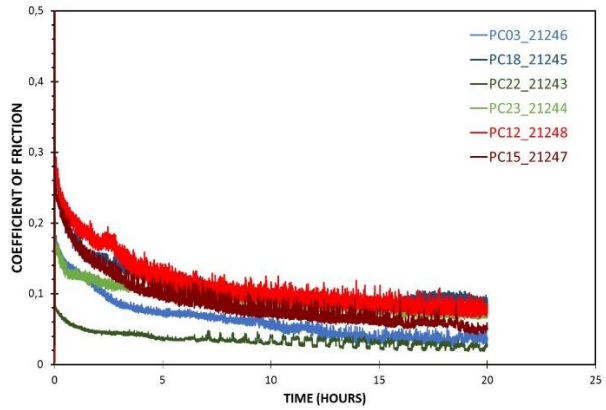

Figure 4. *COF evolution in Pulse plated Ni-P/SiC rods*

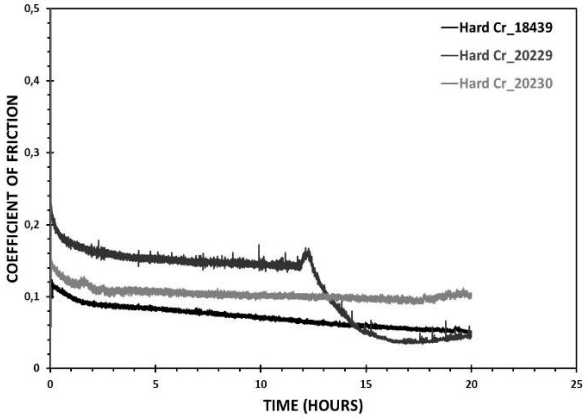

Figure 5. *COF evolution in hard Cr plated rods*

Additionally, a series of geometrical parameters that affect the performance of the plated components were evaluated. These parameters are associated with the thickness and the coating formation on the surface of the substrate. The same series of tests were performed not only in the as plated but to the heat treated as well. As it can be seen in Figure 6, the values vary within the limits of the given specifications. Only two rods are presented for reference. The tests were carried out in the circumference of the rods as well.

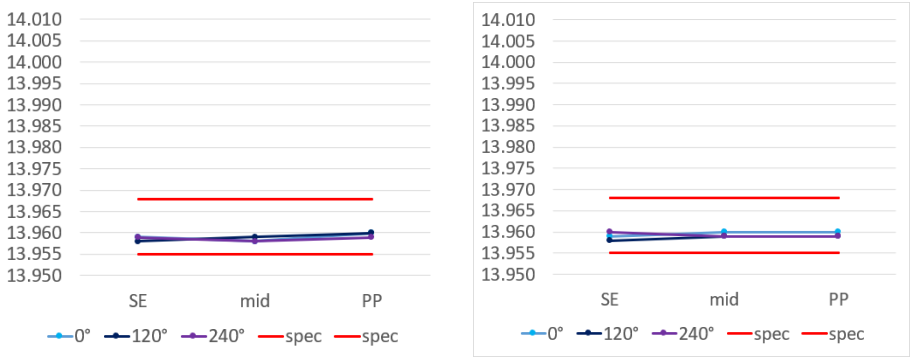

Figure 6. *Evaluation of geometrical parameters of the coated components*

The coated rods were then validated by bending test in order to estimate their peel-off behaviour. Thus, the adhesion of the coating was estimated. in Figure 7 are shown the bending tests and the performance of the coated articles.

Medium and slight peel-off is evident at Figure 7b and Figure 7e respectively.

