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Proceedings of the Institution of Mechanical Engineers, Part N: Journal of Nanoengineering and Nanosystems 2013 227: 105 originally published online 22 April 2013
DOI: 10.1177/1740349912464930

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Institution of MECHANICAL ENGINEERS

Journal of NANOENGINEERING AND NANOSYSTEMS

Proc IMechE Part N:
J Nanoengineering and Nanosystems
227(2) 105–111
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DOI: 10.1177/1740349912464930
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An experimental investigation of corrosion resistance of mild steel by sol-gel process using TiO_2 nanostructure coating and prediction of optimal parameters

Ali Shanaghi[1], AR Sabour Rouhaghdam[2], Seyyed Ahmad Tabatabaei[3], Masoud Shariatpanahi[3], Abbas Rastgoo[3], Akbar Karkhaneh Yousefi[3] and Mostafa Samadzadeh[3]

Abstract

A TiO_2 nanostructure coating has shown to significantly improve the thermal and electrical properties of steel plates and increase their resistance to oxidation, corrosion, and wear, especially in high temperature applications. In this research, the corrosion resistance properties of a mild steel substrate by applying TiO_2 nanostructure coating using the sol-gel method were investigated. The quality of the coating, however, is notably affected by such process parameters as the dip-coating rate, drying time, heat-treatment rate, and the number of coating layers. Moreover, this article presents an integrated approach to the optimal parameter setting for the above process. Using experimental data from a coating process by the sol-gel method, an artificial neural network is trained to map the vector of process parameters onto a measure of corrosion resistance. An evolutionary search algorithm is then employed to find the optimum set(s) of process parameters. The efficiency of the proposed approach is demonstrated using a case study involving a 316L stainless steel substrate.

Keywords

Nanostructures coating, TiO_2, sol-gel, neural networks

Date received: 12 June 2012; accepted: 19 September 2012

Introduction

Nanostructured TiO_2 thin films are used in a wide range of applications such as ultraviolet filters for optics and packing materials,[1,2] antireflection coatings for photovoltaic cells and passive solar collectors,[3] photo catalysts for purification and treatment of water and air,[4,5] anodes for ion batteries,[6] electro chromic displays,[7] transparent conductors, self-cleaning coatings of windows and tiles,[8] humidity sensors,[9] gas sensors,[10] and barrier layer for corrosion protection.[11] It has been shown that some applications greatly benefited from a nanostructured phase for TiO_2. Indeed, the production of nanostructured TiO_2 thin films has been recently carried out by several methods.[12–14]

Several techniques have been used for the preparation of transparent TiO_2 thin films that include sputtering,[15] chemical vapor deposition,[16,17] pulsed laser deposition,[18] laser molecular-beam epitaxy method,[19] and sol-gel techniques.[20,21] The sol-gel technique has distinct advantages over the other techniques due to excellent compositional control, homogeneity on the molecular level due to the mixing of liquid precursors, and lower crystallization temperature. Moreover, the microstructure of the film deposited, that is, the pore size, pore volume, and surface area, by the sol-gel process can be tailored by the control of process variables[22] and a more generic approach to enhance corrosion resistance is to apply

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protective films or coatings without crack. The presence of cracks and defects in coating, with increasing current density, will lead to localized corrosion.[23]

In recent years, sol-gel based Titania coatings have been successfully applied on stainless steel and mild steel substrates to improve their abrasion and corrosion resistance.[24,25] Due to the increasing industrial applications of mild steels, in this work an attempt was made to increase the corrosion and wear resistance properties of a mild steel substrate by applying TiO_2 nanostructure coating using the sol-gel method.[26] Structural and micro-structural characterizations of thin films have been realized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The Tafel polarization curves were employed to measure anticorrosion performance of the TiO_2 coatings in 3.5%NaCl solution and to discuss the mechanism of corrosion resistance for the coatings based on the study of Shanaghi et al.[26] Finally, the experimental results were used to find the TiO_2 nanostructure coating parameter values that would maximize the coating's corrosion resistance. For this, a model-based approach was proposed to solve the multiobjective problem. The approach uses an artificial neural network (ANN) model of the coated plate, trained and tested with experimental data by the sol-gel coating method, to estimate the corrosion resistance of the plate at significantly reduced computational cost.

