



Technical Sciences
Academy of Romania
www.jesi.astr.ro

Journal of Engineering Sciences and Innovation

Volume 9, Issue 1 / 2024, pp. 33 - 46

<http://doi.org/10.56958/jesi.2024.9.1.33>

C. Chemical Engineering, Materials Science and
Engineering

Received 5 December 2023

Accepted 22 March 2024

Received in revised form 5 March 2024

Influence of deposition technology on the morphology of chromium carbide-based powder coatings

Corneliu Munteanu^{1,2}, Daniela-Lucia Chicet^{3*}, Bogdan Istrate¹,
Adrian Stefan¹, Ioan Vida-Simiti^{2,4}

¹*Gheorghe Asachi Technical University of Iasi, Department of Mechanical Engineering, Blvd. Mangeron, No. 61, 700050, Iasi, Romania.*

²*Technical Sciences Academy of Romania, 26 Dacia Blvd, Bucharest, 030167, Romania.*

³*Gheorghe Asachi Technical University of Iasi, Department of Materials Science and Engineering, Blvd. Mangeron, No. 41, 700050, Iasi, Romania.*

⁴*Technical University of Cluj-Napoca, 103-105 Muncii Ave., Cluj-Napoca, 400641, Romania.*

Abstract. Chromium carbide powders are widely used for thermal spray coatings because these hard particles provide improvements of mechanical properties, mainly wear resistance, on the surfaces on which they are deposited. The integration of chromium carbides in a Ni-based matrix provides increased erosion, abrasion, hot wear and corrosion resistance. In this paper, a comparative study is presented between two types of chromium carbide-based coatings made by two different spray deposition methods, namely atmospheric plasma spray (APS) and cold spray (CS). By electron microscopy (SEM) and X-ray diffraction (XRD) analysis, the effect of the deposition technology on the morphology of the coatings and especially on the way chromium carbides are embedded in the deposited layers was analyzed. It was observed that plasma spraying is accompanied by phase transformations of the chromium carbides (e.g. Cr₇C₃ type carbides appear), which can increase the hardness of the coating thus obtained, but also by the appearance of oxides of the component elements (NiO, Cr₂O₃, NiCr₂O₃). By comparison, cold spray coating provides a compact coating with minimal oxidation, which is the main advantage of this deposition technology.

Keyword: chromium carbide, plasma spraying, cold spray, phase transformation, coating morphology.

* Correspondence address: cornelmun@gmail.com

1. Introduction

Hard chromium plating has traditionally been used in several industries: agriculture, steel, mining, energy, oil and gas including the aerospace and military sectors [1]. Hard chromium plating creates a surface that is resistant to corrosion and wear, and is used to improve the surface characteristics of a multitude of parts, from drive shafts and landing gears to hydraulic rods and valves [2]. Despite all the advantages that hard chromium plating offers, there is one unavoidable disadvantage: the presence of hexavalent chromium and the toxic waste that is produced during the chromium plating process, and the impact it has on the environment [3]. The "notorious four Cs" are known as cyanide, cadmium, hexavalent chromium and chlorinated solvents. The latter is a known carcinogen and has the potential to damage major organs such as the kidneys, lungs and heart. Today, product engineers and materials engineering researchers are focusing their efforts on finding a safer and healthier alternative to hard chromium plating (HCP). In fact, due to European regulations, hard chromium plating is almost obsolete today and the rest of the world is following closely behind [4].

In response to these trends, several solutions to replace hard chrome plating appeared in the scientific literature and are already in current production, the most frequently mentioned being thermal spray coating with materials from the same category [5,6].

Thermal spraying is a process by which a coating is applied to a substrate or a component part of an assembly, the newly created surface being a functional one, with a protective or performance-enhancing role. Almost any type of material can be sprayed by this process, so applications of sprayed coatings range from wear, corrosion or heat protection to restoration or repair of components in various industries [7]. The technologies gathered under this name are grouped into several broad categories: Flame Spray processes (Flame Powder, Wire Flame, High-Velocity Oxyfuel, Detonation Gun), Electric Arc processes (Electric Arc Spray), Plasma Spray Arc processes (Conventional Plasma, Vacuum Plasma), Kinetic Energy processes (Cold Spray) [8, 9]. A comparison between the main process parameters, i.e. process temperature and particle acceleration velocity, is shown in Figure 1, from which it emerges that the highest temperatures are encountered in plasma processes and the lowest in kinetic, Cold Spray processes [10].

