

Study on the Microstructural Characteristics of Some Metallic Layers Produced Using the Electrochemical Method and Thermal Spraying

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Abstract: *The paper presents the comparative analysis of the microstructural particularities and the superficial characteristics (microhardness and wear resistance) of 3 methods of producing composite layers on metallic support. The aim of the research was to study the possibility of replacing the hard chromium plating process by the thermal metallization process, in order to produce layers resistant to wear and corrosion. Samples produced by hard chromium plating (layers deposited by electrolysis), samples loaded by thermal metallization with electric arc and G3Si1 wire, and samples loaded by thermal metallization with oxy-gas flame and detonation (HVOF) using tungsten carbide as filler material were used in this study. Hard chromium plating allows for high wear resistance thin layers to be produced, but the process is cumbersome and polluting. Thermal metallization allows the production of composite layers, of a chemical composition selected according to the operational demands, in much shorter times and at lower costs. In order to ensure a higher adhesion and to reduce the mechanical stresses at the support-hard layer interface, an intermediate layer of nickel was deposited in the case of samples loaded by thermal metallization with wire. In the paper, the microstructures in cross-section were analysed, the chemical compositions were determined on micro-zones related to the diffusion from the support material and the microhardness in the deposited metal and in the thermally affected zones was measured. These studies have shown that composite metallic layers displaying satisfactory mechanical and microstructural characteristics can be produced using alternative methods (thermal metallization) if optimum regime parameters are chosen.*

Keywords: *thermal spraying, hard chromium plating, microstructure, chemical composition, microhardness*

1. Introduction

Many industrial applications require the use of high wear and corrosion resistance active surfaces. These surfaces can be produced for both new and reconditioned parts. The area of use of hard chromium plating reconditioning comprises a wide range of parts, including hydraulic subassemblies, engine components, pressure cylinders, etc., whose surfaces are subjected to corrosion and heavy mechanical wear. A chromium layer, of a hardness of at least 1000 HV, is applied on the surface of the parts to protect them against such stresses. Durability and reliability characteristics adapted to the requirements of the beneficiaries can be achieved by varying the thickness of the chromium layer.

The main criteria for choosing alternative processes are: ensuring the prescribed surface mechanical characteristics, good machining by cutting to obtain the desired dimensions, mechanical and chemical

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stability of the layers under different operating conditions and the possibility of restoring them when wear phenomena occur. In the case of hydraulic cylinders, which are extensively used in a wide variety of industrial areas (such as civil, automotive or shipbuilding), the contact surfaces must be smooth (roughness of 1-2 μm) and very hard ($> 1000 \text{ HV}$), so as to ensure the tolerances required for proper sealing and the longest possible service life. Piston rods are usually chromed, but other alternative methods are currently being researched, as hexavalent chromium oxide is produced during the hard chromium plating process, which is a well-known carcinogen by-product.

Thermal spray coating could be considered as an alternative technique for producing complex metallic layers, similar to those produced by hard chromium plating [1]. Metallic layers produced by thermal spraying can withstand various stresses, under aggressive environmental conditions, such as abrasive wear and corrosion [2]. Some surfaces produced by thermal spraying can have better properties than the layers produced by hard chromium plating, and the former process is much more productive. Moreover, laser and powder loading is increasingly becoming a variant used for high precision industrial applications for loading with metallic-ceramic or composite layers [3-4]. The use of high-performance filler materials, such as high entropy alloys [5] or the optimization of the technological parameters of the processing, also allows achieving very good results when depositing complex layers [6-8].

The research carried out in the paper was aimed at achieving improved surface mechanical characteristics by applying the thermal spraying deposition methods, comparable to those achieved by hard chromium plating. The paper analyses two processes for thermal spray coating for obtaining of metallic layers, namely the deposition by HVOF thermal spraying using tungsten carbide (WC/CoCr 86/10-4) and electric arc thermal spraying using two wires as electrode (Fe-based alloy wire G3Si1) and Ni intermediate layer. The loaded parts were then subjected to destructive tests, i.e. cross-sectioning for microstructure and microhardness analyses, as well as local chemical composition analyses on the interface zones between the deposits and the support material.

Thermal spray coating methods

Thermal spray coating methods are mainly distinguished by their performance, i.e. the porosity of the layers (about 10% for electric arc metallization, 10-15% for flame metallization, 2-5% for plasma metallization and 1-2% for flame and HVOF detonation metallization), the maximum temperature reached in the melting zone of the filler material (between 3000 - 4000°C for electric arc or flame processes and 15000°C for plasma processing), the projection rate of the molten particles (between 40 and 200 m/s for classical processes and up to 800 - 2500 m/s for plasma or HVOF processes), respectively the peeling resistance of the deposited layer (10-15 MPa for flame or electric arc processes, over 50 MPa for plasma metallization and over 70 MPa for the HVOF process).

