ESTIMATION OF THE QUANTITATIVE UNCERTAINTY FOR THE CORROSION POTENTIAL AND CORROSION CURRENT DENSITY

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Abstract

This paper briefly describes how to estimate numerically the quantitative uncertainty of potentiodynamic polarization curves obtained from a charge transfer controlled reaction in the case of working electrodes made from C45 steel with specific coatings (WC-Co, WC-Co-Al_2O_3 and a reference without coatings). The processed dataset was created during a real physicochemical experiment, but potentiostat/galvanostat transformed the dataset of measurements into parameters of Tafel's lines without uncertainty estimation. The Monte Carlo simulation with resampling (bootstrap approach) was used to estimate confidence intervals of these parameters.

Keywords: Uncertainty, quantitative estimation, corrosion potential, corrosion current density, bootstrap

1. INTRODUCTION

The carbon steel is very widely used as a construction material in many industries. The corrosion of steel surfaces, especially in acidic solutions, contributes to large costs because of damages and required repairs. The estimation of a corrosion rate and its reduction are problems of the great importance allowing to predict required corrective actions and to reduce their costs.

Several different techniques are applied in industry to reduce the corrosion of metals. One of them, the electro-spark deposition (ESD) process [1-3] is used to create specific corrosion-resistant coatings on the surface of machine's elements. The corrosion resistance of specimens from C45 steel with specific coating created by ESD were investigated and it resulted in the analyzed dataset.

Potentiodynamic polarization curves, obtained from a charge transfer controlled reaction, are used to designate the corrosion potential E_{corr} and corrosion current density j_{corr}. The one of the most popular DC techniques for the estimation of the corrosion rate is an extrapolation of linear Tafel lines. These lines are specific combined linear regressions derived from a logarithm of non-linear potentiodynamic polarization curves [4,5].

Poorqademi et al. [5] considered the issue of the accuracy, but they investigated only an uncertainty originated from experimental sources. They did not refer to the arbitrariness of the choice of linear sections making up Tafel's lines and the impact of this decision on the uncertainty of the obtained parameters.

In the further part of the article, the authors analyze the uncertainty of Tafel's lines parameters using Monte Carlo methods on a dataset obtained from the research of the C45 steel corrosion resistance.

2. MATERIALS AND METHODS

2.1. Experimental

The WC-Co or WC-Co-Al_2O_3 coatings were produced by electro-spark deposition on C45 mild steel (wt.%: C 0.42 - 0.50, Mn 0.50 - 0.80, Si 0.10 - 0.40, P 0.04, S 0.04) surface in four variants of coating compositions (**Table 1**).

Table 1 Composition of electro-spark coatings

Number of variant	Coating composition	Nanopowder mixture
1	WC80-Co20	80 % WC, 20 % Co
2	WC80-Co15-Al2O35	80 % WC, 15 % Co, 5 % Al_2O_3
3	WC80-Co10-$Al_2O_3$10	80 % WC, 10 % Co, 10 % Al_2O_3
4	WC80-Co5-$Al_2O_3$15	80 % WC, 5 % Co, 15 % Al_2O_3

An EIL-8A pulse spark generator was used to deposit coatings on the steel surface (output power 4 kW, voltage 250 V/50 Hz). After the coatings were deposited, specimen surfaces were microscopically observed, by LM [6,7] and SEM [8], and analyzed [9-12].

The solutions were made from distilled and deionized water with addition of FLUKA analytical grade sodium chloride (NaCl) and POCH analytical grade hydrochloride acid (HCl). The corrosive environment (1.2 M of Cl^- ions, pH 1.5) was obtained by mixing sodium chloride (1 M) and hydrochloride acid (1 M). The rectangle working electrode (4.5 cm^2) was polished, rinsed with double distilled water, degreased in ethanol and immediately immersed in the test solution - the experiment had begun 30 min. after immersion. All electrochemical measurements were made using a potentiostat/galvanostat PGSTAT 128N, AutoLab, Netherlands with the NOVA 1.7 software of the same producer. Potentiodynamic polarization curves were recorded in 1.2 M Cl^- acid solution. Measurements, replicated 3 times, were carried out at the temperature of 25±0.5 °C in the potential range from -800 to -50 mV vs. SCE, while the potential scan rate in was 1 mV s^{-1}.

