Characterization of the WC coatings deposited by plasma spraying

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Abstract. Tungsten monocarbide (WC) is deposited using a plasma jet on the martensitic non-corrosive steel support (Z12CNDV12), in three different thicknesses.The characteristics of the coatings are determined by: its chemical composition, optical microscopy, RX analysis, tensile adhesion strength, Vickers hardness, the nature and the processing degree of the substrate and the deposition conditions.The method used for determining the behaviour in a corrosive environment of the WC coatings deposited by plasma spraying consists in measuring the electrochemical potential difference between the coating and the substrate, which are immersed in a solution containing NaCl as a corrosive agent. The experimental results are then mathematically processed in order to determine a law and the mechanisms involved.

1. Introduction

The WC – Co coatings are increasingly certain to be an alternative mean of effectively protecting metal structures and equipment exposed to corrosive and/or abrasive environments. [1], [2], [3].

The characteristics of the coatings are determined by: its chemical composition, optical microscopy, RX analysis, tensile adhesion strength, Vickers hardness, the nature and the processing degree of the substrate and the deposition conditions. The common techniques to attain these depositions are: Air Plasma Spray (APS), Vacuum Plasma Spray (VPS) and High Velocity Oxygen Fuel (HVOF) [4], [5], [6], [7].

The studied coatings in this paper have been deposited by Air Plasma Spray, on a martensitic stainless steel substrate, using a Metco 73 spraying powder.

In order to analyze the behavior of these coatings in a corrosive environment, in literature there are mentioned multiple examples of solutions that can be used in this purpose such as: the 0.1 M NaOH, 0.1 M H2SO4, but also NaCl [7]. We have used NaCl solutions of different concentrations.

Our objective is to characterize the WC coatings and to find a parameter to reflect in a sensitive and easy to quantify way the corrosive action of the corrosion agent upon the coating. This parameter represents the electrochemical potentials of the substrate and the coating immersed into the NaCl solution. Generally, in order to ensure the anti-corrosive action, the coating/substrate couples of choice are those in which the electrochemical potential of the coating is higher than that of the substrate [8], [9].

2. Experimental section

2.1. Experimental conditions at the WC coatings spraying in plasma

The metallic substrate on which the coatings were sprayed is the Z12CNDV12, a martensitic stainless steel whose chemical composition is presented in Table 1.

Table 1. Chemical composition of martensitic stainless steel Z12CNDV12.

Chemical composition (%wt)	C	Si	Mn	S	P	Cr	Ni	Mo	V	N2
	0,06 0,15	$\leq$ 0,35	0,50 0,90	$\leq$ 0,025	$\leq$ 0,035	11,0 12,5	2,00 3,00	1,5 2,0	0,25 0,40	0,02 0,04

Before performing the ceramic coating, the surface of the metallic substrate was prepared in advance by mechanical procedures. During the experimentation, the preparation of the surfaces of the substrate was achieved by blasting aluminum oxide particles. The layer of coatings on the substrate prepared in this way was done almost immediately in order to avoid the contamination of surfaces, which can affect the adhesion between the coat and the substrate.

The coatings were made using a Metco 7MB equipment. The powder used is Metco 73, which contains 83% WC and 17% Co and has the size particle size ranging between 10 and 45 μm.

The plasma deposition was made using the following parameters:
- Primary plasma gas: argon, 0.62 MPa pressure;
- Secondary plasma gas: helium, 0.62 MPa pressure;
- Intensity of the current at the generator: 800A and 45÷55 V tension;
- Spraying distance: 80 mm;
- (deposited) powder flow: 2.7 kg/h.

2.2. Determination of coating adhesion
The tensile adhesion strength is a quantity which characterizes the force necessary to detach the thermally sprayed coating from the substrate.