The experimental work

The reagents were used as in received conditions. Since the water content of the sol has a critical role in the hydrolysis and polycondensation reactions, absolute ethanol (Merck 99%) was used as the solvent, ethyl acetoacetate (EAcAc) (Merck 99%) used as chelating agent, and tetra *n*-butyl orthotitanate (TBT) (Merck 98%) was used as the precursor. The TiO_2 sol was prepared from TBT, ethanol, EAcAc, and distilled water, which were mixed at room temperature as shown in Figure 1. In the experiment, the hydrolysis reaction was carried out by drop-wise addition of deionized (DI) water to prepared solution, while stirring for obtaining yellow and transparent solution.

Plate samples (20 mm × 10 mm) of mild steel were used as substrates in this study. After polishing to an R_a of about 2 μm using Al_2O_3 slurry, the samples were first cleaned with acetone and then ultrasonically cleaned in ethanol. The samples were dip-coated in the specific solution with a dip-coating rate of 0.5 mm/s by a dip-coater rig and then pulled out from the solution with the same dip-coating rate. The samples were dried in a drying rig by decreasing the humidity from 85% to common laboratory atmosphere. Heat treating was performed after drying in a common tube resistance furnace. The XRD pattern for the TiO_2 coating was obtained using an XRD system with Cu Kα radiation (wavelength = 1.5406 Å) at range 10°–60°.

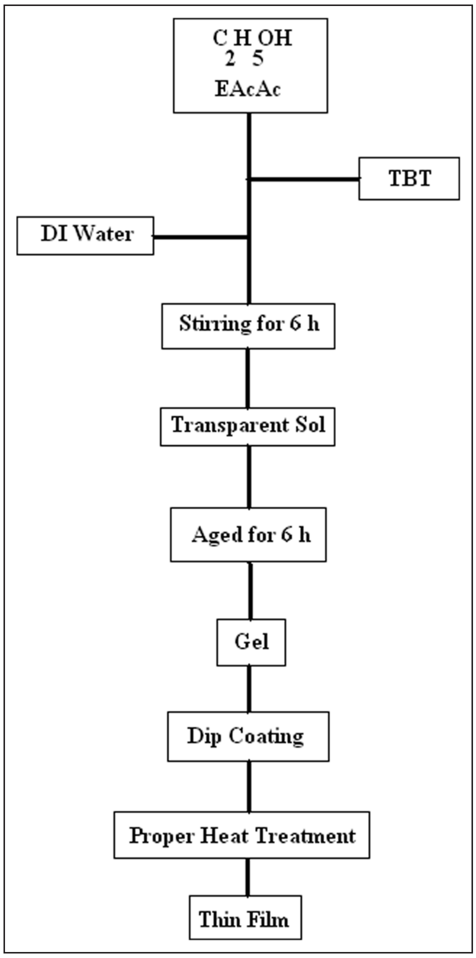

Figure 1. Preparation diagram for sol gel–derived TiO_2 nanostructure coating.
EAcAc: ethyl acetoacetate; TBT: tetra *n*-butyl orthotitanate; DI: deionized.

The "quality characteristic" of concern is the corrosion resistance of the coatings that was assessed by Tafel polarization tests carried out at 298 K using an EG&G 273A Potentiostat/galvanostat with 352 SoftCorrIII software. A three-electrode cell with the coated samples as a working electrode, saturated calomel electrode as a reference electrode, and a platinum plate as a counter electrode was used in the tests. The ratio of the volume of 3.5 wt% NaCl solution/sample area was 200 mL/cm^2.

After the electrochemical testing system became stable (about 1 h), scans were conducted at a rate of 0.1 mV/s from −0.25 V versus open-circuit potential to +0.25 V versus open-circuit potential. The surface morphology, uniformity, homogeneity, and crack-free coated samples were examined by XL-30 (PHILIPS) SEM.