Most thermal spray coating processes are carried out at ambient temperature and pressure, with the exception of plasma metallization, which requires plasma generating gases (argon, nitrogen or helium) supplied at high pressure (over $5\text{m}^3\text{min}^{-1}$) [9]. The filler material can be supplied as powder, metal bars, wire or metal melt, the final version being chosen depending on the performance of the process (the maximum temperature, the particle projection rate) and the design requirements (thickness of the layer, adhesion). The main issues that arise in the thermal metallization are: the metallized layer lacks homogeneity and is produced by the mechanical adhesion of the molten metal droplets between them and upon reaching the substrate; the microstructure of the metallized layer includes oxide films and pores [10, 11] as a result of the rapid cooling upon impact with the cold substrate, the metallization deposits have unique crystalline microstructures that are not usually formed in conventional metallic alloys. The disadvantages of the wire metallization process include the following effects: overheating and oxidation of the materials sprayed on a metallic substrate, unevenness of the thickness of the deposited layer. The main advantage of the electric arc spraying method is the high productivity of the process and the possibility of depositing performance materials. Thus, at high current intensity, for example 750 A, the productivity for alloyed steel is 36 Kg/h, exceeding by several times the productivity of oxy-gas flame

spraying, and layers with significantly higher adhesion can be produced on various types of substrates. Pseudo-alloys can be produced when wires made of differing metals are used [2].

Plasma metallization is a process widely applied due to the special quality of the deposits, made with both wire and powder. The main disadvantages are the high price of the plant and the processing costs incurred with the use of plasma generating gases. The plasma torches allow the use of gas mixtures such as: Ar, Ar-H₂, Ar-He, Ar-He-H₂, N₂ and N₂-H₂. Most plasma torches are provided with a cathode, supplied with power ranging between 30 and 90 kW and powder feeding rate between 3 and 6 kg/h at a deposition efficiency of around 50% [9].

The flame spraying method allows composite, metallic or metallic-ceramic deposits to be produced. The large amount of heat emitted by the flame and the resulting gases can lead to a significant combustion of the alloying elements in the filler material. Thus, the carbon concentration in the layers formed by spraying is by 40-60% lower than that of the original material and by 10-15% lower than that of silica and manganese. The main advantage of the method is the high flexibility and low cost of applying the process. Unfortunately, the quality of the deposited layer is often inferior compared to other metallization techniques (at a layer thickness above 6 mm the flaking effect may occur, Figure 1) [10, 11].

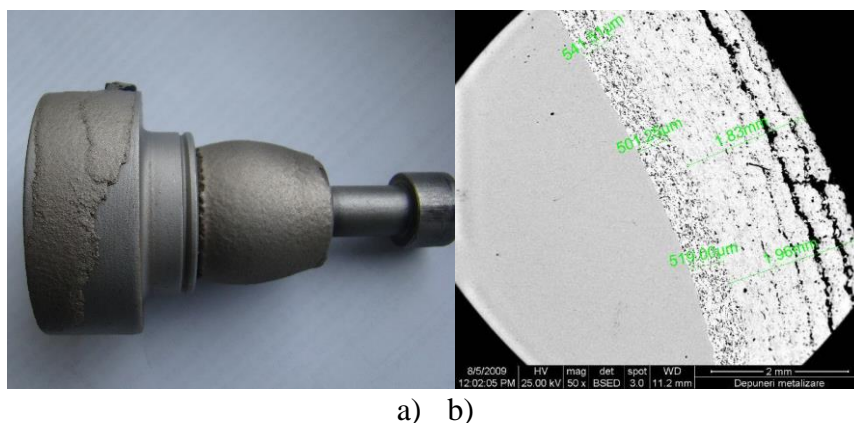


Figure 1. Unsatisfactory appearance of a flame metallization deposit:
a) peeling off the substrate; b) flaking

The HVOF (High Velocity Oxy-fuel Flame), HVOF (High Velocity Air-fuel Flame) and D-gun (Detonation gun) procedures were developed to improve the performance of flame metallization deposits. In the case of these processes, the deposited layers are very finely structured and extremely dense, using metallic or metallic-ceramic powders at very high sputtering rates and high carrier gas pressure. The rapid combustion of hydrocarbon molecules or of liquefied gases (kerosene) is produced by mixing with oxygen which reaches high pressures in the combustion chamber (0.24 and 0.82 MPa). In order to obtain high rates of projection of the molten particles (up to 2000 m/s), the system is provided with a Laval-type convergent-divergent nozzle, the power level ranging between 100 and 120 kW, with a deposition efficiency of about 70% for powder flow rates up to 7.2 kg/h for gas-fuel guns [9]. Although the performance of the deposits yielded by these processes is extremely good, it does not apply to substrates of low strength or high brittleness, as the shock produced upon hitting the support can cause overheating, deformation or cracks [12, 13]. The choice of filler materials for producing composite layers greatly influences the corrosion resistance characteristics [14]. Some new metal alloys, called high entropy alloys, tend to replace conventional alloys used in special applications, due to their special mechanical and microstructural characteristics [15]. Moreover, welding deposition processes can be applied to achieve heterogeneous layers of superior mechanical strength characteristics [16, 17]. At the same time, the development of new methods for depositing nanostructured layers allows to reduce their thickness and improve the technological performance [18-24].