The tensile test is a quasi-direct measure of the adhesion force. The device used is presented in Figure1.
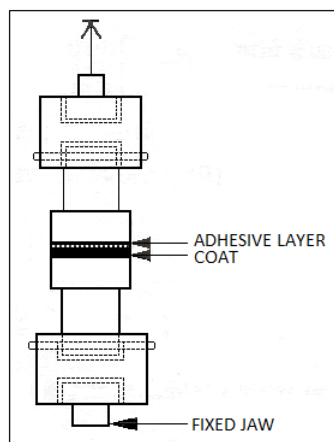

Figure 1. The static method of determining the adhesion of the sprayed coatings.

In the case of its application to plasma coatings, according to the region where rupture occurs, it is necessary to differentiate cohesive ruptures that occur inside the coating of adhesive fractures which appear at the interface.

The test consists in subjecting the coating on the substrate, by means of two glued test pieces on both sides of the coating and the substrate, to a force at a constant speed. The value of the tensile adhesion strength is the ratio between the maximum force achieved at breaking point and the surface of the coating, the stress needing to be evenly distributed over the surface. [10]

In practice, this test is advantageous because of its rapidity, but a poor alignment of the assembly can induce types of stresses other than traction, such as the shearing stress. In the case of very porous deposits, it is difficult to obtain precise results because of the adhesive which can touch the substrate, as the coating is thinner.

2.3. Corrosion resistance determined by the potentiostatic method
The couple made of the coating (WC-Co) and the substrate (stainless steel) has been immersed in NaCl solutions having concentrations between 0,172 and 2,85 M. In each case, the electrochemical

potential between the coating and the substrate has been determined using as a reference the calomel electrode [11], [12].
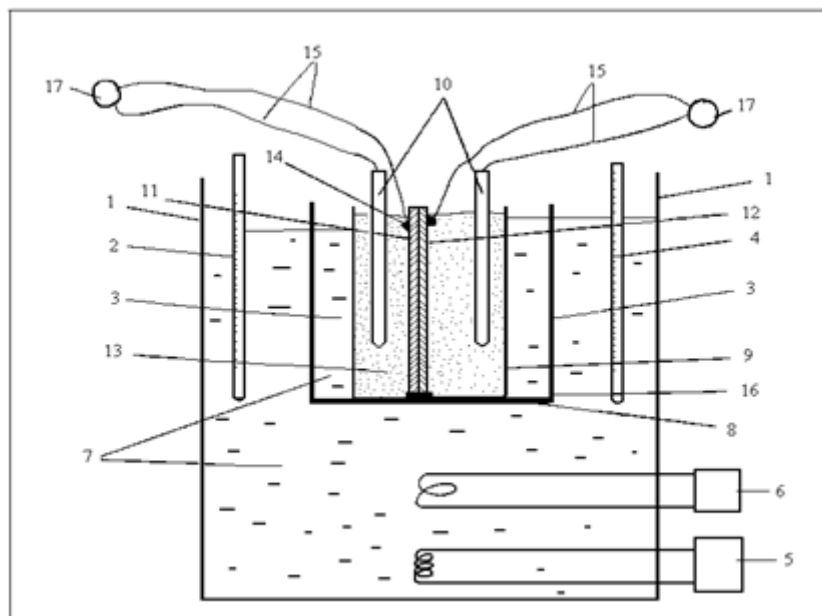
The scheme of the installation used is shown in Figure 2.

Figure 2. The assembly used for the determination of the corrosion resistance.
1-Thermostate; 2-Measurement thermometer; 3-Fixing device of the support; 4-Contact thermometer; 5-Heater; 6-Water recycling pump; 7-Water; 8-Support; 9-Berzelius glass; 10-Reference (calomel) electrodes; 1-Coating; 12-Metallic substrate; 13-Electrolite (NaCl solution); 14-Contact; 15-Conductors; 16-Silicon (adhesive for sealing); 17-Milivoltmeter

The measurements were made for three different values of the coat thickness (0,05 mm, 0,10 mm and 0,25 mm).

The difference between the electrochemical potential of the coating and that of the substrate represents the measure of the protection degree the coating can provide. The greater the difference, the better the protection of the metallic substrate.