The multiobjective optimization algorithm

There are several ways to treat problems with multiple, possibly conflicting objectives. The "conflict" among

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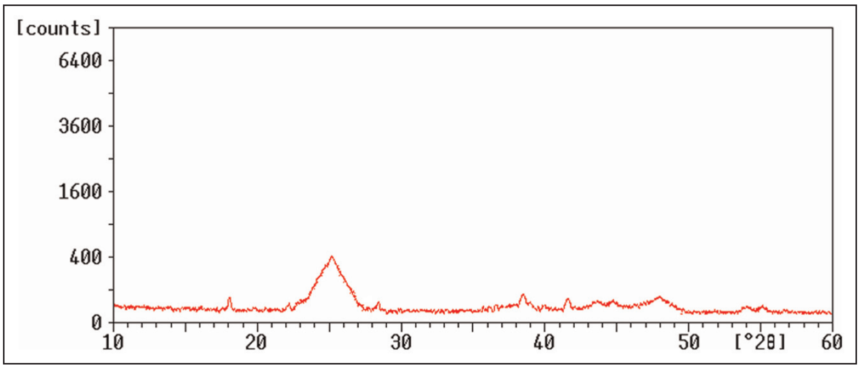

Figure 2. X-ray diffraction curve of TiO_2 coating on mild steel.

the objectives implies that there is usually no single "best" point in the solution space that surpasses all other points with respect to all objectives. Points that surpass others according to some criteria may well fall inferior to them according to other criteria. This brings up the notion of Pareto-optimality, where multiple, nondominated solutions, collectively referred to as the "Pareto set" are sought, rather than a single best point.[27] The Pareto-optimality has found wide applications in real-world problems, as it provides the user with the opportunity to choose from a variety of plausible solutions according to his/her preferences. Many search/optimization algorithms have adopted the notion of Pareto-optimality in their quest for optimal solutions when multiple measures of desirability need to be considered. With the emergence of evolutionary algorithms (*EA*s), more researchers were encouraged to employ the notion, thanks to the population-based structure of *EA*s that made it possible for multiple candidate solutions to be processed simultaneously and to their exploration power that considerably reduced the computational cost of finding nondominated points.

Being among the first *EA*s applied to problems with multiple objectives, the multiple-objective genetic algorithms (*MOGA*s) soon made their way to the top of users' lists in practical applications, as their easily tunable genetic operators proved to be quite efficient in spotting the often-scattered nondominated points. A rank-based fitness assignment scheme was commonly used to map the multidimensional space of the objectives to the unidimensional space of fitnesses, where individual solutions were "ranked" based either on the number of solutions they dominated or on the order of the nondominated layer of solutions they belonged to.[28]

Of the many variants of *MOGA*s, a modified version of Srinivas and Deb's nondominated sorting genetic algorithm (*NSGA*), which is referred to as *NSGA-II*,[29] has perhaps been the most popular. In an attempt to enhance the diversity of the evolving populations of potential solutions, the *NSGA-II* replaced the classical "sharing" mechanism of *NSGA* with a direct "elitist" mechanism. This modification improved the exploration power of the algorithm and enabled it to find wider spectrums of Pareto-optimal solutions. The *NSGA-II* has been widely adopted as a general purpose multiobjective optimizer, despite of some recent attempts to further improve its performance.[30,31]

Data gathering

The XRD spectrum indicates strong diffraction peaks of anatase phase. It shows that anatase is the major phase in coating and there is not any another phase in the coating; so there is no other stress in the structure, and anatase (101) and rutile (110) reflections can be seen at 25.4° and 27.4° (Figure 2).

These results are in good compliance with the thermodynamic and heat-treatment properties of titanium oxide in 550 °C. The anatase phase has good stability and corrosion-protective characteristic on metals. In addition, the quality control of anatase phase was easier compared with the rutile phase at 800 °C. Therefore, in this article, the anatase phase was chosen as the protective coating layer.[26]

The important factors in corrosion protection of coated samples are high quality of coating, such as thickness, crack, and uniformity. Moreover, in sol-gel process, essential factors such as relevant factors of sol-gel preparation process and heat-treatment rate are contributing in obtaining coatings with high quality, and each of them has specific effect in coating quality.[26] Figure 3 illustrates the SEM micrograph of TiO_2 nanostructure coating. This figure exhibits a uniform and complete coating with no cracking and results in corrosion resistance improvement of metals. The homogeneous, crack-free, optically transparent, and uniform coatings (as shown in Figure 3) with thicknesses on the order of 500–700 nm were produced in this investigation.

