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APPLICATION OF REGRESSION ANALYSIS AND GENETIC ALGORITHM TO THE OPTIMIZATION OF NITRIC ACID PASSIVATION OF 316L STAINLESS STEEL

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Abstract: Passivation of a biomedical grade 316L stainless steel by mean of nitric acid treatment was used to improve a protective oxide layer on the surface and to increase resistance to pitting corrosion in physiological solution. Both regression analysis and genetic algorithm were employed to reveal the effects of operating parameters of the nitric acid passivation (HNO3 concentration. temperature and passivation period) on the corrosion resistance of AISI 316L stainless steel in Hank's solution. The experiment designed as full factorial with three factors and three levels. The responses were the pitting potential values (Ep) obtained from potentiodynamic tests. Mathematical model was determined by using regression analysis. According to the model, the effects of each variable and interactions between them were calculated. Optimal intervals of the parameters were estimated by mean of genetic algorithm.
Keywords: stainless steel, passivation, nitric acid, regression analysis, genetic algorithm

1. INTRODUCTION

Pitting corrosion, one of the most severe and destructive types of localized attack, represents a serious problem related to the stability of stainless steels used in various applications, ranging from industrial to medical applications. The susceptibility of stainless steels to pitting attack depends largely on the type of stainless steel used and on the subsequent chemical composition of the protective passive layer. It is a common agreement that an increased content of chromium in the surface passive film results in an increased resistance of the stainless steel to pitting corrosion [1-4]. On the other hand, the presence of some inclusions on the material's surface, such as sulfide inclusions, represents a major problem due to their negative role in pitting corrosion.

The passive films which are formed on the surface play an important role in corrosion stability of stainless steel. The study of electrochemical behaviour of that kind of steel in aggressive conditions, when a considerable dissolution of the metal takes place even in a passive state, is significant for the creation alloys, which are stable in corrosive media. In order to increase corrosion resistance, some protocols of passivation have been used for the stainless steel.

A number of research groups have done extensive research on the improvement of both general and pitting corrosion resistance of stainless steels by developing techniques for the modification of the material's surface and passive film. Nitric acid has been used as one of the most popular chemical passivating reagents for surface treatment of stainless steels. Extensively cited works have emphasized a beneficial effect of nitric acid solution on chromium enrichment in the modified passive layer [5-8].

The ASTM-F86 protocol defines a protocol for stainless steel implant immersion in nitric acid solution due to reduce their surface reactivity and consequently their potential for dissolution [9]. The knowledge of the effect of these operating conditions of passivation is essential for achieving a controlled process. Experimental design techniques, such factorial design and optimization are useful tools in the characterization of electrochemical processes to study the effects of variables which affect them and their possible interactions [10]. The aim of this work was to determine the effects of the passivating solution concentration, its temperature and the period of treatment on the corrosion resistance of the passivated 316L stainless steel, namely pitting potential by using multiple regression analysis (MRA) and genetic algorithm (GA).

2. MATERIALS AND EXPERIMENTAL METHODS

2.1 Materials

Prior to each test, the exposed surface of the samples (6 mm diameter and 10 mm high) were wet ground with silicon carbide paper up to 1200 grit, successively polished with diamond paste grain size up to 0.25 μm, rinsed with distilled water and then washed with ethanol in an ultrasonic cleaner. After the final polishing and cleaning, the samples were immersed in nitric acid (HNO_3) solutions. After the passivation, the samples were rinsed in double distilled water and alcohol respectively.

2.2 Electrochemical measurements

The experiments were carried out using a three compartments cylindrical glass cell equipped with a saturated calomel electrode (SCE) as reference electrode and a platinum foil as a counter electrode. The measurements were made using Potentiostat–Galvanostat device (Princeton Applied research EG&G Typ 273A) which was connected to the electrochemical cell. Data registration and testing process conduction were performed on an interfaced computer using appropriate software.

The potentiodynamic polarization curves of the test specimens were measured from -400 mV with a scan rate of 0.25 mV/s. The tests were finished when the current density reached about 0.2 mA/cm^2. The pitting potential (Ep) in the polarization curve was obtained when the passive film broke down. Namely, the anodic current density increased very quickly and pits were observed on the surface of specimen after corrosion test.

