Influence of the Stand-off Distance and of the Layers Thickness on the Adhesion and Porosity of the 97MXC Deposits Obtained by Arc Spraying Process

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Abstract. In this paper, the surfaces of some weakly alloyed steel specimens were covered, by arc spraying process, with a layer of high alloyed steel: 97MXC, using core wires. The technological parameters, used to spray the high alloy steel, were kept constant except for the spray stand-off distance (SOD) which varied on three levels. The research was performed on deposits with a thickness between 0.2-2.4 mm. The microstructure of the deposits, the chemical composition, the physical properties of the layers were investigated by SEM analyzes, X-ray diffraction, microhardness tests and adhesion tests. The porosity of the deposits was determined by optical microscopy. The adhesion of the layer to the substrate was researched by the tensile test. Studies have shown the fact that SOD significantly influences the adhesion and porosity of the deposits. Thus, the increase of SOD determines the decrease of the adhesion of the layer to the substrate by approximately 21.4%, the increase of the porosity of the deposits by approximately 14.2% and variations up to 5% of the microhardness.

1. Introduction

The versatility and economic efficiency of the arc spray process (ASP) make it often to be used in obtaining surfaces with new physical and mechanical properties, or in restoring the surfaces of used parts [1-4].

In the ASP, the raw material - in the form of wire, is melted in the electric arc developed at the contact between the tops of the wires [5-7]. A jet of compressed air divides the drop formed into fine particles, which it projects onto the surface of a substrate, [8-12]. The sprayed particles collide with the surface of the substrate and flatten on it [13-17], finally resulting in a layer that presents a lamellar structure and contains various chemical compounds, oxides, pores or unmelted particles [18-23]. It is known that the physical, chemical and mechanical properties of the deposits are strongly influenced both by the intrinsic properties of the addition material [24-27] and by the technological parameters of the ASP, [28, 29]. The latter are defined as being the sum of the parameters that directly or indirectly influence the melting process, the flight characteristics (speed, temperature and particle size) [30] and the kinematic spraying parameters, that influence the process of layer formation. The spraying distance, generically defined spray stand-off distance (SOD) - represents the distance between the nozzle of the spray device and the surface of the substrate [31-34]. It belongs to the category of kinematic parameters that dictate the state of the particles before impact, the heat and mass transfer at the substrate surface being specified to each sprayed material [35-38].
The purpose of this study is the influence of the spray stand-off distance and the thickness of the deposits on the physical-mechanical characteristics of the 97MXC layer obtained by arc spray process.

2. Experimental procedure

2.1. Materials and equipment

Substrates made of low alloy steel C15 –EN10083, with dimensions of 40x40x10 were covered by ASP using the 97MXC filler material - in the form of cored wires, a product of the company Praxair-Tafa, USA. The chemical composition of the sample material, as well as that of the additive material are presented in Table 1.

Table 1. Chemical composition of the materials used.

| Materials | Elements (wt%) |
|-----------|----------------|
|           | C  | Si  | Cr  | Ni  | Mn  | B  | WC | TiC | Fe  | P  | S  |
| C15       | 0.14 | 0.15 | 0.3 | 0.3 | 0.43 | -  | -  | -   | 0.04 | 0.04 |    |
| 97MXC     | -   | 1.25 | 14.0 | 4.5 | 0.55 | 1.87 | 26.0 | 6.0  | balance | -  | -  |

For the carrying out the deposits, we used a Tafa CoArc System electric spray installation (manufactured by Praxair-Tafa, USA), equipped with a 9935-spraying gun, before spraying.

Before deposits carrying out, the surface of the samples was cleaned by sandblasting using alumina powders (alumina Al₂O₃) with an average diameter of 536 ± 24μm, sprayed with the pressure of 4 bar at the distance of 30 mm. To remove residues left on the surface, the specimens were ultrasonically cleaned by immersion in an ethanol bath (C₂H₆O) for 10 minutes and dried under compressed air. All the samples examined were deposited at a constant speed, at the same value of pressure and current intensity.