Among the materials used to obtain coatings with characteristics that are at least equivalent to those obtained by hard chromium plating, presented in the scientific literature, the following can be mentioned: WC/17Co, Cr₃C₂-20NiCr, Co-28Mo-17Cr-3Si (Triballoy 800), Metco 73F-NS-1, Metco 66F-NS [11], WC-12Co, Diamalloy 2002 (55/45 mixture of WC-Co in self-fluxing binder), W 20Cr 6Ni 6C (WC-496) and so on [6].

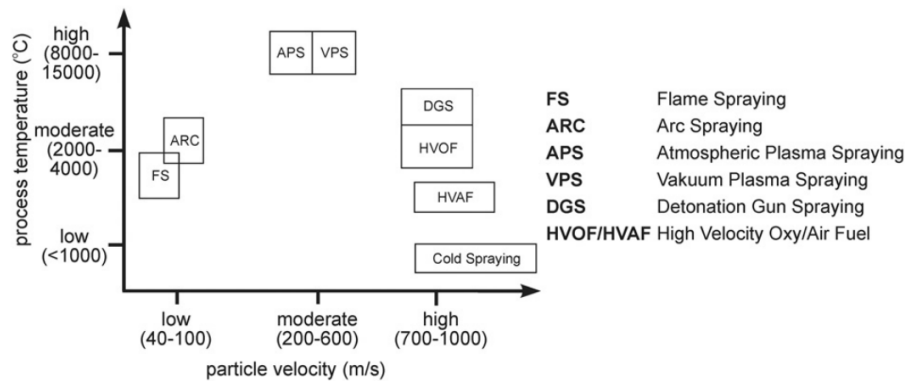


Fig. 1. Comparative presentation of the main thermal spray deposition technologies in terms of process temperature and particle acceleration rate [10].

In this study we have analyzed the influence of the deposition technology, through specific parameters (temperature and particle acceleration rate) on the morphology of the coating, considering layers produced by plasma spraying in normal atmosphere (APS) and by Cold Spray. Microscopic analysis (SEM) and X-ray diffraction (XRD) were used as analysis methods, and the presence of chromium carbides in the deposited layers, the phase transformations produced (e.g. Cr_7C_3 carbide appears, which can bring with it an extra hardness), and the appearance of oxides of the component elements (NiO , Cr_2O_3 , NiCr_2O_3), in the case of plasma jet deposition, were investigated. In comparison, cold spray coating provides a compact layer with minimal oxidation, which is the main advantage of this deposition technology.

2. Experiment

2.1. Materials and methods used for APS coatings

The deposition of the powders on the surfaces of the samples was carried out by plasma jet deposition technology in normal atmosphere, using the SPRAYWIZARD 9MCE equipment belonging to the Materials Study Laboratory of the Faculty of Mechanics of the Technical University "Gheorghe Asachi" of Iasi. A representative image of the experiment is presented in Figure 2 and the working parameters used are listed in Table 1.

The characterization of the materials used to obtain the studied coatings was carried out in terms of morphology and chemical composition by scanning electron microscopy (SEM) and qualitative, semi-quantitative elemental chemical analysis type EDS (energy dispersive X-ray spectroscopy), using the scanning electron microscope type Quanta 200 3D (FEI Company, Netherlands, 2008). The image acquisition was performed using the necessary working parameters for soft

conducting materials: Low Vacuum working mode at 60 Pa pressure, LFD (large field detector).

Morphology and chemical analysis performed with scanning electron microscope were complemented by phase and constituent characterization using XPERT PRO MRD 3060 diffractometer (Panalytical, Almelo, The Netherlands, 2008), with a Cu X-ray tube ($K\alpha = 1.54051 \text{ \AA}$), 2 theta: $10^\circ - 90^\circ$, step size: 0.13, time/step: 51 s, and a scan speed of $0.065651^\circ/\text{s}$.