2. Materials and methods

Hard chromium plating process

In order to produce layers deposited electrochemically by hard chromium plating, the following steps were carried out: mechanical processing of the surfaces of the part made of Cr low alloy steel; cleaning the processed surfaces (degreasing and washing in an ultrasonic tank for 10 min) followed by hot air drying; the chromium plating itself in the electrochemical tank; surface washing with hot water and final hard chromium plating processing.

The mechanical processing was first performed by grinding, in order to achieve the lowest roughness possible, specific to the hard chromium plating process, i.e. $R_a = 3\mu\text{m}$. It was followed by sanding with abrasive paper (360 - 1500 grit) and polishing with fine abrasive paste (chromium oxide), to eliminate the scratches left by the mechanical processing. In order to keep the parts at the required distance from the chromium anodes, the parts were mounted in special supports during the electrochemical deposition process. The surfaces were cleaned by chemical degreasing in aqueous solution of 70 g/L NaOH and 30 g/L Na₂CO₃, at 80°C, and electrochemical degreasing in aqueous solution of 100 g/L NaOH and 3 g/L soluble glass (NaSiO₃). The current density for degreasing was set at 7 A/dm² and the temperature of the bath was of approximately 85°C. After degreasing, the parts were washed with hot water to remove any trace of electrolyte that may affect the quality of the chromium deposition. The anodic etching was performed in the chromium bath, using an electrolyte made of 150 g/L CrO₃ and 1.5 g/L H₂SO₄. The solution for the actual chromium was made as follows: 200 g/L electrolyte in the form of CrO₃ powder, 35 mL for 1 kg of CrO₃ additional additives of catalytic chromium, 4 g/L ultrapure sulfuric acid, 20 mL/L of solution chromium of HN25 catalytic purity. The parameters of the chromium plating regime were set as follows: current density, $D_c = 40\text{ A/dm}^2$, solution temperature, $T = 60\text{--}80\text{ }^\circ\text{C}$ and 10 min loading time.

Two-wire thermal spraying process

In order to produce the specimens loaded by thermal spraying, a 12 mm thick support made of S235 structural steel was used. Successive layers were deposited using G3Si1 wire, whose chemical composition is shown in Table 1. To ensure the adhesion of the hard layer and to avoid any flaking phenomena, a nickel alloy buffer layer was deposited prior to depositing by thermal spraying using G3Si1 wire.

The technological parameters used in the thermal spraying process by electric arc metallization plant were: 0.4 - 0.5 MPa compressed air spraying gas, 28 V electric arc voltage, 200 A current intensity, 1.6 mm wire diameter, 100-110 mm spraying distance, 150 m/s sprayed particle rate, 90° spraying angle.

Table 1. The chemical composition of the G3Si1 wire

Wire	Chemical elements, wt. %									
	C	Si	Mn	P	Cu	Cr	Ni	Mo	S	Al
G3Si1 (RYWAL RHC)	0.08	0.82	1.51	0.011	0.21	0.11	0.12	0.10	0.012	-

HVOF thermal spraying process

The substrate material chosen for producing the samples loaded by HVOF spraying was made of 8 mm thick S275 structural steel (Figure 2). Tungsten carbide powder WC/CoCr 86/10-4 was used as filler material, having the chemical composition shown in Table 2.

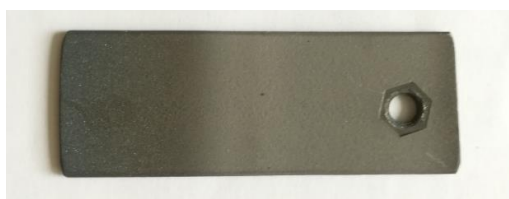


Figure 2. The aspect of the sample loaded by HVOF thermal spraying

Table 2. The chemical composition of the WC/CoCr 86/10-4 powder

Sintered powder	Chemical elements, wt. %					
	W	Co	Cr	C	O	Fe
WC/CoCr 86/10-4 (GTV)	Ballance	10	4	5.3	0.03	0.005

The parameters of the HVOF spraying metallization process were: 7 bar fuel gas (propane) pressure, 10 bar oxygen pressure, 7 bar spraying air pressure, 45g/min powder flow rate, 280 mm spraying distance, 1600-2000 m/s particle spraying rate range, 90 ° spraying angle.

