Mathematical modelling in Matlab of the experimental results shows the electrochemical potential difference - temperature of the WC coatings immersed in a NaCl solution

M L Benea¹ and O D Benea²

¹Politehnica University of Timisoara, Department of Engineering and Management, Hunedoara, Romania
²The National Institute of Applied Sciences: Department of Informatics, Lyon, France
E-mail: laura.benea@fih.upt.ro

Abstract. The method used for purchasing the corrosion behaviour the WC coatings deposited by plasma spraying, on a martensitic stainless steel substrate consists in measuring the electrochemical potential of the coating, respectively that of the substrate, immersed in a NaCl solution as corrosive agent. The mathematical processing of the obtained experimental results in Matlab allowed us to make some correlations between the electrochemical potential of the coating and the solution temperature is very well described by some curves having equations obtained by interpolation order 4.

1. Introduction
The simplest way of an interpolation consists in knowing the points \{x_i\} \in [a, b], i=1, 2, ..., n, called the interpolation points and the points \{y_i\} \in [a, b], i=1, 2, ..., n, given by an interpolation function F(x) that belongs to a known class that needs to satisfy the relations F(x_i)=y_i, i=1, 2, ..., n. In this case, for a value \xi \neq x_i, i=1, 2, ..., n, we can determine the value \eta=F(\xi). If \xi \epsilon [a, b] the problem is called interpolation [1].

The mathematic interpolation can also be used with success for the interpolation of experimental data. In this case we used the data gathered using the potentiostatic method for the electrochemical resistance of the coating formed in plasma [2], [3].

Our preoccupations to find a parameter to reflect in a sensitive and easy to quantify way the corrosive action of the corrosion agent upon the coating led to the electrochemical potentials of the substrate and the coating immersed into the NaCl solution. Generally, in order to ensure the anti-corrosive action, there are preferred the coating/substrate couples in which the electrochemical potential of the coating is higher than that of the substrate [4].

The WC – Co coatings are designed to protect machines parts (roll cylinders, turbine shuffles, parts of diesel engines) during the combined wear and chemical corrosion stresses [5-7].
2. Experimental part

2.1. Experimental condition at the WC coatings spraying in plasma

The coated metallic substrate is the martensitic stainless steel Z12CNDV12. Before being coated, the surface of the substrate has been prepared by sanding with corundum powder.

The coatings have been made using a Metco 7MB equipment. The powder used is Metco 73, with 83% WC and 17% Co and particle size between 10 and 45 μm.

There have been working 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;
- coating thickness: 0.10 mm

2.2. 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 1 and 15%, at temperatures between 20 and 48˚C. In each case there has been determined the electrochemical potential of the coating and substrate, using as reference electrode the calomel electrode.

The difference between the electrochemical potential of the coating and that of the substrate represents a measure of the protection degree the coating provides. The greater this difference, the better the protection of the metallic substrate. [4]

3. Results and discussion

The results of the experimental determinations are shown in Table 1.

The standard deviation for the parabolic interpolations has been calculated with the relation (1).

\[
\sigma = \sqrt{\frac{1}{15} \sum_{i=1}^{15} (y_i - a \cdot x_i^4 - b \cdot x_i^3 - c \cdot x_i^2 - d \cdot x_i - e)^2}
\]  

where a, b, c and d are the coefficients in the obtained regression equations, and y_i, x_i are pairs made of the values of the electrochemical potential differences between the coating and the metallic substrate and the concentration of the NaCl solution, for the same temperature.

Table 1. The values of the electrochemical potential differences [mV] between the coating and the substrate, when varying the temperature and the concentration of the NaCl solution.