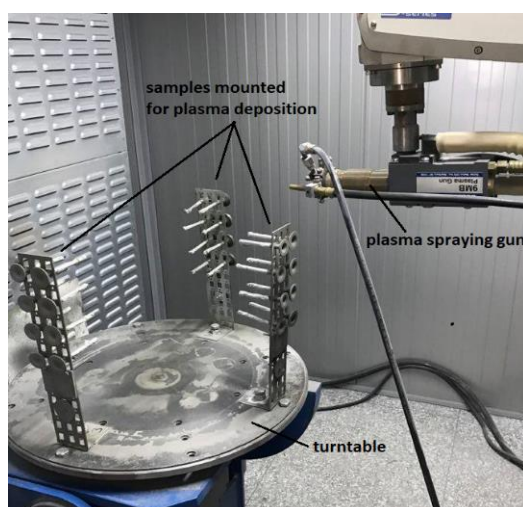


Fig. 2. The final appearance of the sample installation on the turning table.

Table 1. Working parameters of the APS deposition process of the studied powders [12].

Nr.	Parameters	Values	
	Powder type	Al ₂ O ₃ -30(Ni20Al) (410NS)	Cr ₂ C ₃ -Ni20Cr (81NS)
1	N ₂ flow (bar)	3,4	3,4
2	H ₂ flow (bar)	3,4	3,4
3	Ar flow (powder feeder gas) (NLPM)	5,66	5,66
4	Voltage (V)	70-80	74-80
5	Intensity (A)	500	500
6	Standoff distance (mm)	153	90
7	Powder feed rate (g/min)	68	91

The studied coating is composed of two layers, the first one being the base coat made of a cermet powder - Al₂O₃ - 30(Ni20Al), produced by Metco - Oerlikon and commercialized under the code Metco 410NS. For the Top Coat a chromium carbide-based powder - Cr₂C₃ - Ni20Cr, produced by Metco - Oerlikon and commercialized under the code Metco 81NS, was used.

Since the study is focused on the analysis of the influence of the deposition method on the morphology of the coatings, we only considered the characteristics of the top layer, made of chromium carbides and nickel-based matrix.

Chromium carbide powders are made by mechanical mixing of chromium carbide and nickel-chromium particles. The nickel-chromium alloy serves as a matrix that ensures overall coating integrity and corrosion resistance, while the chromium carbide constituent serves as a hard phase that ensures wear resistance [13]. These coatings effectively address solid particle erosion, high-temperature wear (abrasion, erosion, fretting and cavitations) and hot corrosion. In terms of chemical composition, 81NS is composed of: 18.75 wt% Ni, 9.95% C, < 2.25 wt% other elements, and balance Cr. The particle size ranges from 106 - 11 μm , the color is light grey and the shape is irregular polygonal.

The characteristics of coatings made from 81NS powder by APS, according to the product sheet, are as follows: microhardness HV0.3 = 550 - 800; macrohardness = 40 - 55 HRC; porosity = 1 - 5%; density = 6.0 - 6.6 g/cm^3 , maximum working temperature = 870°C, maximum coating thickness: 0.4 mm, deposition efficiency = 30 - 70%. The aspects presented in the product sheet were observed and analyzed by electron microscopy, the results are shown in Figures 5 and 6.

2.2. Materials and methods used for Cold Spray coatings

Within the framework of a collaboration project between the team of the Faculty of Mechanics of the Technical University "Ghe. Asachi" of Iasi and Northeastern University, Boston, USA, the morphological and mechanical characteristics (friction, wear and fatigue resistance) of cold spray coatings provided by the partner on 4340 steel substrate [14] with an average thickness of 450 μm were studied. AISI 4340 steel (equivalent to 36CrNiMo4/1.6511 according to EN10250) is a medium carbon, low nickel-chromium-molybdenum alloyed steel known for its hardness and strength in relatively large sections. Its chemical composition, according to ASTM A29, is as follows: 0.38 - 0.43% C, 0.60 - 0.80% Mn, max. 0.035% P, max. 0.040% S, 0.15 - 0.35% Si, 1.65 - 2.00% Ni, 0.70 - 0.90% Cr, 0.20 - 0.30% Mo.