3. Results and discussions

The powder used in plasma jet coatings was Metco 73, which has a grain size of 10-45 μm. For this powder, the granulometric distribution was also determined by means of microphotography obtained with an LMA 10 Carl Zeiss Jena optical microscope.
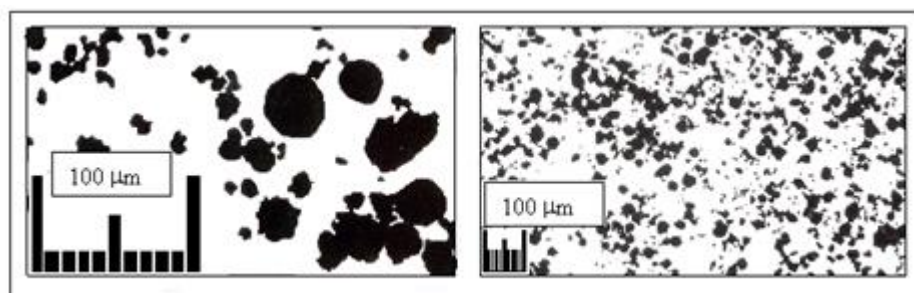

Figure 3. Microphotography of Metco 73 powder: a) x 256; b) x 64.

In order to determine the structure of the wolfram carbide covering layers, the photographies takes used 50x, 100x, 250x and 400x magnifying order, by means of a NEOPHOT-2 microscope; these photos are shown in Figure 4.

a) x 50
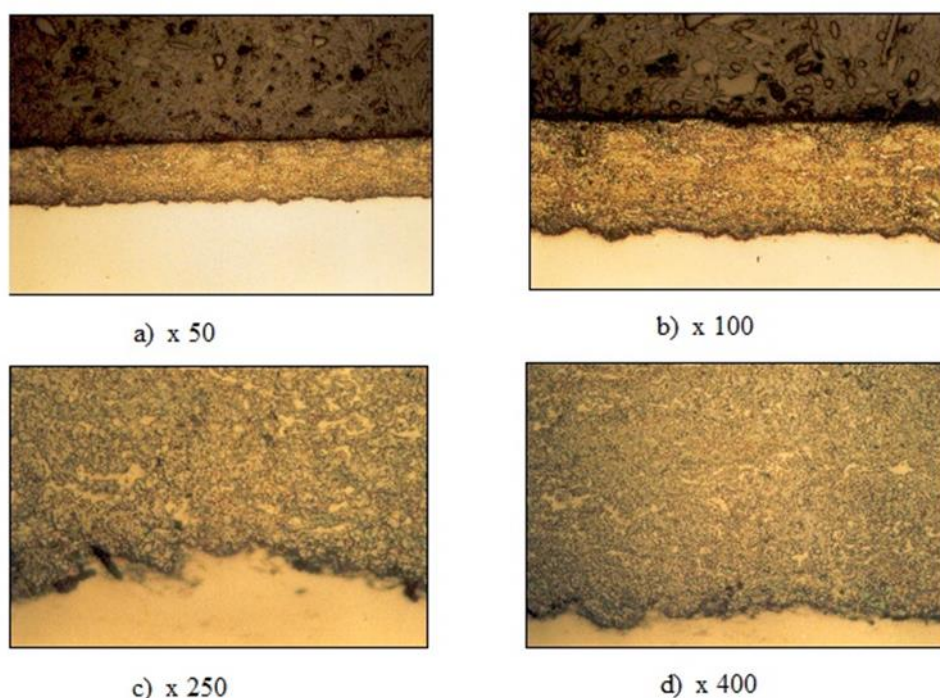
b) x 100

c) x 250

d) x 400

Figure 4. Microphotographies of the Metco 73 powder covering layer.

It is noticeable in all the images that the substrate (the martensitic stainless steel) has a very light color, while the polymer used in attaching the probe to the microscope, above the layer, is dark colored.

The covering layers have a blade structure.

The dark spots represent the pores in the substrate and one can notice that they have an irregular shape. The particles that are not melted can be easily noticed at 250x or 400x magnifying as they have a lighter color and preserve the rounded shape of the initial grains.

In the carbide strata the percentage of unmelted particles is low.