3. Results and discussions

Microstructural examination

The microstructural examination was performed on surfaces sampled from cross sections. The samples were cut using an abrasive wheel and coolant in the IsoMet 4000 precision cutting machine, the wheel being positioned perpendicular to the metallic deposit. For further processing, the samples were embedded in phenolic resin (Figure 3) using the IPA 40 press. The layer that was thermally and mechanically affected by cutting was removed by metallographic grinding on the Buehler automatic machine using abrasive paper (with progressive 360, 600 and 1000 grit). The surfaces were polished using fine alpha alumina abrasive powder of 3.0 - 0.25 μm grain size. The polished surfaces were degreased with ethanol and then dried with hot air jet. There was not applied a chemical attack with metallographic reagent, in order not to affect the chemical composition of the samples subjected to metallographic analysis.



Figure 3. Samples embedded in phenolic resin for metallographic processing P1 chromed specimen; P2 specimen loaded by electric arc and G3Si1 wire; P3 specimen loaded with tungsten carbide

The optical microscopy examination was aimed at the microstructural analysis of the zones adjacent to the layers deposited by metallization and at measuring the thickness of the layers. The metallographic analysis was performed by optical microscopy, according to SR EN 1321:2000, using an Olympus GX51 microscope equipped with the AnalySIS specialized software for image processing. The SEM electron microscopy analysis was performed according to SR EN 1321:2001 using a Quanta Inspect S, FEI Netherlands electron microscope equipped with a Z2e EDAX sensor. The analysed samples were coded (P1, P2, P3) and data on the materials, the thermal spraying processes and the thickness of the layers is presented in Table 3.

Figure 4 shows the cross-section through the layer deposited by hard chromium plating. The deposited layer is even, compact and free of major flaws. The parallel striations along the chromium layer were caused by grinding. There is noted the occurrence of a thermally affected zone at the interface with the support material, extending over approximately 20 μm .

Table 3. Data on samples subjected to metallographic analysis

Sample code	Process for producing hard layers	Layer thickness [μm]	Substrate material	Deposited material
P1	Hard chromium plating	~ 18	Heat-resistant steel, containing about 2% Cr	Chromium with Gadolinium
P2	Electric arc spraying and 2 wires	100 - hard layer 75 - adhesion layer	Structural steel S 235	G3Si1 wire for wear layer and Ni for adhesion layer
P3	High rate spraying with oxygen-propane flame (HVOF)	~ 575	Structural steel S 275	WC/CoCr86 powder 10-4 participation

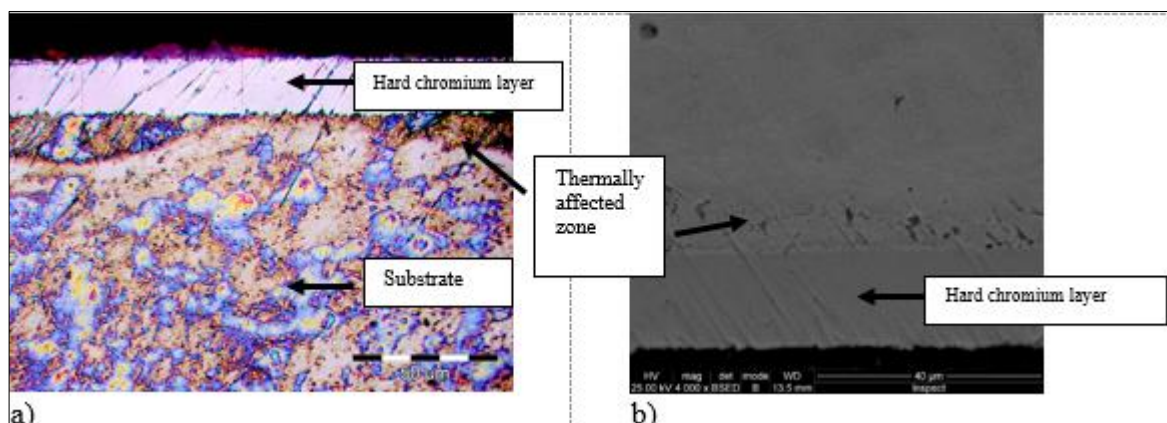


Figure 4. Cross-section of the sample loaded by hard chromium plating (P1).
a) optical microscopy; b) SEM electron microscopy