| C [%] | 20  | 22  | 24  | 26  | 28  | 30  | 32  | 34  | 36  | 38  | 40  | 42  | 44  | 46  |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1    | 253 | 250 | 248 | 245 | 240 | 245 | 237 | 235 | 233 | 225 | 225 | 225 | 225 | 227 |
| 2    | 225 | 215 | 209 | 205 | 198 | 199 | 195 | 194 | 192 | 191 | 190 | 188 | 190 | 198 |
| 3    | 210 | 200 | 195 | 190 | 180 | 175 | 174 | 180 | 172 | 171 | 170 | 170 | 172 | 172 |
| 4    | 195 | 179 | 168 | 170 | 159 | 159 | 157 | 155 | 152 | 154 | 149 | 152 | 154 | 154 |
| 5    | 190 | 176 | 161 | 150 | 142 | 144 | 143 | 142 | 141 | 141 | 140 | 140 | 141 | 142 |
| 6    | 185 | 160 | 152 | 150 | 141 | 142 | 135 | 134 | 133 | 132 | 132 | 133 | 133 | 135 |
| 7    | 184 | 181 | 165 | 151 | 140 | 135 | 134 | 132 | 132 | 131 | 130 | 131 | 132 | 132 |
| 8    | 183 | 165 | 150 | 143 | 140 | 137 | 133 | 132 | 132 | 131 | 131 | 132 | 133 | 134 |
| 9    | 184 | 160 | 155 | 145 | 142 | 138 | 137 | 140 | 133 | 132 | 132 | 133 | 135 | 136 |
| 10   | 183 | 160 | 160 | 143 | 140 | 135 | 134 | 133 | 132 | 131 | 131 | 132 | 133 | 135 |
| 11   | 183 | 177 | 168 | 157 | 150 | 143 | 132 | 140 | 137 | 135 | 132 | 132 | 133 | 137 |
| 12   | 183 | 170 | 159 | 155 | 140 | 137 | 135 | 135 | 133 | 131 | 132 | 132 | 132 | 137 |
| 13   | 183 | 172 | 165 | 151 | 145 | 142 | 139 | 138 | 140 | 134 | 133 | 135 | 138 | 139 |
| 14   | 183 | 170 | 160 | 153 | 150 | 148 | 142 | 139 | 136 | 135 | 135 | 137 | 140 | 139 |
| 15   | 180 | 168 | 157 | 150 | 145 | 143 | 140 | 137 | 136 | 135 | 135 | 137 | 139 | 140 |
In order to obtain some mathematical correlations between the corrosion behavior – estimated by the electrochemical potential differences and the concentration of the NaCl solution (for each temperature), the experimental data have been processed with Matlab program.

For each concentration of the NaCl solution it has been established the dependence: electrochemical potential differences between the coating and the substrate, noted as deps (y), and the temperature of the NaCl solution (x), by interpolation order 4. Table 2 shows the results of this interpolation.

In Figures 1-14 there are graphically represented the variations of the electrochemical potential differences between the Metco 73 coating and the metallic substrate related to the concentrations of the NaCl solution, for constant temperature.

**Table 2.** The results of the 4th order interpolation of the variation of the electrochemical potential difference between the coating and the metallic substrate vs. the concentration of the NaCl solution, in isothermal conditions.

| Temperature of the NaCl solution [°C] | The dependence relation: electrochemical potential difference between the coating and substrate (y) and the concentration of the NaCl solution(x) | Correlation coefficient | Standard deviation |
|--------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------|------------------------|--------------------|
| 20                                   | y=0.0077305·x⁴-0.3526·x³+5.7991·x²-40.8716·x+287.7816                                                                             | 0.99892                | 0.92062            |
| 22                                   | y=0.0059597·x⁴-0.31722·x³+5.9078·x²-45.3062·x+287.955                                                                            | 0.96932                | 5.8117             |
| 24                                   | y=0.0056683·x⁴-0.34677·x³+6.8183·x²-2.4896·x+293.2594                                                                          | 0.98489                | 4.4212             |
| 26                                   | y=0.0025746·x⁴-0.22919·x³+5.4366·x²-7.7457·x+285.8302                                                                          | 0.99091                | 3.7052             |
| 28                                   | y=0.0099036·x⁴-0.47267·x³+8.1471·x²-8.8958·x+290.5068                                                                         | 0.99329                | 3.1822             |
| 30                                   | y=0.012105·x⁴-0.53799·x³+8.8511·x²-62.679·x+297.1169                                                                         | 0.99586                | 2.6753             |
| 32                                   | y=0.009306·x⁴-0.44414·x³+7.739·x²-57.2276·x+285.6101                                                                          | 0.99678                | 2.2682             |
| 34                                   | y=0.0065474·x⁴-0.35716·x³+6.8111·x²-3.5447·x+281.4159                                                                          | 0.99381                | 3.1659             |
| 36                                   | y=0.0083619·x⁴-0.41563·x³+7.4291·x²-5.7598·x+280.4742                                                                          | 0.99781                | 1.8473             |
| 38                                   | y=0.0058911·x⁴-0.31456·x³+6.0075·x²-8.0569·x+267.1885                                                                         | 0.99877                | 1.3242             |
| 40                                   | y=0.0092604·x⁴-0.42376·x³+7.186·x²-52.7556·x+271.1275                                                                         | 0.99884                | 1.2881             |
| 42                                   | y=0.009237·x⁴-0.41715·x³+7.0324·x²-51.572·x+269.1572                                                                          | 0.99841                | 1.4764             |
| 44                                   | y=0.0082825·x⁴-0.38485·x³+6.6865·x²-0.2447·x+268.7306                                                                          | 0.99727                | 1.9199             |
| 46                                   | y=0.0061802·x⁴-0.33071·x³+6.3076·x²-9.9541·x+272.6797                                                                         | 0.99876                | 1.3315             |