The determination of the crystalline structure of the covering layers was done by means of RX spectra obtained of a DRON-3 refractometer. Radiation Cu K_{α}, was used at a voltage of 30 kV and a current of 30 mA. The detector movement rate was 1°/min.

By comparing the RX spectra for the Metco 73 powder and for the covering layer obtained with this powder (Figure 5), one can notice that in the covering layer there are no more drops that characterize cobalt, therefore the covering layer contains nothing but wolfram carbide.

Vikersmicrohardness (HV 0.3) was determined by applying a 2.94 N force to the samples for a given period of time, using a square-based, straight pyramid diamond penetrator having the angle between the opposed sides of 136°. The arithmetic mean of the diagonals of the print was 0.025 mm and the values of the microhardness ranged between 800 and 950 N/mm2.

The adherence of the wolfram carbide layers was determined as described in paragraph 2.2. The resulting values of traction resistance ranged between 45-50 MPa. These values point to the fact that such coatings have a high adherence.
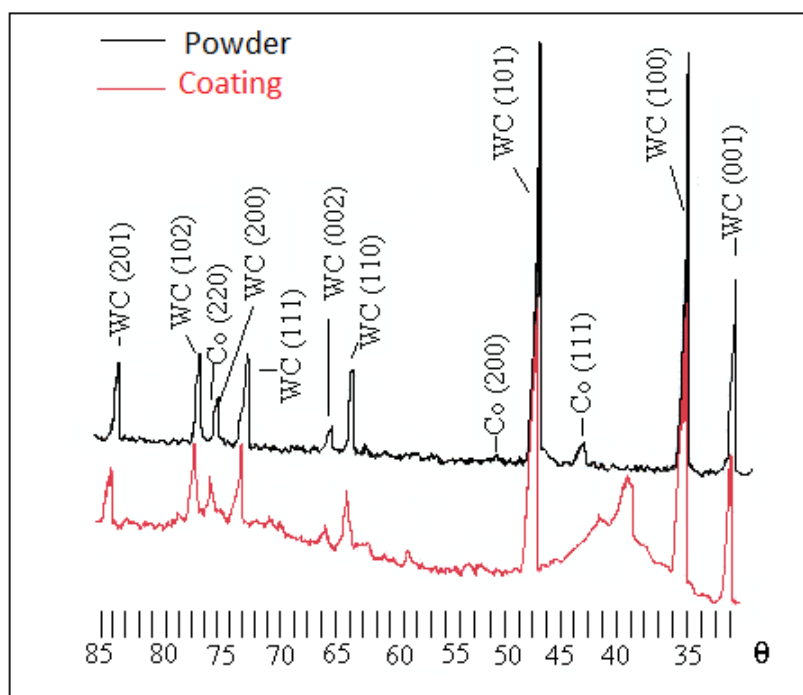
Figure 5. Comparison of the RX spectra obtained with the powder and
covering layer achieved withMetco 73 (WCCo17).

The results of the experiments meant to determine the corrosion resistance by potentiostatic methods (in module) are shown in Table 2.

Table 2. The variation of the difference of the electrochemical potential [mV] between the coat and substrate, with the thickness of the coat and the concentration of the sodium chloride.