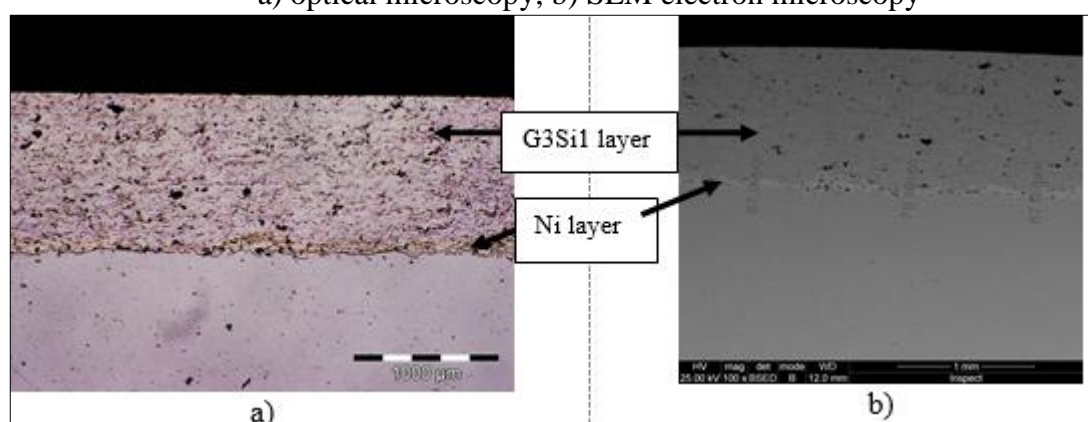


Figure 5. Cross-section of the sample metallicized using an electric arc (P2).
a) Optical microscopy. b) SEM electron microscopy

The metallic layer is even, compact and has small imperfections (isolated pores, inclusions and crusts of oxides). The deposited layer has a quasi-even thickness and the interface with the support material is continuous, free of peeling or other unacceptable flaws. There is noted an intermediate layer of Ni, very thin and uneven, deposited at the interface with the support material.

The cross-section of the layer deposited by thermal spraying with oxy-propane flame and WC/CoCr86 powder is shown in Figure 6. The metallic layer is even, compact and has small imperfections (isolated pores, inclusions and crusts of oxides).

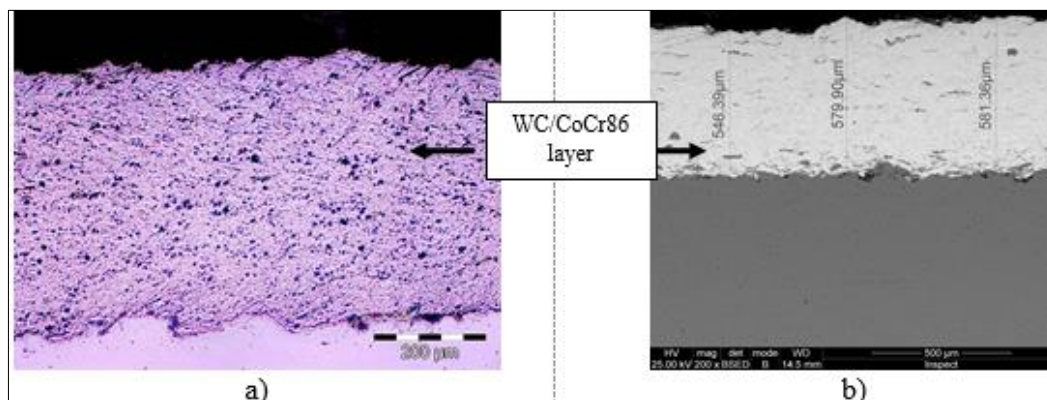


Figure 6. Cross-section of the sample metallicized using the HVOF process (P3).
a)optical microscopy; b) SEM electron microscopy

As a result of the high impact energy, small fragments from the surface of the support material flaked off and were embedded in the first metallized layers. Some inclusions of various shapes (elongated or rounded) are present in the upper layers as well (Figure 7).

A flaking zone on the surface of the support material and inclusions of various shapes (dark-coloured) embedded in the material deposited by metallization are highlighted in Figure 7a. At higher magnifications (10000x, Figure 7b), there can be seen polyhedral grains of light-coloured tungsten carbide (200 nm and 1.84 μm grain size) and the bonding zones between them, consisting of CoCr alloy.

There can also be seen a massive inclusion caused by the flaking of the surface of the support material, dark-coloured.

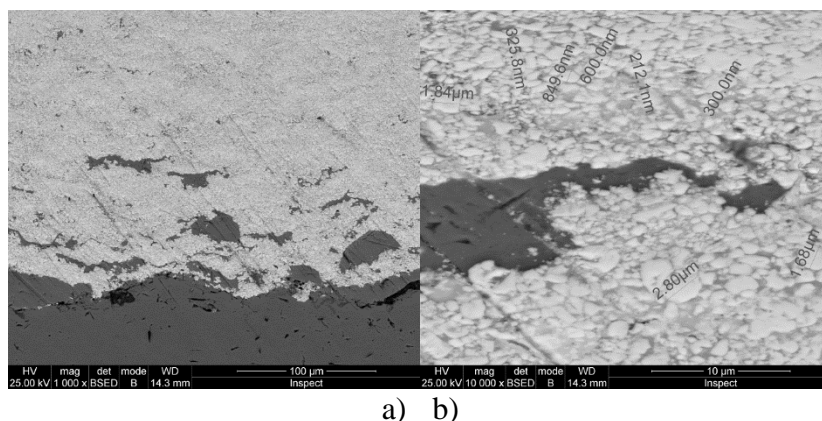


Figure 7. Detail on the interface between the layer deposited by HVOF metallization and the steel substrate for sample P3.