Table 2. Technical parameters of magnetron sputtering.

| Parameters                  | Value       |
|-----------------------------|-------------|
| Current intensity (A)       | 220         |
| Voltage (U)                 | 32          |
| Air pressure (bar)          | 6.0         |
| Movement speed of the gun (m/s) | 0.14       |
| Coating thickness (mm)      | 0.53/1.24/2.22 |
| Stand-off distance (mm)     | 100/125/150 |
| Spray angle                 | 90⁰         |

During the experiments the spray distance varied on three levels. In Table 2 are presented the parameters of the arc spraying.

2.2. Deposits characterization

The investigations on the qualitative elemental chemical analysis and on the morphology of the 97MXC layers were performed using the scanning electron microscope (SEM): FEI - Quanta 200 SEM-EGF. The crystalline spectra of the deposits were highlighted by X-ray diffraction, using X-ray diffractometer - type XPERT PRO MRD made by PANalytical Holland, using Cu Ka radiation (λ = 0.15406 nm), with an emission current of 40mA and acceleration voltages of 40kV. The tensile test of the flat samples was used to determine the adhesion of the layer to the substrate, in accordance with EN 582. With the help of the CV Instruments 400 DM micro-hardness tester - by using a load of 300g for 10s, we determined the Vickers micro hardness of the deposits. We performed a number of 15 investigations in the cross section of the layers and reported the average values of the measurements. With the help of the micrometre we determined the deposits thickness and we reported its average values - obtained after performing a number of 5 determinations on the surface of each sample. The
layers porosity was determined in the cross section of the test samples, by image analysis, using the IQ Materials program (Japan).

3. Results and discussions
Microstructures of the 97MXC deposits - made by thermal spraying in electric arc, at different values of the spraying distance, are presented in Figure 1. It is observed that the deposits obtained at short SOD presents a homogeneous structure, the tungsten and titanium carbides are evenly distributed and they are well anchored in the metal matrix.

Figure 1. SEM micrographs showing the cross-section of 97MXC deposits obtained at p = 6.0 bar, I = 220 A and under the following conditions: (a) SOD = 100 mm; (b) SOD = 150 mm.

By increasing the spraying distance, the structure of the deposits becomes inhomogeneous and in the structure of the deposits appear particles of unmelted material. The electric arc formed at the contact between the electrodes melts, by Joule Lentz effect, the metallic material outside the wires and the powder inside it. The jet of compressed air sprays the particles on the surface of the substrate interacting with the outer surface of the particles. Their flight time and implicitly the contact time between the particles and the jet of compressed air, is shorter when the SOD is shorter, reason for which the particles arrive on the layer surface in a liquid phase.

Figure 2. Variation of the porosity of the 97MXC layers with the SOD.
The increase of SOD determines the increase of the flight time of the metallic particles, respectively of the particle-compressed air interaction time, reason for which the particles reach the value of the solidification temperature and reach the surface of the substrate in solid, semi-molten or molten state.

The variation of the porosity of the 97MXC deposits with the spray distance (SOD) is presented in Figure 2. It can be seen that denser coatings are obtained when the spray distance is shorter. The increase by up to 14.2% of the porosity of the 97MXC deposits obtained at SOD = 150mm, the presence of less flattened (thick) lamellae and of unmelted particles inside the deposition presents a clear proof of the fact that at high SOD, the pulverized particles cool and reach the surface of the substrate in a predominantly solid state.

X-Ray diffraction investigations carried out on 97MXC layers, deposited by ASP in demonstrate that their structure consists of hard compounds such as WC and TiC, ferroborides, ferrite alloyed with Ti or ferrite alloyed with tungsten (FeW) or titanium alloy ferrite, as well as complex compounds of the type FeNiCrW, FeNiCrTi - ferrite alloyed with Ti or ferrite alloyed with tungsten (FeW) or titanium alloy ferrite, as well as complex compounds of the type FeNiCrW, FeNiCrTi - independent of the SOD, reason for which only one was exposed - Figure 3.

Thus, the solidification mechanism is complex, depending on the concentration and the number of component elements of the filler material. During the flight, inside the pulverized particles diffusion phenomena appear. Some of the dissolved tungsten and titanium is alloying with carbon, forming WC or TiC - an aspect which is in concordance with the reports of Tillman et al. [35]. As the temperature decreases, in the layer are formed substitution solid solutions as type of ferrite alloyed with tungsten or ferrite alloyed with titanium.