c (%wt)	ρ (g·cm^{-3})	CM (mol·L^{-1})	0,05 mm			0,10 mm			0,25 mm		
			$\varepsilon_s{}^a$ (mV)	$\varepsilon_d{}^b$ (mV)	$\Delta\varepsilon$ (mV)	$\varepsilon_s{}^a$ (mV)	$\varepsilon_d{}^b$ (mV)	$\Delta\varepsilon$ (mV)	$\varepsilon_s{}^a$ (mV)	$\varepsilon_d{}^b$ (mV)	$\Delta\varepsilon$ (mV)
1,00	1,0072	0,1722	253	281	28	73	326	253	3	361	358
2,00	1,0145	0,3468	278	330	52	106	370	264	105	406	301
3,00	1,0217	0,5239	335	346	12	146	393	247	83	416	333
4,00	1,0290	0,7036	348	360	12	228	415	187	88	416	328
5,00	1,0366	0,8860	360	376	16	246	396	150	115	420	305
6,00	1,0440	1,0707	376	386	10	221	406	185	128	423	295
7,00	1,0513	1,2580	385	391	6	246	426	180	141	431	290
8,00	1,0585	1,4475	380	398	18	231	415	184	188	433	245
9,00	1,0659	1,6398	393	401	8	225	416	191	241	433	192
10,00	1,0733	1,8347	391	393	2	230	413	183	216	425	209
11,00	1,0809	2,0325	396	403	7	230	420	190	221	415	194
12,00	1,0886	2,2330	401	410	9	233	423	190	243	428	185
13,00	1,0962	2,4360	405	411	6	236	420	184	198	426	228
14,00	1,1039	2,6418	406	411	5	240	425	185	215	437	222
15,00	1,1115	2,8500	406	411	5	251	428	177	235	440	205

[a] the electrochemical potential [mV] of the substrate
[b] the electrochemical potential [mV] of the coat

In order to obtain some mathematical correlations between the corrosion resistance, estimated by the electrochemical potential difference, and the concentration of the NaCl solution (for each

thickness), the experimental data have been processed usingMatlab.The graphical representations are shown in Figures 6, 7 and 8. All measurements were made at a constant temperature of 20°C (293K).
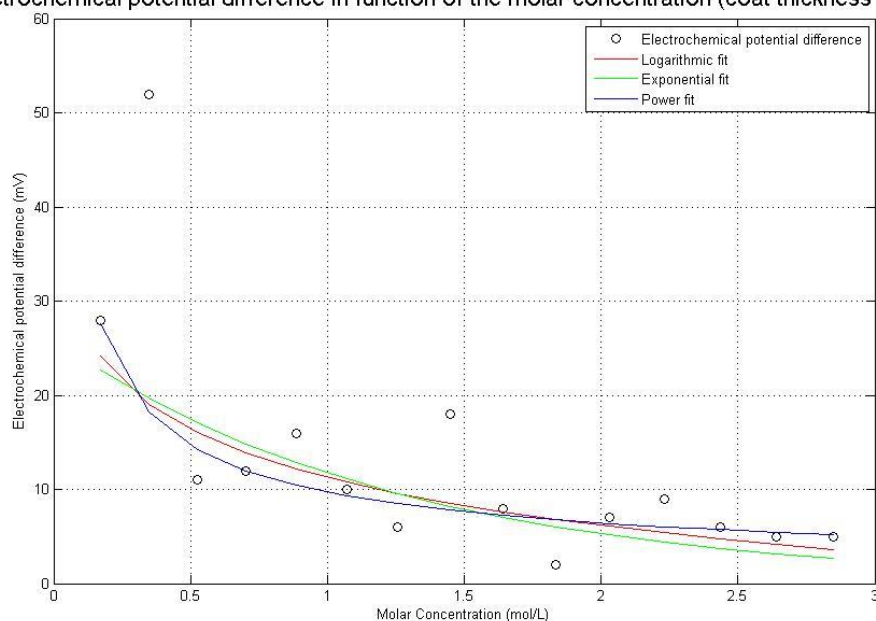