A neural network with *dip-coating rate* (mm/s), *heat-treatment rate* (°C/min), *drying time* (min), and the number of dip coatings as inputs and corrosion resistance as output was designed.[26] A series of experiments were carried out to produce sufficient training data. A total of 81 experiments were performed and the corrosion resistance of the plate was measured for each input vector.[26] The experimental results, partially presented in Table 1, were used to train the neural network. For

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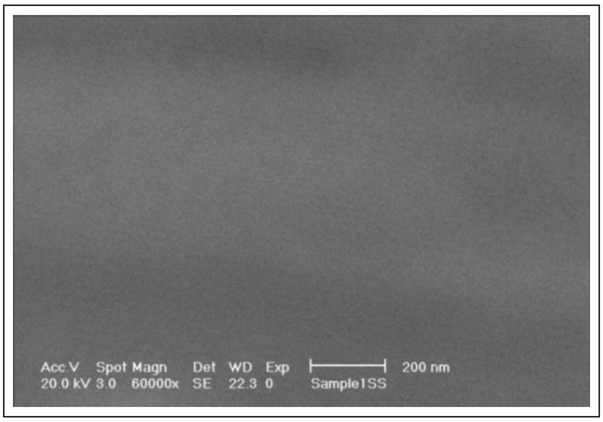

Figure 3. Scanning electron microscopy micrograph of sol-gel TiO_2 nanostructure–coated steel surface.

the sake of brevity, only the results of 10 tests (of 81) are presented here.

The ANN was trained using the Levenberge–Marquart algorithm. Overall, 70% of the experimental data was used for training, 20% for testing, and 10 % for validating the network.

The performance and convergence history of the developed ANN for training and test data sets are demonstrated in Figures 4 and 5, respectively.

Formulating the coating design as a multiobjective optimization problem

We wish to find the TiO_2 nanostructure–coating parameter values that would maximize the coating's *corrosion resistance*. However, the mapping from the parameters space to the objective space is not one-to-one, meaning that there is generally more than one input vector resulting in the same objective value. Therefore, we wish to find the one input vector that would maximize the plate's corrosion resistance (R_p) with minimal *dip-coating rate* (*dcr*), *heat-treatment rate* (*htr*), and *drying time* (*dt*), and maximal *number of coatings*.

To do this, we define a second objective comprising three of the four input parameters. The inclusion of this second objective would mean that the solution to the two-objective optimization problem would not only give the maximum value of the plate's corrosion resistance but also the corresponding input vector with minimum *dcr, htr, dt*, and maximum number of coatings.

A *weighted-sum* approach is used to turn the three distinct, yet interrelated parameters into a single objective. Each parameter is normalized, multiplied by a weight factor, and summed up to form the second objective. To comply with the monotonicity requirements, the three minimizing parameters, namely *dcr, htr*, and *dt* were transformed into maximization ones using the following formulas

$$dcr \leftarrow max\_dcr - dcr$$
$$htr \leftarrow max\_htr - htr$$
$$dt \leftarrow max\_dt - dt$$

where *max_dcr, max_htr*, and *max_dt* represent the "maximum possible dip-coating rate" and "maximum possible heat-treatment rate," and "maximum possible *drying time*," respectively. This way, the collective maximization of the second objective results in the minimization of its first three components, *dcr, htr*, and *dt*.

In order to find the Pareto-optimal solutions to the multi-objective problem just outlined, a real coded version of the well-known *NSGA-II* algorithm with a population size of 100, cross-over rate of 0.9, and mutation probability of 0.02 was employed. An intermediate gene-altering cross-over and a random-replacement mutation scheme[32,33] were used as genetic operators.

Optimization results

The Pareto set of points resulting from a typical run of the optimization code is presented in Figure 6. The so-called "Pareto front" enables the user to choose from the set of nondominated solutions according to his or her priorities. Nonetheless, to pick a single representative solution from the set, it is common practice to pick the one with the shortest distances from the "utopia point" in the objectives space where the utopia point is an imaginary point with the best

Table 1. The experimental results.

