Influence of the thickness of the Tungsten Carbide (WC) coating deposited on martensitic stainless steel on corrosion resistance

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Abstract. On the martensitic non-corrosive steel support (Z12CNDV12) it is deposited by plasma jet, tungsten carbide, in three different thicknesses. We determined the electrochemical potential of both the coating layer and the substrate for different concentrations of NaCl in a solution. The experimental results are mathematically processed. From each protective coating a 1, 2 and 3 degree polynomial fit were obtained. Also, the comparison between the three obtained thicknesses mathematical function is realized.

1. Introduction
As a replacement of hard chrome plating, thermal-sprayed WC (tungsten carbide) based cermet coatings have been widely used in several industries, such as aerospace, automobile and energy, due to their excellent performance of wear resistance [1–3]. The hard WC particles in the coatings provide hardness and wear resistance while the metal binder (CoCr, NiCr, Ni, Co, etc.) gives the necessary coating toughness [4].

Transition metal carbides such as WC present high interest because of their specific physical and mechanical properties [5]. Tungsten carbide has high melting point and exhibits extreme hardness, low friction coefficient, chemical inertness, oxidation resistance, and good electrical conductivity [5–10].

Tungsten carbide-cobalt (WC-Co) based materials are used extensively in the industry in their sintered as well as thermal sprayed forms for applications requiring abrasion, sliding, fretting, and erosion resistance. The hard WC particles form the major wear-resistant constituent of these materials, while the cobalt binder provides toughness and cohesion. Properties such as hardness, wear resistance, and strength has been influenced primarily by the WC grain size and volume fraction and, with thermally sprayed coatings, also by varying the porosity and (often unintentionally) the carbide and binder phase composition [11], [12].

As the WC-based cermet coatings have been widely used, it is realized that the corrosion resistance becomes increasingly important besides wear resistance because the potential service environments for these WC-based cermet coated components are inherently corrosive in nature.

However, the corrosion resistance of WC-based cermet coatings is not so desirable [13]. In recent years, optimization of processing parameters and incorporating anti-corrosive materials have been tried to improve the corrosion resistance. References [13], [14] reported that minimization or partial elimination of intrinsic defects, such as porosities, microcracks and oxide phase by optimization of processing parameters, helped to improve the corrosion resistance.
The considerations that led to the study of the corrosion resistance in a sodium chloride environment of tungsten carbide achieved by plasma jet spraying on a martensitic stainless steel substrate in sodium chloride environment by potentiostatic methods.

2. Experimental considerations in performing plasma jet coatings

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

| Chemical composition | C  | Si | Mn | S  | P  | Cr | Ni  | Mo | V  | N  |
|----------------------|----|----|----|----|----|----|-----|----|----|----|
|                      | 0.06 | ≤   | 0.50 | ≤  | 11.0 | 2.00 | 1.50 | 0.25 | 0.02 |
|                      | 0.15 | 0.35 | 0.90 | 0.025 | 0.035 | 12.5 | 3.00 | 2.00 | 0.40 | 0.04 |

Before performing 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 with aluminium oxide particles.

The pulverisation of coatings on substrate prepared in this way was done almost immediately in order to avoid the impurification of surfaces, which can affect the adhesion between coat and substrate.

The technical conditions of performing the coatings as well as the values of the main parameters of processing are presented below:

- Equipment used: METCO 7MB;
- Ceramic powder: WC – 87 %, Co – 17 %, tip METCO 73;
- Size of particles: 10 – 45μm;
- Parameters of spraying gun:
  - Current: 800 A;
  - Voltage: 44-55 V;
  - Spraying rate: 2.7 kg/h.
- Parameters of plasma gas:
  - Primary gas (Ar):
    - Pressure (MPa): 0.620;
    - Volume (m³): 4.53;
  - Secondary gas (He):
    - Pressure (MPa): 0.620;
    - Volume (m³): 0.566.

3. The determination of the corrosion resistance and the interpretation of the experimental results

The determination of the corrosion resistance of the coating layer performed by METCO 73 dust was made by potentiostatic methods, in sodium chloride solutions of various concentrations.

The electrochemical potential of the coat and of the substrate was determined versus an electrode of reference of calomel, in solutions of sodium chloride of various concentrations. The difference between the electrochemical potential of the coat and of the substrate is a measure of the degree of protection, which the coat achieves for the substrate. The greater the difference, the better the coat protects the metallic substrate.

The determinations were made for three different values of thickness of the coat (0.05 mm, 0.10 mm, 0.25 mm) and different concentrations of the solution of sodium chloride.

The experimental results are given in Table 2.

It may be noted that the electrochemical potential of the coat is bigger than that of the substrate, which leads us to the conclusion that an anodic protection takes place. The experimental results were processed in Matlab.
In the beginning the processing of data for each thickness of coat was made, and interpolation curves of order 1, 2 and 3 were obtained. The graphic representation is given in Figures 1–3.

All the measurement was made at a temperature of 20 °C. The results of the mathematical processing are given in Table 3.