Chemical composition analysis

The local chemical composition was analysed using the EDAX (Energy Dispersive Spectroscopy) method, a Z2e-type energy dispersive X-ray spectrometer fitted to an Inspect S (FEI Netherlands) electron scanning microscope within the UPB's LAMET laboratory. The measurement micro-zones and the determined values of the chemical compositions are shown in Figure 8 (P1), Figure 9 (P2) and Figure 11 (P3).

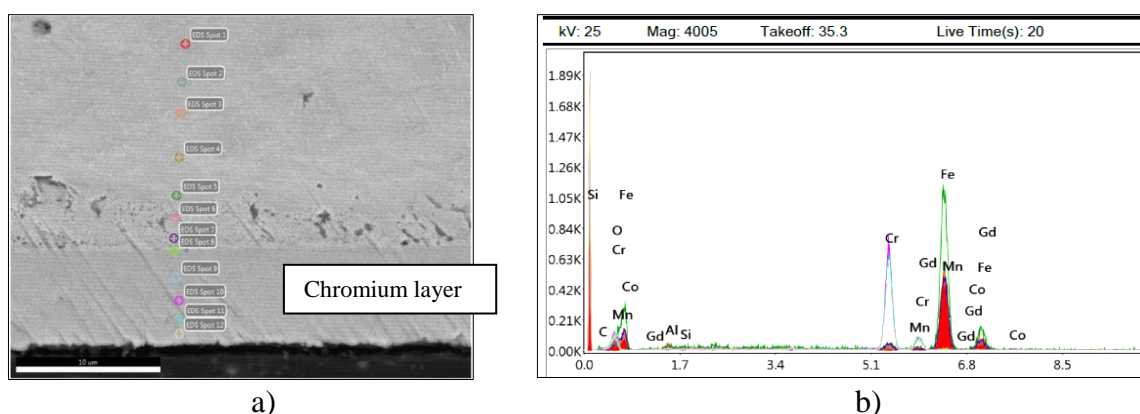


Figure 8. The location of the chemical composition measurement zones on the chromed layer cross-section (a) and the energy dispersive X-ray (EDAX) spectra cumulated for all the measurement points associated with the microzone (b)

The local chemical composition analyses revealed the presence of alloying elements in each zone in Figure 8, as follows: Fe (84.15 - 70.95 wt.%), Mn (4.7 - 1.18 wt.%), Si (2.67 - 0.95 wt.%), Al (6.4 - 5.99 wt.%), Cr (11.64-2.11 wt.%), in the support material, noting that higher values of chromium

concentrations were ascertained on the zones near the interface with the electrochemical deposition (transition zone); Cr (93.66 - 89.88 wt.%), Co (4.06 - 1.53 wt.%) and Gd (9.18 - 6.34 wt.%) on the interface with the steel support; Cr (98.25 - 90.20 wt.%), O (1.13 - 0.94 wt.%) and Gd (7.50 - 6.34 wt.% in electrochemical chromium deposition.

The presence of oxygen in relatively small quantities shows that the deposition was performed in good conditions, as confirmed by the higher wear resistance characteristics of the chromed layer. For the sample with thermal spraying deposition using an electric arc and G3Si1 wire, the chemical composition analyses reconfirmed the presence of the nickel adhesion intermediate layer, where the Ni concentration ranged from 67.32 to 79.54 wt.%.

The chemical composition of the layer deposited by thermal spraying (Figure 9) was similar to that of the wire used, containing the main alloying elements: Fe (63.26 – 42.70 wt.%), Si (1.42 – 0.83 wt.%), Mn (2.07 – 1.46 wt.%), Cr (39.05 – 28.59 wt.%), Mo (1.42 – 0.47 wt.%).