**Figure 1.** The variation of the potential difference deps [mV] depending on the concentration of the NaCl solution, for 20°C temperature
Figure 2. The variation of the potential difference $d_{eps}$ [mV] depending on the concentration of the NaCl solution, for 22°C temperature.

Figure 3. The variation of the potential difference $d_{eps}$ [mV] depending on the concentration of the NaCl solution, for 24°C temperature.
Figure 4. The variation of the potential difference $\text{deps [mV]}$ depending on the concentration of the NaCl solution, for 26°C temperature.

Figure 5. The variation of the potential difference $\text{deps [mV]}$ depending on the concentration of the NaCl solution, for 28°C temperature.
Figure 6. The variation of the potential difference $d_{eps}$ [mV] depending on the concentration of the NaCl solution, for 30°C temperature.

Figure 7. The variation of the potential difference $d_{eps}$ [mV] depending on the concentration of the NaCl solution, for 32°C temperature.
**Figure 8.** The variation of the potential difference $\text{deps} \,[\text{mV}]$ depending on the concentration of the NaCl solution, for $34^\circ\text{C}$ temperature

**Figure 9.** The variation of the potential difference $\text{deps} \,[\text{mV}]$ depending on the concentration of the NaCl solution, for $36^\circ\text{C}$ temperature
Figure 10. The variation of the potential difference $d_{e}p$s [mV] depending on the concentration of the NaCl solution, for 38°C temperature.

Figure 11. The variation of the potential difference $d_{e}p$s [mV] depending on the concentration of the NaCl solution, for 40°C temperature.
Figure 12. The variation of the potential difference $d_{eps}$ [mV] depending on the concentration of the NaCl solution, for 42°C temperature

Figure 13. The variation of the potential difference $d_{eps}$ [mV] depending on the concentration of the NaCl solution, for 44°C temperature
4. Conclusion
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 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 of the temperature of NaCl solutions, the dependence between the electrochemical potential difference and the solutions concentrations is very well described by some curves having equations obtained by interpolation order 4 with the coefficients varying between 0.96932 and 0.99892.

References
[1] Maksay S 2001 Matematici speciale, Sigma Publishing House, Deva, Romania (in Romanian)
[2] Benea M L, Maksay S, Laziu R I and Becherescu D 2003 Using the potentiostatic method in order to purchase the corrosion behavior of the WC coatings deposited by plasma spraying. I: The influence of the NaCl solution concentration, respectively of the temperature, upon the coating/substrate electrochemical potential difference, Materials engineering 4(2) 127-140
[3] Benea M L, Maksay S, Laziu R I and Becherescu D 2003 Using the potentiostatic method in order to purchase the corrosion behavior of the WC coatings deposited by plasma spraying. II: The combined influence of NaCl solution concentration and temperature upon the coating/substrate electrochemical potential difference, Materials engineering 14(2)141-155
[4] Benea M L and Benea L P 2015 Characterization of the WC coatings deposited by plasma spraying, IOP Conf. Ser.: Mater. Sci. Eng. 85 012004
[5] Kasai S, Yanagisawa A, Ichihara A, Shimoyama Y, Ochiai K and Onishi H 1988 An investigation of oxide cermet coatings for hearth roll aplicatin in a continous amelling fournace, 1st Plasma Technik Symposium, Lucerne, Switzerland, May 18-20, pp 205-215
[6] Smith R W and Mutasim Z Z 1992 Reactive plasma spraying of wear – resistant coatings, *Journal of Thermal Spray Technology-ASM International* 1(1) 57-63

[7] Kvernes I, Lugscheider E and Norholm O 1988 *Potential of thermal and wear resistant coatings in combustion engines*, 1st Plasma Technik Symposium, Lucerne, Switzerland, May 18-20, pp 41-53