In Table 3 on can notice that in cubic interpolation, for all the values of thickness of the coat, we have the highest coefficient of correlation and the lowest medium square diversion.

**Table 2. The variation of the difference of the electrochemical potential**

| The concentration of sodium chloride solution [%wt] | The thickness of the coat | 0.05 mm | 0.10 mm | 0.25 mm |
|---------------------------------------------------|--------------------------|---------|---------|---------|
| 1                                                 | 28                       | 253     | 365     |
| 2                                                 | 23                       | 225     | 245     |
| 3                                                 | 12                       | 210     | 333     |
| 4                                                 | 12                       | 195     | 328     |
| 5                                                 | 11                       | 185     | 305     |
| 6                                                 | 10                       | 184     | 295     |
| 7                                                 | 9                        | 183     | 290     |
| 8                                                 | 8                        | 184     | 245     |
| 9                                                 | 8                        | 183     | 255     |
| 10                                                | 7                        | 183     | 245     |
| 11                                                | 7                        | 183     | 240     |
| 12                                                | 8                        | 183     | 230     |
| 13                                                | 7                        | 183     | 228     |
| 14                                                | 5                        | 183     | 222     |
| 15                                                | 5                        | 180     | 220     |

**Figure 1.** Cubic interpolation for 0.05mm thickness of coat
Figure 2. Cubic interpolation for 0,10mm thickness of coat

Figure 3. Cubic interpolation for 0,25 mm thickness of coat

Table 3. The results of the mathematical interpolation

| Thickness of coat, [mm] | Interpolation | The relationship of dependence: difference of potential (y) [mV] and the concentration of NaCl solution (x), [%] | Coefficient of correlation r | Medium square diversion |
|------------------------|---------------|-------------------------------------------------------------------------------------------------|-----------------------------|-------------------------|
| 0,05                   | Linear        | y = -1,175x+20,07                                                                                  | 0,8127                      | 3,64                    |
|                        | Parabolic     | y = 0,1649 x^2 -3,814 x +27,54                                                                     | 0,9231                      | 2,402                   |
|                        | Cubic         | y = -0,03146x^3 +0,9201x^2 -8, 804x+36,25                                                        | 0,9742                      | 1,411                   |
| 0,10                   | Linear        | y =-3,468x +22,13                                                                                  | 0,7545                      | 13,03                   |
|                        | Parabolic     | y =0,6707x^2-14, 2x+251,7                                                                        | 0,9397                      | 6,794                   |
|                        | Cubic         | y =-0,1052x^3+3,196x^2–30.89x+277,5                                                              | 0,9951                      | 1,969                   |
| 0,25                   | Linear        | y =-10,71x+362,1                                                                                  | 0,97                        | 11,6                    |
|                        | Parabolic     | y =0,5449x^2-19, 43x+386,8                                                                        | 0,9883                      | 7,274                   |
|                        | Cubic         | y =0,04033x^3-0, 4229x^2-3,04x+376,9                                                              | 0,9897                      | 6,834                   |
Medium square diversions in the regression curves obtained were calculated by means of the formulas given:

- for linear interpolation:

\[ s = s_1 = \sqrt{\frac{1}{15} \sum_{i=1}^{15} (y_i - ax_i - b)^2} \]  

(1)

- for parabolic interpolation:

\[ s = s_2 = \sqrt{\frac{1}{15} \sum_{i=1}^{15} (y_i - ax_i^2 - bx_i - c)^2} \]  

(2)

- for cubic interpolation:

\[ s = s_3 = \sqrt{\frac{1}{15} \sum_{i=1}^{15} (y_i - ax_i^3 - bx_i^2 - cx_i - d)^2} \]  

(3)

where a, b, c and d are the coefficients in the regression equations obtained, and \( y_i \) and \( x_i \) are pairs of values of the difference of potential between the coat and the metallic substrate and the concentration of NaCl solution. Figures 4, 5 and 6 render a superposition of the three interpolation graphs for three different values of thickness of coat.

**Figure 4.** The comparison of the linear interpolation with the three values of thickness of the coat

**Figure 5.** The comparison of the parabolic interpolation with the three values of thickness of the coat
It may be seen that, the bigger the thickness of the coat, the difference of electrochemical potential between the coat and substrate and consequently, the protection is better.

4. Conclusions
The corrosion resistance was determined for the layers of coating performed with powder Metco 73 by spraying on a martensitic stainless steel substrate, by means of potentiostatic methods. The main conclusions of this study are outlined below:

- 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 biggest difference of electrochemical potential is met in very small concentrations of NaCl solutions. With the increase of the concentration, the difference of potential decreases. Hence, the best protection is achieved in small concentrations of NaCl solutions;
- For all values of the coat thickness, the highest coefficient of correlation and the lowest medium square diversion are in a cubic interpolation;
- In a cubic interpolation with the coat thickness of 0,10 mm a correlation coefficient of 0,9951 was obtained, which made us choose this coat thickness for further research.

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