In Figure 4 is presented the variation of the HV micro hardness of the 97 MXC deposit with SOD. It is remarked that the HV microhardness decreases with the increasing of SOD value, due to both the phenomenon of rapid solidification of particles before hitting the surface of the substrate and the inhomogeneous and porous structure of the deposit.

The variation of the deposition adhesion of 97MXC with the layer thickness, for the three considered values of the spraying distance is presented in Figure 5. It is observed that the adhesion of the carried-out deposits decreases with the spraying distance, on average by 21.4%. This aspect is due to the existence of pores, the high speed of the particles when the spraying distance is small, as well as the presence of solidified particles in the layer. The increasing of the deposits thickness determines the adhesion decreasing, on average by up to 11.5%.
Figure 4. The effect of SOD on the microhardness of 97MXC coatings obtained by ASP.

This aspect is due to the fact that the adhesion of 97MXC deposits - obtained by the electric ASP with two wires, is mainly mechanical and the presence of hard carbides and complex solid solutions stiffens it - detailed aspect by Haraga et colab., [17].

Figure 5. Variation of adhesion of 97MXC coatings with deposits thickness and SOD.

It can be suggested that by reducing the spraying distance the particles speed is high, the particles are in a liquid state, collide the substrate and fix in its asperities - aspect in concordance with the reports of Toma et colab. [9].

4. Conclusion and perspectives
The study performed on the influence of the spraying distance (SOD) and of the thickness of the deposits on the physical-mechanical properties of the 97MXC deposits, obtained by arc thermal spraying highlights the following aspects:
− at small values of the spray distance, uniform, homogeneous deposits are obtained in which the carbides are uniformly embedded in the metal matrix. The deposits obtained at higher values of the spraying distance (SOD) have inhomogeneous structures, present unmelted pores and particles and the tungsten and titanium carbides are unevenly distributed inside the layer - see Figure 1. Regardless of
the SOD value, the layers contain ferrite alloyed with W or Ti, WC, CTi, complex compounds such as FeNiCrW, FeNiCrTi:
- the porosity of the deposits increases by approximately 14.2%, when the SOD increases from the value of 100mm to the value of 150mm - see Figure 2. Increasing the porosity of 97MXC deposits has a negative effect both on the micro hardness - see Figure 4 and on the adhesion of the layer to the substrate - see Figure 5;
- the presence of hard carbides in the layer influences its elastic properties, which is why the increase in the thickness of the deposits determines the decreasing of the layer adhesion to the substrate.

All these aspects suggest the fact that in the moment of increases the spraying distance, the interaction time between the compressed air jet and the molten particles increases, the latter cool intensely and hit the substrate surface in a predominantly solid or semi-molten state having negative effects on mechanical properties.