The electrochemical tests were conducted in Hank's solution, which is a simulated body fluid. The temperature was maintained at 37±1°C (typical body temperature) during the experiments.

2.3 Methodology

Three variables (X_1: HNO_3 concentration. X_2: temperature of passivation solution and X_3: passivation period) were selected in this study. As the experiments were easy to carry out, we decided to assign three levels for each variable and to perform the 27 experiments corresponding to a full factorial design 3^3.

Table 1. Passivation factors and their levels used in experimentation

Factors	Level -1	Level 0	Level 1
HNO_3 concentration (vol. %)	10	30	65
Temperature of solution (°C)	17	40	60
Passivation period (min)	20	40	60

This procedure allowed us to measure 27 values for the response (pitting potential Ep) and to efficiently estimate the coefficients of second order model, which revealed a link between the passivation phenomena and experimental variables X_j. We chose a reduced second order.

It can be represented as follows:

$$\breve{Y} = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2$$

where: Y - response function, X_j - coded variables of the system, b_0 - model constant, b_j - first degree coefficient, b_{jk} - crossproducts coefficients and b_{jj} - quadratic coefficient.

The model coefficients b_0, b_j, b_{jk} and b_{jj} were estimated by a least squares fitting of the model to the experimental results obtained in the design points. The computed values of the response were designated by $\breve{Y}$.

3. RESULTS AND DISCUSSION

3.1 Experimental results

As the main results from the experiment are pitting potentials for all 27 combinations of the three factors (X_1, X_2 and X_3) on the three levels (-1, 0, 1). Graphical review of the experimental results as contour plots of E_p (Y in graphs) versus X_1 and X_2 (a) and E_p versus X_2 and X_3 (b) is presented in figure 1. On the basis of the contour plots can be concluded that maximal pitting potential E_{pmax} = 1.47 V was measured for the middle (0) level of the factors. In other words, the best measure combination of factors was concentration about 30% vol. HNO3 solution in distilled water, temperature 40 ^{0}C for period passivation about 40 minutes.

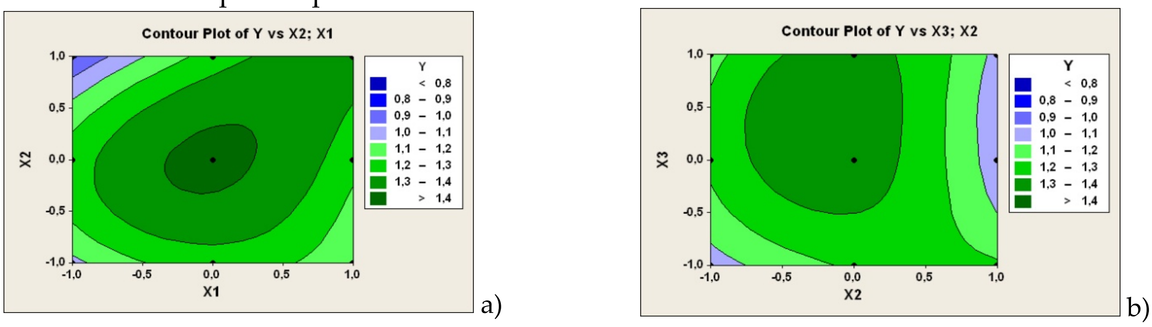

Figure 1. Contour plot of experimental results for pitting potenti al (Y) and passivation factors

3.2 Mathematical model and analysis

Multiple regression analysis (MRA) was applied to develop mathematical model for the combined effect of passivation factors, namely nitric acid concentration, temperature and passivation perion on the pitting potential. First and second order main effects and interaction effects were accounted in the mathematical model. The regression model coefficients were determined using least square method and the adequacy of model fit is assessed by coefficient of determination (R^2). The mathematical model relating the passivation parameters and pitting potential (Ep) was obtained as:

$$\hat{Y} = 1.45 + 0.072X_1 + 0.0036X_2 + 0.0194X_3 + 0.0911X_1X_2 - 0.0364X_1X_3 - 0.0576X_2X_3 - 0.169X_1^2 - 0.155X_2^2 - 0.0537X_3^2 \quad (1)$$