Figure 6. Electrochemical potential difference in function of the molar concentration(coating thickness 0,05 mm).
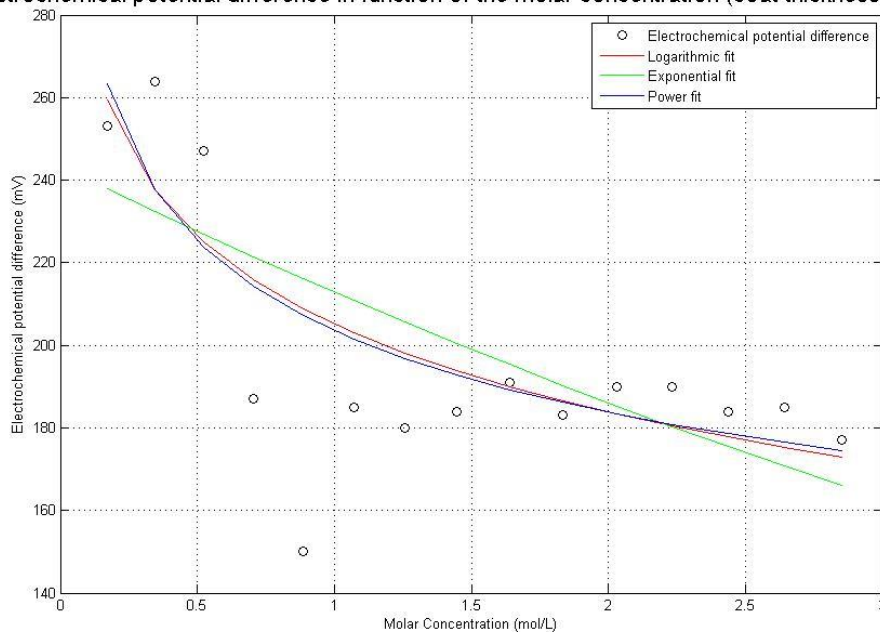

Figure 7. Electrochemical potential difference in function of the molar concentration (coating thickness 0,1 mm).
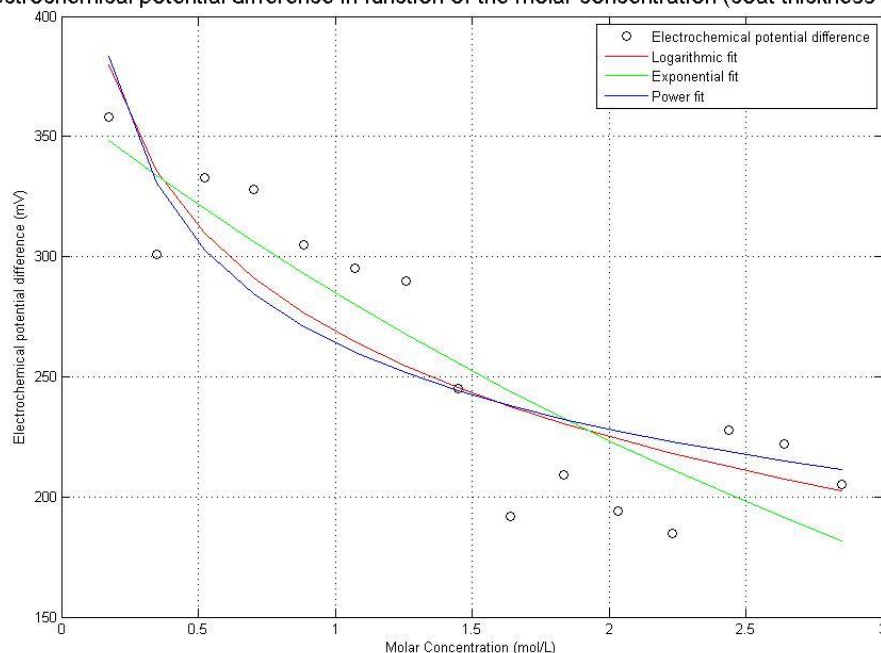
Figure 8. Electrochemical potential difference in function of the molar concentration
(coating thickness 0,25 mm).

The experimental points were used in order to find a law that could relate the electrochemical potential to the concentration of the NaCl solution. There were three types of functions proposed for this purpose: exponential, logarithmic and power. The last one seems to fit the best the experimental points, because the coefficient of determination (R^2) is most of the time higher than or very close to the coefficients obtained for the other functions (as seen in Table 3). This shows that the phenomenon is related to the adsorption/desorption of the ions at the surface, which is also coherent with the decrease of the electrochemical potential. This also explains the important noise obtained for the measurements which is related to the lack of a mechanism that would impose a continuous flow of electrolyte in the experimental setup.

It may be also observed that the thicker coatings introduce a greater electrochemical potential difference which indicates a better protection of the substrate. Moreover, the surface saturation is reached for higher concentrations of NaCl.