The test samples were coated with a mixture of chromium carbide and Ni powder using a VRC, Gen-III cold spray machine (VRC Metal Systems, LLC, SD, USA). The parameters used for spraying the mixture are shown in Table 2.

Table 2. Ni-Cr coating deposition parameters [15]

Parameter	Value
Gas	Azot
Pressure	6.2 MPa (900 psi)
Temperature	675°C
Nozzle type	WC NNZL0060
Nozzle throat size	2 mm
Powder feeder speed	8 rpm
Powder feeder gas flow	105 slm

Parameter	Value
Standoff distance	25 mm
Spray angle	90°
Nozzle traverse speed	250mm/s
Nozzle step distance	0.25 mm
Target coating thickness	0.508 mm
Powder	WIP – C1
Bond coat powder	WIP – BC1 și 60°

The powder mixture is known commercially as WIP-C1, the appearance of the powder is shown in Figure 3. Before the surface was coated with the WIP-C1 powder, a thin layer of WIP-BC1 bonding powder was applied to the surface (see Figure 4) with a nozzle orientation of 60 degrees. The WIP-C1 powder is a chromium carbide with the composition Cr-31Ni-3C, whose composition is: 0.02%Co, 68.45%Cr, 0.08%Fe, 27.84%Ni, 0.01%W, 0.06%Al, 0.04%B, 0.01%Mo, 0.43%Si, 0.01%V, 3.00%C [16].

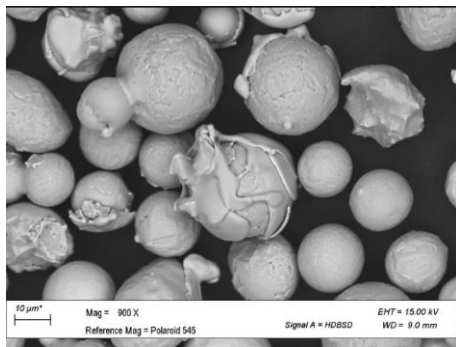


Fig. 3. WIP-C1 powder particles aspect (900x) [17]

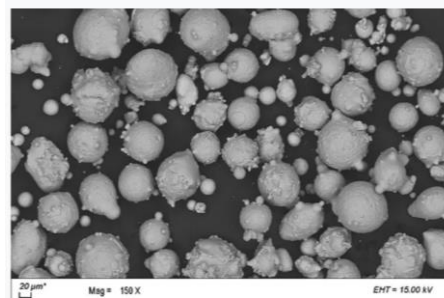


Fig. 4. WIP-BC1 powder particles aspect (150x) [18]

For the analysis of the coatings morphology, the conventional analysis methods were used: direct observation, optical and electron microscopy, supplemented by elemental chemical analysis using the EDS method. Two working modes were used for electron microscopy image acquisition: Low Vacuum mode, with LFD (Large Field Detector) detector at 20kV and High Vacuum mode, with ETH (Everhart–Thornley) detector at 30kV.

The morphology of the coatings has been analysed both in cross-section, longitudinally (on the surface) and in fracture, with all approaches aimed at providing a complete picture of the deposited layer structure.

3. Results and discussions

3.1. Coatings produced by atmospheric plasma spray (APS)

Figure 5 shows the morphology of the component particles of the analysed powder: most of them have an irregular, polygonal appearance, with visible porosity and

sizes between 40 - 140 μm , and the others have a spheroidal appearance with medium sizes (60 - 80 μm). The chemical composition of each of the two types of particles shown in Figure 6 reveals that the polygonal particles have a high percentage of Cr in their chemical composition, while the spheroidal particles have higher percentages of Ni and Cr, and the presence of Si, but not oxygen, is also reported.