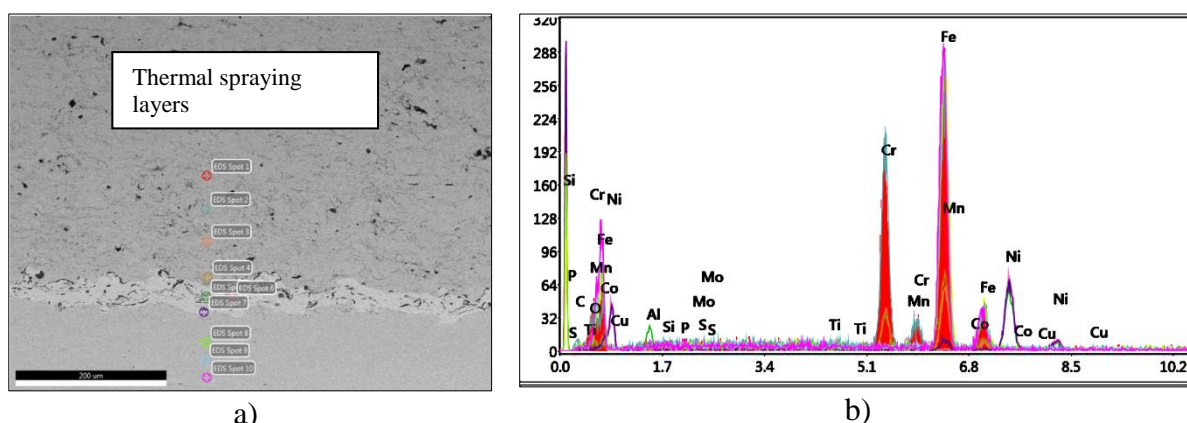


Figure 9. The location of the chemical composition measurement zones on the cross-section of the layer deposited by thermal spraying using an electric arc (a) and the energy dispersive X-ray (EDAX) spectra cumulated for all the measurement points associated with the microzone (b)

The chemical composition analysis on micro-zones for the sample produced by thermal spraying with oxy-propane flame (HVOF) and WC/CoCr86 powder mixture is shown in Figure 10. The chemical composition of the layer deposited by thermal spraying contained the following main alloying elements: Co (24.85 – 7.23 wt.%), Cr (23.74 – 4.08 wt.%), W (82.79 – 3.63 wt.%), C (5.66 - 4.54 wt.%). In this case as well, the percentage of oxygen is low, the highest measured value being 3.02 wt% at the interface with the substrate material.

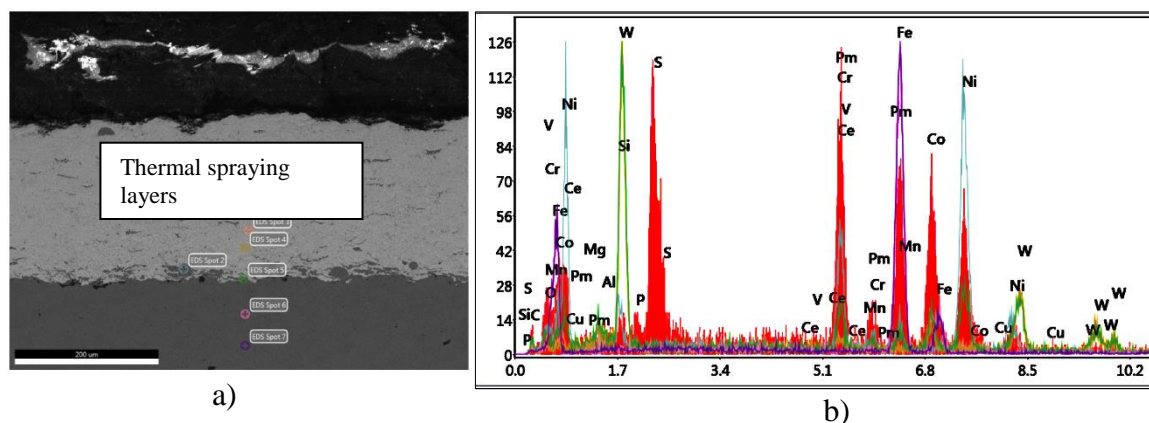


Figure 10. The location of the chemical composition measurement zones on the cross-section of the layer deposited by thermal spraying using an oxy-propane flame (HVOF) (a) and the energy dispersive X-ray (EDAX) spectra cumulated for all the measurement points (b)

Microhardness measurements

The microhardness measurements were performed using the Shimadzu HMV 2T microhardness tester within the LAMET laboratory, according to SR EN ISO 6507-1:2006. The measurements were performed in line, with distances between prints of at least 500 μm . Several measurements were performed on the deposited layers and on the zones bordering the support material, both in cross-section and on the deposited layer, after a prior processing carried out by grinding, at a pressing force of 0.98 N (HV 0.1) and pressing time of 10 seconds. The evolution of the microhardness values measured on the surface of the deposited layers is shown in Figure 11.