Table 3. The results of the mathematical processing of experimental data.

Coat thickness (mm)	Type of Law / Form / Coefficient	Logarithmic a·ln(x)+b	Exponential a·exp(b·x)	Power a·xb
0.05	a	-7.328	25.99	9.712
	b	11.27	-0.795	-0.5948
	R^2	0.7839	0.7066	0.8447
0.10	a	-30.75	243.5	203.5
	b	205.2	-0.1344	-0.1466
	R^2	0.7362	0.5744	0.7478
0.25	a	-63.08	363.2	264.1
	b	268.8	-0.2428	-0.2118
	R^2	0.7598	0.7986	0.7204

A comparison of the experimental results for the three thicknesses of the covering layer is depicted in Figure 9.
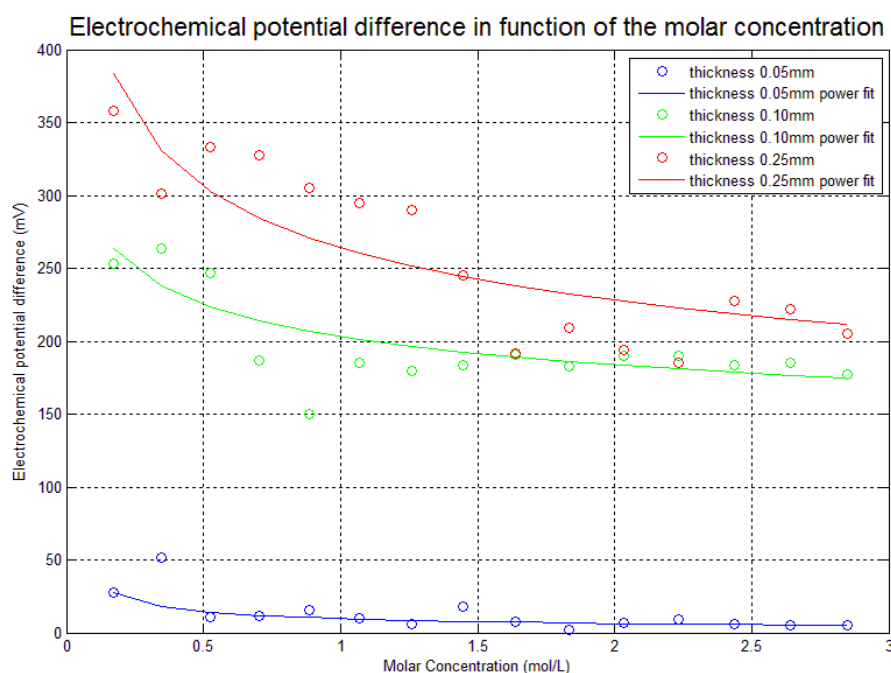

Figure 9. Electrochemical potential difference in function of the molar concentration for different thicknesses of coating.

4. Conclusions

The paper presents the principal characteristics and an original method to describe the behavior in a corrosive environment of the WC coatings deposited by plasma spraying on a stainless steel substrate; the method is based on measuring the electrochemical potential of the coating, respectively that of the substrate, immersed in a NaCl solution (corrosive agent), related to a reference calomel electrode.

The characteristics of the coatings are determined by: its chemical composition, optical microscopy, RX analysis, tensile strength, Vickers hardness, the nature and the processing degree of the substrate and the deposition conditions.

The obtained experimental results show that the coating/substrate electrochemical potential difference is a sensible parameter, which reflects the protection provided by the coating and may be used in quantifying coatings protection activity, in constant conditions concerning the nature of the couple coating/substrate and the spraying parameters.

The bigger the thickness of the coat, the greater the difference between the electrochemical potential of the coat and that of the substrate and consequently the coat protects the substrate better.

The values of the potential differences between the coating and the substrate are decreasing when raising the concentration of the NaCl solution, which shows a decrease of the protection provided by the coating.

The mathematical processing of the experimental results shows that for all the concentrations of the used NaCl solutions, the dependence between the electrochemical potential difference is very well described by some curves having equations.

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