Table 2. Significance of effects by ANOVA for Y

Main and interaction effects	Coefficient	Standard deviation	t.exp	Signif. %
Constant	1.44656	0.09118	15.86	0.000
X1	0.07198	0.04155	1.73	0.104
X2	0.00364	0.04314	0.08	0.934
X3	0.01942	0.04155	0.47	0.647
X12	0.09105	0.05217	1.75	0.101
X13	-0.03636	0.05217	-0.70	0.496
X23	-0.05761	0.05217	-1.10	0.287
X11	-0.16900	0.07251	-2.33	0.034
X22	-0.15536	0.07043	-2.21	0.043
X33	-0.05367	0.07251	-0.74	0.471

Results of analysis of variance indicated that the regression was significant at the probability level 99.9%. Moreover, the R^2 for the model is equal to 0.81 for Y implied that about 81% of the variability in the data for each response were explained by the models. Combined with the satisfactory residual analysis, this indicated that each model was a very good fit to the data.

Complete analysis of variance was summarized in Table 2. The statistical test allowed us to conclude that the main effect on the nitric acid passivation of 316L was X_2 – temperature as the most significant factor on the passivation.

3.3 Genetic algorithm (GA) optimization

Modern methods for optimization are powerful and popular tools for solving complex engineering optimization problems. GA is a modern optimization method for finding the optimal values of the function with many variables, such as those modeling the passivation process. Pitting potential of passivated 316L stainless steel, depending on HNO_3 concentration, its temperature and passivation period was maximized. The possibility of finding the maximum of the second order function, obtained by using MRA, and the fact that derivatives or other additional information of the function are not necessary are basic advantages of GA optimizatiom method.

In this paper, three variable function given by equation (1) was optimized (maximized) by using GA. Graphical review of the results is presented in figure 2. Since, GA always looks for the minimum of the function, an algorithm for finding function maximum can be used as follow:

$$\max Q(x) = -\min(-Q(x)) \quad (2)$$

According to the previous equation, maximum of the function Y obtained in 51 iteration by GA is 2.35. Coded values for the predictors corespond to maximum of the response are: X_1=0.541, X_2=1 and X_3=-0.539. In real parameters, passivation in 49% vol. HNO_3 solution, at the temperature 60 ^{0}C for a period of 31 minutes are predicted values of parameters for the most effective passivation treatment .

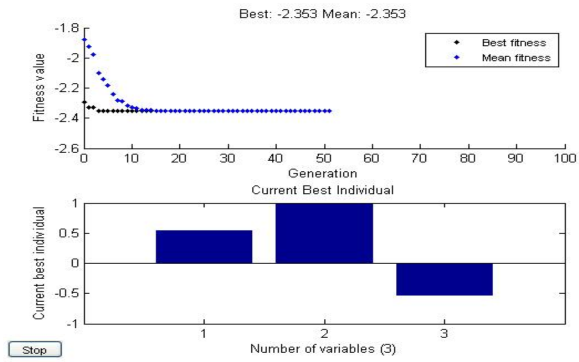

Figure 2. GA optimization results

4. CONCLUSION

The effects of nitric acid concentration, temperature and passivation period on the pitting potential of AISI 316L stainless steel are reported in this work. Within the range of operating conditions, the following conclusion can be drawn:

- Maximal pitting potential E_{pmax} = 1.47 V was measured for the middle (0) level of the factors (30% vol. HNO3 solution in distilled water, at the temperature 40 ^{0}C for period passivation about 40 minutes).
- Multiple regression analysis was applied to develop second order mathematical model.
- On the basis of the mathematical model and ANOVA analysis, it can be concluded that temperature had a major effect on the pitting potential**.**
- Passivation period had a secondary, while nitric acid concentration was the factor with the lowest signification on the pitting potential.
- Genetic algorithm was applied to optimized mathematical model
- Predicted optimal values for the pitting potential as response, nitric acid concentration, temperature and passivation period are 2.35 V, 49% vol. HNO_3 water solution, 60 ^{0}C and 31 minute, respectively.

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