2.2. Tafel's lines

Potentiodynamic polarization curves were used to designate the corrosion potential (E_{corr}) and corrosion current density (j_{corr}). Extrapolation of Tafel lines [4,5] is one of the most popular DC techniques for estimation of corrosion rate. According to the Tafel's law [5] the linear cathodic branch of a polarization curve is as following:

$$E - E_{0,c} = b_c \log\left(j_c / j_0\right) \quad (1)$$

while the linear anodic branch of polarization curve is:

$$E - E_{0,a} = b_a \log\left(j_a / j_0\right) \quad (2)$$

where $E_{0,c}$, $E_{0,a}$, j_0, b_c and b_a are constant parameters describing polarization curves.

2.3. Bootstrap simulations and statistical analysis

Potentiodynamic polarization curves were recorded into five datasets, separately for each specimen. Subsequently, cathodic and anodic Tafel's lines were determined for them. From the mathematical point of view, these lines are two independent linear regressions with the additional assumption that the corrosion potential (E_{corr}) and corrosion current density (j_{corr}) have to be exactly the same for both lines, cathodic and anodic branch. This condition leads to the construction of the special approximation criterion, where typical minimization of the least squares criterion is extended into the constrained Karush-Kuhn-Tucker's form [13] while the regression branches are defined in the form previously shown in equations (1) and (2).

After some transformations and resolving, this formulation gives four parameters to determine: E_{corr}, j_{corr}, b_c, b_a and two of them, E_{corr} and j_{corr} are the same for both branches. These four parameters are random variables and their values and dispersion may be estimated, however analytical approach may give results far from observed due to differences between theoretically assumed normal distribution and really observed variability.

To avoid this inconsistence, the bootstrap approach [14-16], being the Monte Carlo resampling-based simulation procedure, was selected as a numerical tool to estimate uncertainty distribution without additional assumptions. The two-branches model of Tafel's lines was assumed as a base for the bootstrap iterations. Next, the residuals were calculated and then used for bootstrap resampling [14]. Bootstrap iteration count was set to 10,000, because such value makes 95 % confidence intervals estimation very easy.

3. RESULTS AND DISCUSSION

The potentiodynamic experiment resulted in a dataset of measurements: 501 records for each variant of the coating with the potential of corroding metal varying from -800 mV up to -50 mV with the rate 1 mV/s. **Figure 1** shows obtained results in a plot with logarithmic scale conformed to equations (1) and (2).

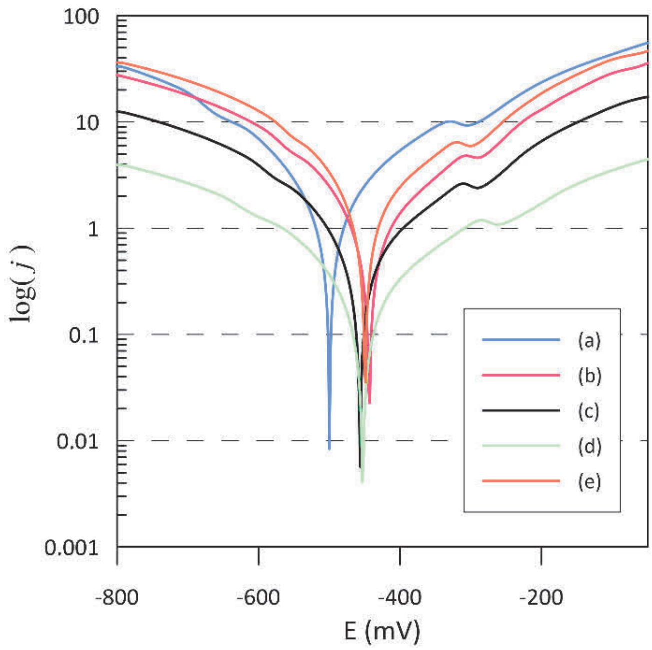

Figure 1 Potentiodynamic polarization curves for C45 mild steel: (a) without coating, (b) WC80-Co15-$Al_2O_3$5, (c) WC80-Co10-$Al_2O_3$10, (d) WC80-Co5-$Al_2O_3$15, (e) WC80-Co20. Logarithmic scale, density of current j (mA·cm^{-2})

The equations (1) and (2) were fitted to measurement dataset and mean values of parameters were obtained. Next, predicted values were compared with real measurements and residual dataset (501 records) was created. According to the bootstrap methodology, these residuals were randomly resampled, added to predicted values and such new dataset was a source for a new bootstrapped fitting. This step (random resampling, adding, fitting) has been iterated 10,000 times and a large dataset of simulated values was obtained. This dataset has been analyzed and 95 % confidence intervals were identified for all considered parameters (**Table 2**). It is worth noting that although all the histograms were bell-shaped e.g. **Figure 2**, they were significantly different from the normal distribution (Shapiro-Wilk test, $p < 0.05$).