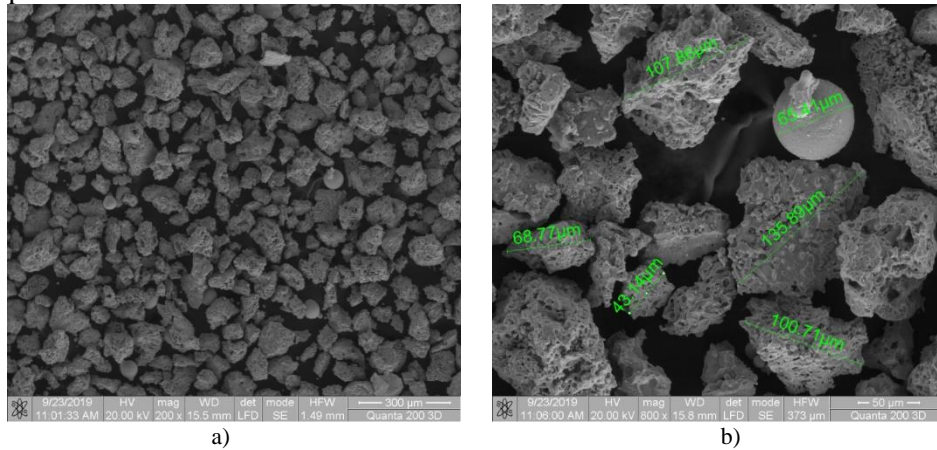


Fig. 5. SEM images of Cr_2C_3 - Ni20Cr powder, at different magnifications: a) 200x; b) 800x.

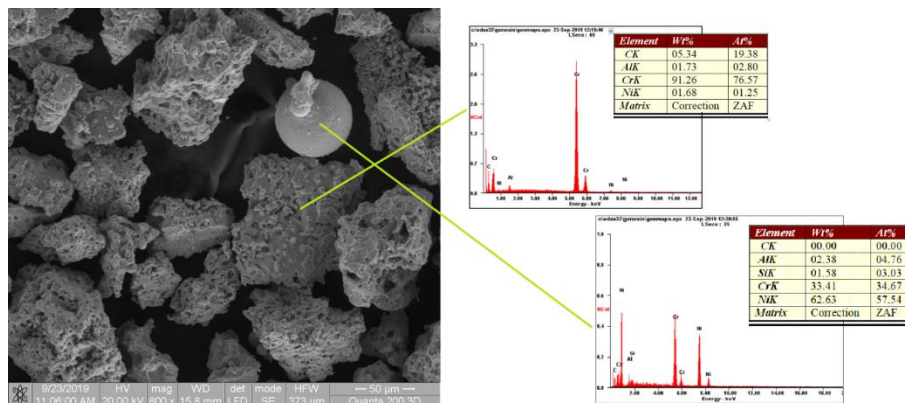


Fig. 6. Chemical elemental EDS point analysis performed on two Cr_2C_3 - Ni20Cr powder component particles.

X-ray diffraction analysis revealed two main component phases of the powder used: a chromium carbide crystallized in the orthorhombic system (Cr_3C_2) and an intermetallic compound formed between Ni and Cr crystallized in the cubic system (CrNi_3), as shown in Figure 7.

Figure 8 shows the surface morphology obtained by thermal plasma spraying of 81NS powder with Cr_2C_3 - Ni20Cr composition.

The layered lamellar structure is observed, formed by the successive deposition of accelerated splats towards the substrate, a structure specific to coatings made by thermal plasma deposition [19]. Some semi-molten particles, some particle

agglomerations and a partially porous appearance with deeper areas at the boundaries of some splats are also visible on the surface.

Figure 9 shows the X-ray diffractogram of the coating made by thermal plasma spraying. Analysing the component phases of the deposited coating compared to those present in the powder used (Table 3), the formation of C_3Cr_7 carbide is detected following the deposition process, a phase that increases the hardness of the coating, together with the carbide already present.