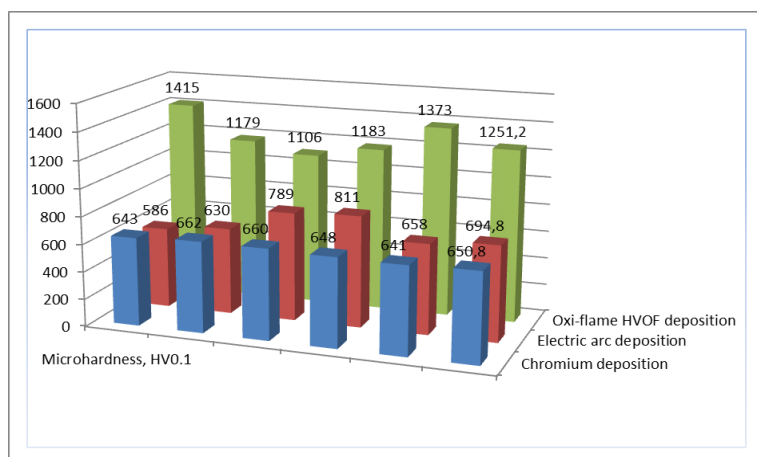


Figure 11. Microhardness values measured on the surface of the deposited metallic layers

The microhardness evolution analysis shows that the highest values were determined at the surface loaded by spraying with WC/CoCr86 (1251 HV_{0.1}) powder mixture, compared to the values achieved in the other two types of deposits, respectively an average of 650 HV_{0.1} for electrochemical deposition with chromium and 695 HV_{0.1} for loading by spraying with G3Si1 wire. The measurements were then performed on the cross-sections of the specimens processed by metallographic procedure and the values are summarized in Tables 4 to 6.

Table 4. Microhardness values determined in cross-section for sample P1

Individual values	P1			
	Chromium layer		Transition zone	Substrate material
	HV _{0.05}	HRC	HV _{0.1}	HV _{0.1}
1	595	55	147	154
2	548	52.2	162	155
3	549	52.3	154	149
4	555	52.6	151	167
5	626	56.6	164	156
Average value	575	53.74	156	156.2

Table 5. Microhardness values determined in cross-section for sample P2

Individual values	P2			
	Arc spraying layer		Ni buffer layer	Substrate material
	HV _{0.1}	HRC	HV _{0.1}	HV _{0.1}
1	894	66.8	104	174
2	665	58.6	155	193
3	654	57	151	178
4	858	65.7	140	171
5	674	59	156	183
Average value	749	61.42	141.2	179.8

Table 6. Microhardness values determined in cross-section for sample P3

Individual values	P3			
	HVOF layer		Transition zone	Substrate material
	HV _{0.1}	HRC	HV _{0.1}	HV _{0.1}
1	1011	-	235	165
2	911	67.2	212	150
3	995	64.8	216	168
4	1067	-	203	166
5	910	61.4	205	148
Average value	978.8	-	214	159

There is found that the microhardness in cross-sections is lower for the samples loaded electrochemically and using the HVOF process, which shows that the manner of formation of the layers using these methods determined the occurrence of the anisotropy of the hardness characteristics in different directions. In contrast, in the case of deposition by thermal spraying with electric arc, there is found an increase of the average hardness in cross-section, from about 650 HV_{0.1} to 749 HV_{0.1}.

4. Conclusions

The deposition of composite metallic layers using various methods allows the assessment and selection of their fields of use, according to the mechanical and microstructural characteristics achieved. The comparative analysis of 3 different methods of depositing composite metallic layers allowed highlighting the microstructural particularities thereof.

In the case of electrochemical deposition of the chromium layer, there was found an evenness of the deposition, its good adherence to the base material and the lack of major flaws such as cracks, flaking or pores. Chromium concentration in the layer was over 98 wt.% ensuring good mechanical characteristics (hardness between 575 and 650 HV_{0.1}) and high corrosion resistance.

For the sample performed by spraying with electric arc and G3Si1 wire, the microhardness values are slightly higher compared to those obtained by electrochemical deposition method. The productivity of producing the layers is higher, considering the lower cost per unit area and the much shorter processing time, the number and size of the pores are low, ensuring good operating behaviour.

The deposited layer performed by spraying with oxy-propane flame and metallic-ceramic powders (WC/CoCr 86/10-4) contains cobalt (over 25 wt.%), chromium (over 23 wt.%) and carbides. The microstructure of the deposited layer highlights the presence of partially melted and flattened particles. There were observed fine and evenly distributed pores as well as the incorporation of particles from the surface of the base material. The deposited layer (average thickness of 550 µm) is even, adherent and relatively compact. There were found no cracks or flaking in the deposited layer.

The microhardness measured on the surface of the layer deposited with WC/CoCr 86/10-4 powders is significantly higher than the microhardness determined on the layers chromed or metallized using an electric arc, the average value being over 1250 HV. The formation of oxides during spraying may cause a decrease in hardness, but the oxygen level detected by chemical composition analyses on micro-zones showed relatively low oxygen levels (below 3wt% O).

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