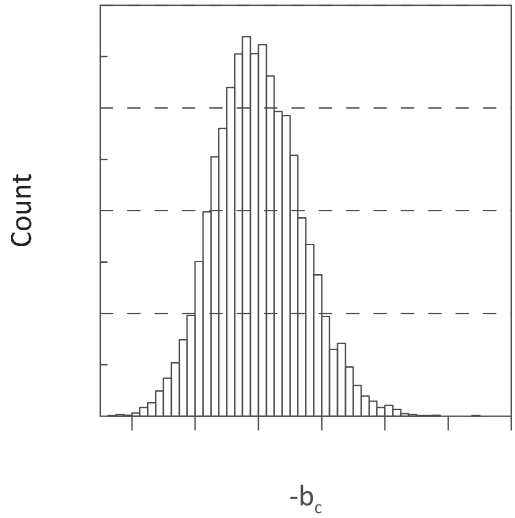

Figure 2 The distribution of the bootstrapped values: the variant with absence of coating and *-b*$_c$ parameter. Descriptive statistics: mean 160; std. dev. 5.5; -95 % quantile 150; +95 % quantile 171; Shapiro-Wilk test of normality $p < 0.005$

Table 2 Identified values of Tafel's parameters together with descriptive statistics obtained from the bootstrap numerical simulation

Material	Parameter	Mean	Std. dev.	-95 %	+95 %
Absence	E_{corr}	-498	1.2	-501	-495
	j_{corr}	1.78	0.1	1.67	1.89
	$-b_c$	160	5.5	150	171
	b_a	190	8.7	174	208
WC80-Co20	E_{corr}	-449	1.1	-451	-446
	j_{corr}	1.48	0.05	1.38	1.58
	$-b_c$	145	4.0	137	152
	b_a	180	4.4	171	189
WC80-Co15-$Al_2O_3$5	E_{corr}	-443	1.2	-446	-441
	j_{corr}	0.89	0.03	0.82	0.96
	$-b_c$	135	3.6	127	142
	b_a	170	3.8	163	178
WC80-Co10- $Al_2O_3$10	E_{corr}	-456	1.1	-458	-454
	j_{corr}	0.49	0.02	0.46	0.52
	$-b_c$	140	3.8	132	147
	b_a	240	4.1	232	248
WC80-Co5- $Al_2O_3$15	E_{corr}	-452	1.1	-455	-449
	j_{corr}	0.19	0.01	0.18	0.20
	$-b_c$	155	4.7	145	164
	b_a	255	5.5	244	267

The consolidated results, means and descriptive statistics obtained from the bootstrap procedure for all variants of coating, are presented in **Table 2**. As can be seen in **Figure 2**, the histogram is sufficiently smooth for the limits of the confidence interval to be determined stably. Additional processing of the whole bootstrap procedure i.e. many times by 10,000 iterations gave the variability of confidence interval bounds less than the precision expressed in **Table 2**. This means that increasing the number of iterations above the assumed 10,000 will not significantly improve the results.

4. CONCLUSION

The surface of C45 mild steel was modified by electro-spark deposition (ESD), using of WC-Co or WC-Co-Al_2O_3 electro-spark electrodes. All variants of a coating together with reference specimen (non-coated steel) were tested on a corrosion resistance in NaCl and HCl solution. The corrosion resistance was estimated in potentiodynamic experiment and the dataset of pairs, potential *E* and current density *j*, was recorded by a potentiostat/galvanostat. Parameters of Tafel's equation were identified and their uncertainties were estimated in the bootstrap numerical simulation. Such approach avoids having to make many initial assumptions about distributions of variables so it makes the whole procedure a data-driven automata.

Further investigation will involve more sophisticated analytical techniques like wavelet analysis and time-series [17-20] to remove time-dependent noises and trends not explained by controlled factors.

Such resampling methodology address the issues with an uncertainty estimation in those research areas where datasets are relatively small because of large cost of data acquisition: in the materials science [21-24] and the mechanical engineering [25,26], especially using fuzzy assessment [27,28]. Additionally, it almost completely removes typical theoretical assumptions on distributions except one: the assumption that residuals conforms i.i.d. what means "independently and identically distributed" [14].

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