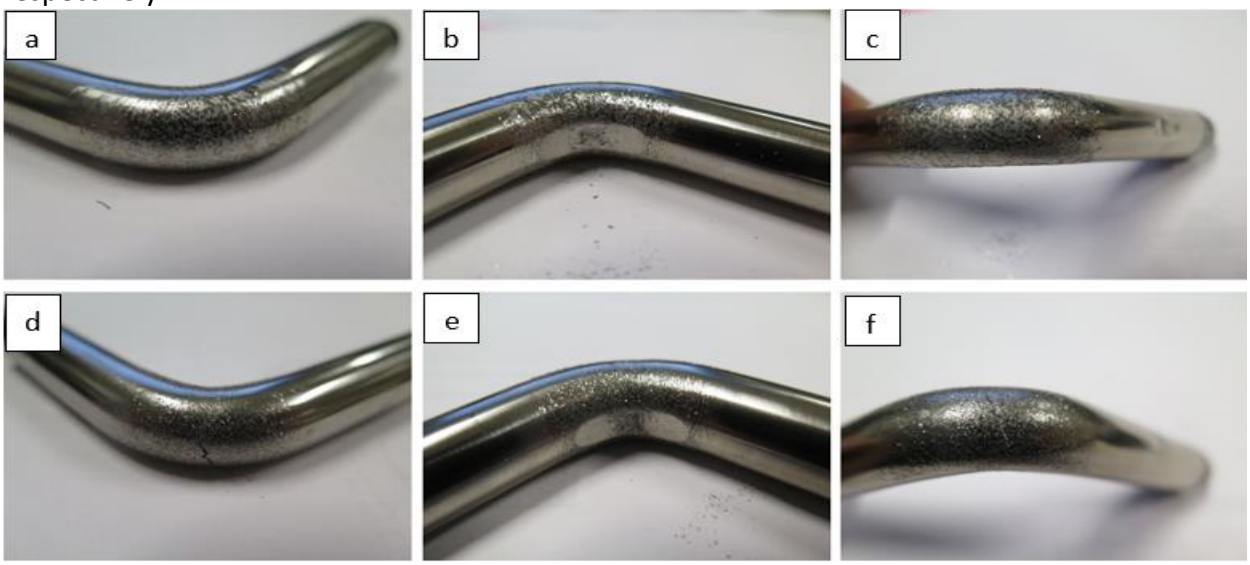

Figure 7. *Bending test of the Ni-P/SiC pulse plated components*

CONCLUSIONS

Pilot scale of pulse electrodeposition process to produce nano-composite Ni-P/SiC (100 nm) coatings has been delivered. The pulse electrodeposited articles were characterized via SEM-EDS in order to evaluate the surface microstructure and the chemical composition of the components respectively. Fine grained and compact coatings were observed while the P content remained rather stable at 3-5 wt%. The SiC was detected and reached values up to 9 wt%. The hardness values approached the hard Cr standards in the as plated form, while the heat treated exhibited an increase of 20% in average. The COF exhibited similar behaviour as the hard Cr during 20h of testing. Medium and slight peel-off was observed after the bending test. Overall, the results were promising, and further studies have to be performed in order to control the nanoparticles suspension within the electrolyte in greater volumes. Pulse plating in higher volumes exhibits better results that direct current processes in terms of particle incorporation and overall behaviour of the coating in industrial testing.

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REFERENCES

[1] Walsh FC, Ponce de Leon C. (2014). *Trans. IMF*, 92(2): 83-98.
[2] Roos JR, Celis JP, Fransaer J, Buelens C. (1990). JOM, 42(11): 60-63.
[3] Zoikis-Karathanasis A, Pavlatou EA, Spyrellis N. (2010). J. Alloys Compd., 494(1-2):396-403.
[4] Wang Q, Callisti M, Kosanovic Milickovic T, Zoikis-Karathanasis A, Deligkiozi I, Polcar T. (2016). Wear, 356-357:86-93.
[5] http://www.procets.eu/
[6] Risk & Policy Analysts Ltd, Environmental risk reduction strategy and analysis of advantages and drawbacks for hexavalent chromium,2005
[7] Y.L. Shi, Preparation of electroplate Ni-P-ultrafine diamond, Ni-P-carbon nanotubes composite coating and their corrosion properties, Journal of Materials Science, 08/2004; 39(18):5809-5815
[8] A. Zoikis Karathanasis, E.A. Pavlatou, N. Spyrellis, The effect of heat treatment on the structure and hardness of pulse electrodeposited NiP-WC composite coatings, Electrochimica Acta, 54 (2009) 2563
[9] E. Pompei, L. Magagnin, N. Lecis, P.L. Cavallotti, Electrodeposition of nickel-BN composite coatings, Electrochimica Acta, 03, 2009,54 p.2571
[10] M. Lekka, C. Zanella, A. Klorikowska, P.L. Bonora, Scaling-up the electrodeposition process of nano-composite coating for corrosion and wear protection, Electrochimica Acta, 11, 2019, 55 p.7876
[11] https://imagej.nih.gov/ij/