5. References

[1] Sacriste D, Goubot N, Dhers J, Ducos M and Vardelle A 2001 J. Therm. Spray Technol. 352 35-358
[2] Pawlowski L 2008 in: 2nd ed., The Science and Engineering of Thermal Spray Coatings, Ed. Wiley, Chichester, England
[3] Toma B F, Baciu R E, Bejinariu C, Cimpoieșu N, Ciuntu B M, Toma S L, Burduhos-Nergis D P and Timofte D 2018 IOP Conf. Series: Mat. Science and Engineering 374 012017
[4] Cazac A M, Bejinariu C, Ionita I, Toma S L and Rodu C 2014 Applied Mechanics and Materials 657 193-197
[5] Tillmann W, Walther F, Luo W F, Haack M, Nellesen J and Knyazeva M 2018 J. of Therm. Spray Technol. 27 50-58
[6] Popovici R, Scripcariu I S, Himiniuc I, Murarasu M and Grigore M 2019 Med. Surg. J.-Rev. Med. Chir. Soc. Med. Nat. 123(1) 97-101
[7] Irimiciuc S A, Agop M, Nica P, Gurlui S, Mihaleanu D, Toma S and Focsa C 2014 Japanese Journal Of Applied Physics 53(11) 173-179
[8] Panadda S and Hathaipat K 2014 Wear 317 194–200
[9] Toma S L 2013 Surf & Coat. Technol. 220 261–265
[10] Timovasanu M, Onofriescu M, Timovusan V, Timovusan V, Ciuntu B M, Timofte V, Himiniuc L and Toma B 2020 Med. Surg. J.-Rev. Med. Chir. Soc. Med. Nat. 124(1)107-112
[11] Matz M M, Aumiller M P 2014 Journ. of Thermal Spray Technology 23(8) 1470-1477
[12] Bloch K, Titu M A and Sandu A V 2017 Rev. de Chimie 68 2162-2165
[13] Guilemany J M, de Paco J M, Nutting J and Miguel J R 1999 Metall. Mater. Trans. A 30 1913
[14] Cazac A M, Bejinariu C, Baciuc C, Toma S L and Florea C D 2014 Applied Mechanics and Materials 657 137-141
[15] Tugui C A, Vizureanu P, Perju M C, Savin C, Nejneru C, Baltatu S M, Bejinariu C and Benchea M 2018 IOP Conference Series-Materials Science And Engineering 374 012029
[16] Toma S L, Bejinariu C, Eva L, Sandu I G and Toma B F 2015 Key Engineering Materials 660 86-92
[17] Haraga R A, Bejinariu C, Cazac A, Toma B F, Baciuc C and Toma S L 2019 IOP Conference Series: Materials Science and Engineering 572 012056
[18] Arif Z U, Shah M, Rehman E and Tariq A 2020 International Journal of Advanced and Applied Sciences 7(7) 25-39
[19] Tănase A E, Toma B, Himiniuc L, Petrica M, Hutanu D and Onofriescu M 2020 Med. Surg. J. Rev. Med. Chir. Soc. Med. Nat. 124 (1) 86-93
[20] Baltatu M S, Tugui C A, Perju M C, Benchea M, Spataru M C, Sandu A V and Vizureanu P 2019 Rev. Chim 70(4) 1302
[21] Li S, Wang Y, Xiang D et al 2016 Rare Metal Materials And Eng. 45 2555-2560
[22] Nanu C, Poeata I, Popescu C, Eva L, Toma B F and Toma S L 2018 Materiale Plastice 55 85-90
[23] Berger L M, Saaro S, Naumann T, Wiener M, Weihnacht V, Thiele S and Suchánek J 2008 Surf. Coat. Technol. 202 4417
[24] Nurisna Z T, Muhayat N and Wijayanta A T 2016 Book Series AIP Conference Proceedings 1717 040012
[25] Toma S L, Badescu M, Ionita I, Ciocoiu M and Eva L 2014 Applied Mechanics and Materials 657 296-300
[26] Nedeff V, Mosnegutu E, Panainte M, Ristea M, Toma S and Agop M 2012 Powder Technology 221 312–317
[27] Calin M A, Curtea A, Toma S and Agop M 2013 Metalurgia International 18 19-22
[28] Toma S L, Bejinariu C, Gheorghiu D A and Baciu C 2013 Advanced Materials Research 814 173-179
[29] Sroka M, Nabialek M, Szota M et al 2017 Revista de Chimie 68 737-741
[30] Tillmann W, Hagen L and Kokalj D 2017 Journal of Thermal Spray Technology 26 1685-1700
[31] Katranidis V, Kamnis S, Allcock B and Gu S 2019 J Therm Spray Tech 28 514–534
[32] Masoumeh G, Shahrooz S, Mahmood G and Ahmad S E 2018 J. Theor Appl Phys 12 85–91
[33] Tanase A E, Tibeica A, Tanase G V, Toma B, Nhambasora F, Nemescu D and Onofriescu M 2018 Filodiritto Publisher 799-803
[34] Przybyl A, Wnuk I and Wyslocki J J 2019 Rev. Chim. 70(11) 4086-4088
[35] Nejneru C, Cimpoesu N, Stanciu S, Vizureanu P and Sandu AV 2009 Metalurgia international 14(7) 95-98
[36] Burduhos-Nergis D -P, Vizureanu P, Sandu A V and Bejinariu C 2020 Applied Sciences 10(8) 2753 doi:10.3390/app10082753
[37] Achitei DC, Vizureanu P, Minciuna MG, Sandu AV, Buzaiianu A and Dana DI 2015 Materiale Plastice 52(2) 165-167
[38] Tillmann W and Abdulgader 2012 Journal of Thermal Spray Technology 22 352-362