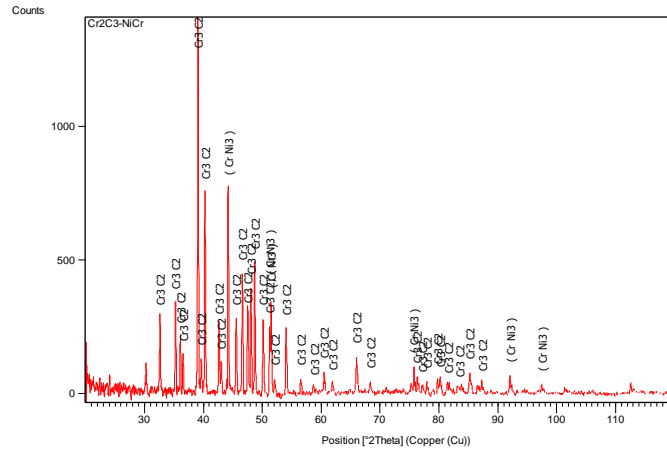


Fig. 7. X-ray diffractogram of Cr_2C_3 - Ni20Cr powder (component phases).

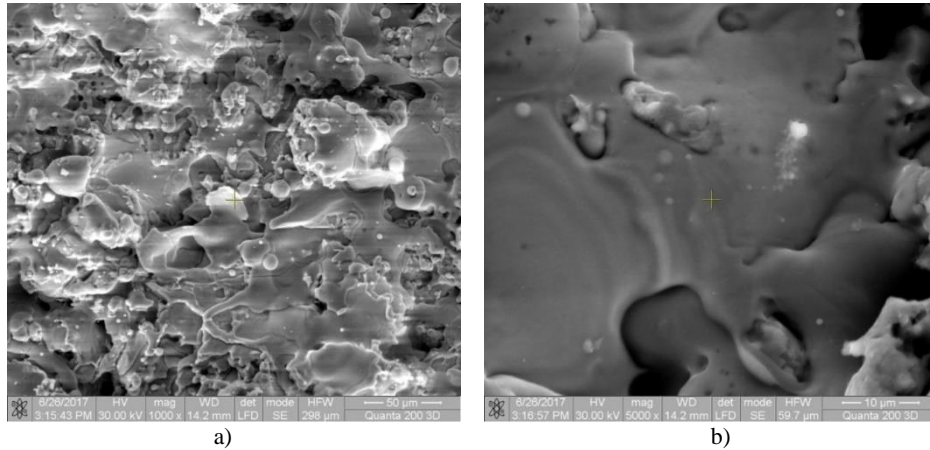


Fig. 8. SEM images of the coating at different magnification powers: a) 1000x; b) 5000x [12].

The presence of the sigma - Cr_7Ni_3 intermetallic phase [20], which is usually formed in the transition metal alloys, especially in Fe - Cr systems [21], in a wide variety of compositions and morphologies, is also observed. It is reported in the scientific literature that, due to the intermetallic tetragonal closed-packed phase (tcp) packing mode, the presence of this phase is unfavorable to the properties of the alloys in which it forms [22].

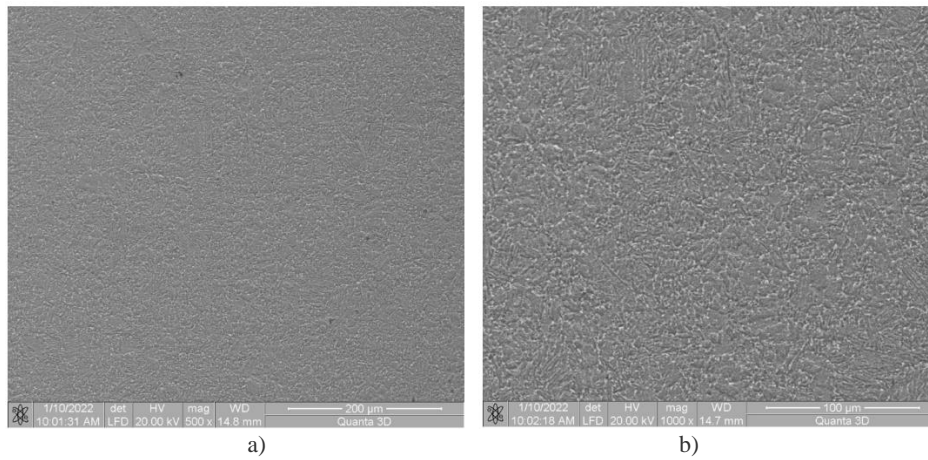


Fig. 10. SEM images of AISI 4340 steel substrate cross-section: a) 500x, b) 1000x.

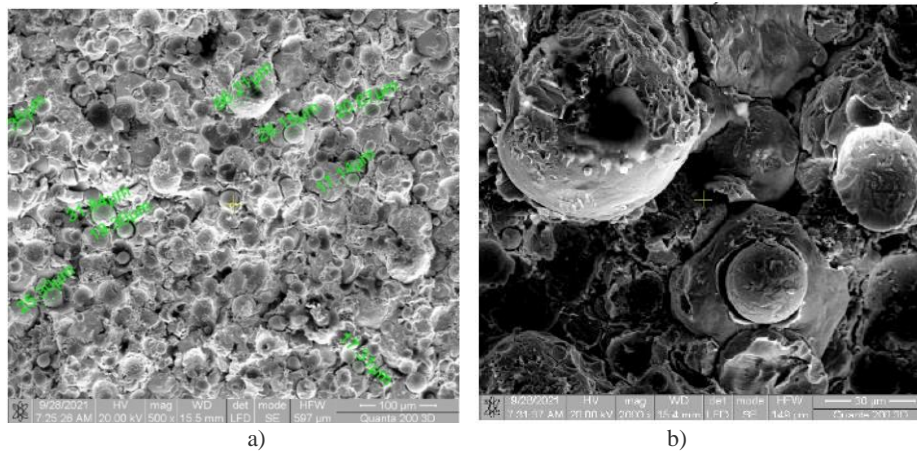


Fig. 11. SEM images on the surface of a deposited layer of WIP-C1: a) 500x, b) 2000x.

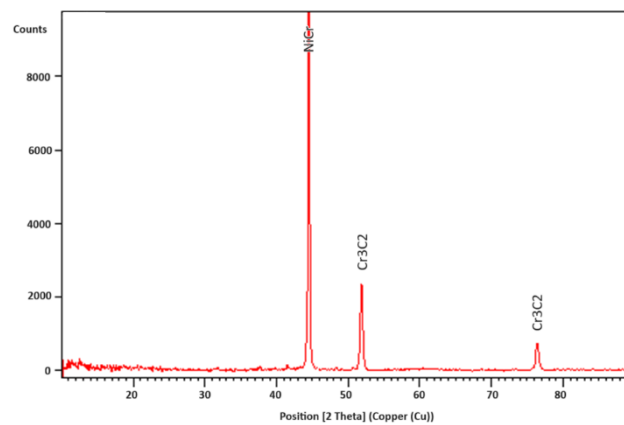


Fig. 12. X-ray diffractogram of Cold Spray deposited coating.

Figure 13 shows secondary electron images taken in several areas on the surface of the investigated samples. An irregular appearance specific to Cold Spray coatings is observed, which is due to the successive deposition of pulverized particles, which either kept their shape due to their high specific hardness (case of chromium carbide particles) or were highly deformed creating an embedding layer of the previous ones (case of Ni-based particles). With increasing magnification power, the plastically deformed matrix and the undeformed spheres are more and more clearly observed, which together generate the roughness of the coating surface.

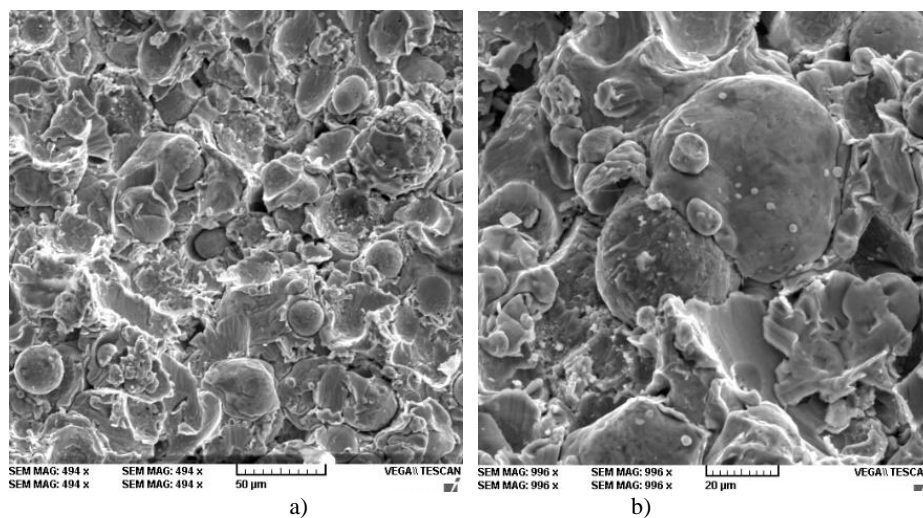


Fig. 13. SEM images of the coating surface: a) 500x, b) 1000x.

The distribution map of the chemical elements on the coating surface (Figure 14) shows a uniform distribution of the elements, i.e. the pulverized particles that formed the coating. The resulting mass values show a high percentage of the Ni element, a plausible result because chromium carbide particles being mostly spherical are not stable unless fixed in the Ni-based matrix.

Also, although traces of oxygen were found in the EDS analysis, its presence is not confirmed by XRD analysis, the conclusion is that the surface has been contaminated following metallographic preparation for the tests performed in the study.

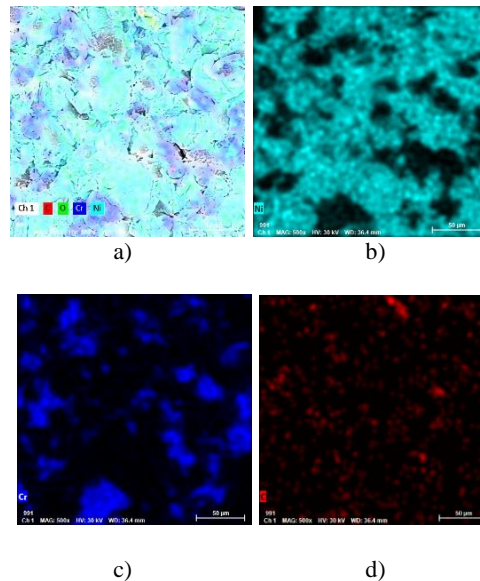


Fig. 14. Chemical element distribution map on the coating cross-section from Figure 12 a) overlapping distribution of C, O, Cr, Ni, b) Ni distribution; c) Cr distribution; d) C distribution.

4. Conclusions

Thermal spraying is a versatile process, both in terms of the sprayed material, which can be almost any, but also in terms of applications, as it is the way to create a new functional coating on a substrate or on a component part of an assembly, with the role of protection or performance improvement.

The technologies grouped under this term are mainly classified according to the temperature of the process - from temperatures below 1000°C (Cold Spray process) to temperatures above 15000°C (Plasma processes), but also according to the acceleration speed of the sprayed particles - from speeds of about 40m/s (Flame Spray process) to supersonic speeds above 1000 m/s (Cold Spray process).

Two types of coatings produced from similar Ni and Cr-based powders by the plasma jet and Cold Spray processes were studied. It was observed that, in terms of phase transformations and chemical composition, the largest transformations occurred in the case of plasma deposition, due to the high process temperatures that generated new carbide-type phases, metastable intermetallic phases and simple and complex oxides of the basic component elements.

Another observation is related to the morphology of the coatings, which differs significantly, in the case of plasma jet coating being of a layered lamellar type (due to total or partial melting of the sprayed particles), compared to the one obtained after the Cold Spray process where the particles either kept their shape due to their high specific hardness (Cr_3C_2), or deformed a lot creating an embedding layer of the previous ones (case of NiCr particles).

Both technologies have produced uniform, continuous coatings that can significantly improve the wear resistance of the substrates on which they have been deposited to replace hard chromium plating layers, the choice of one of them being dictated by the surface geometry, the degree of permitted oxidation (much higher in the case of APS), the required thickness (much higher in the case of CS), and the economic factor that currently disadvantages the younger CS technology.

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