	Dip-coating rate (mm/s)	Drying time (min)	Heat-treatment rate (°C/min)	Number of coatings	R_p (KΩ cm^2)
1	1	1	1	2	268.35
2	1	1	2	2	240.71
3	1	1	1	3	205.11
4	1	1	2	3	211.09
5	1	1	3	2	198.52
6	1	1	3	3	201.83
7	1	1	1	1	193.14
8	1	1	2	1	193.09
9	1	1	3	1	170.28
10	2	1	1	2	3892.21

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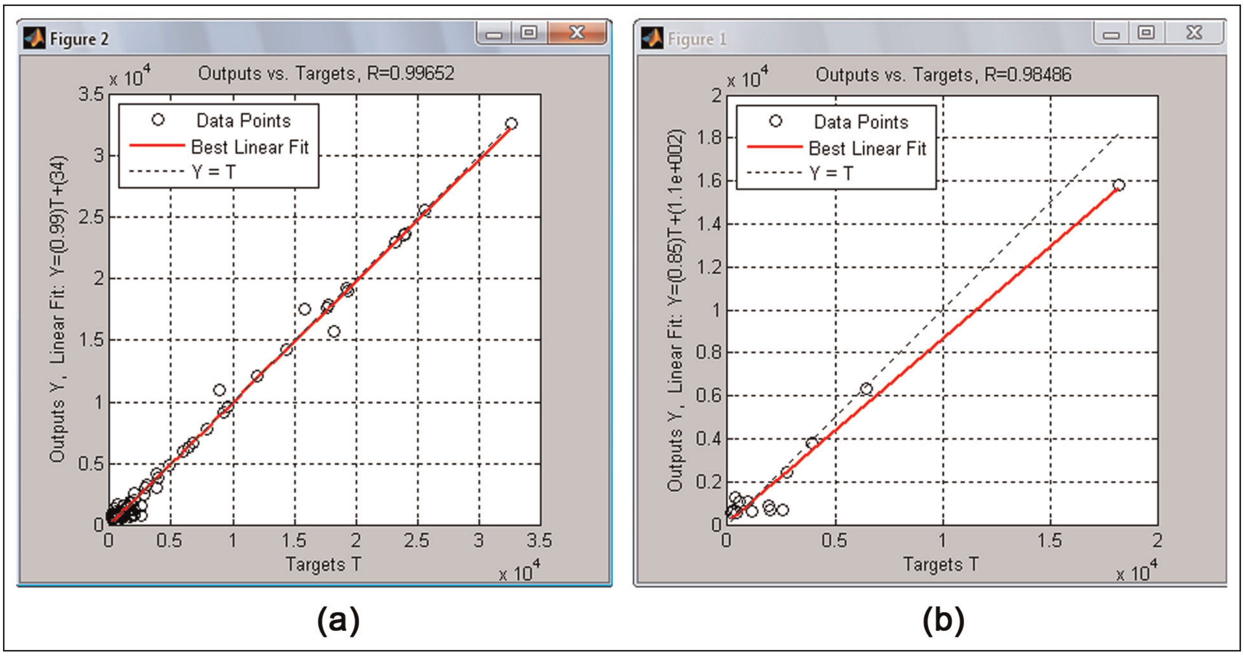

Figure 4. Performance of the artificial neural network for: (a) training data samples and (b) test data samples.

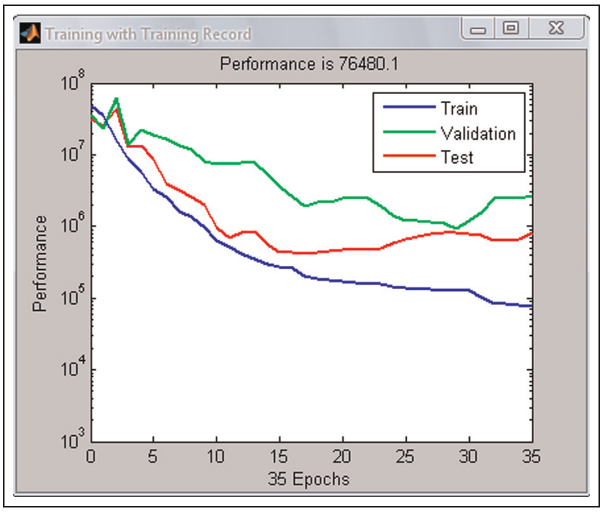

Figure 5. The convergence history of the developed neural network.

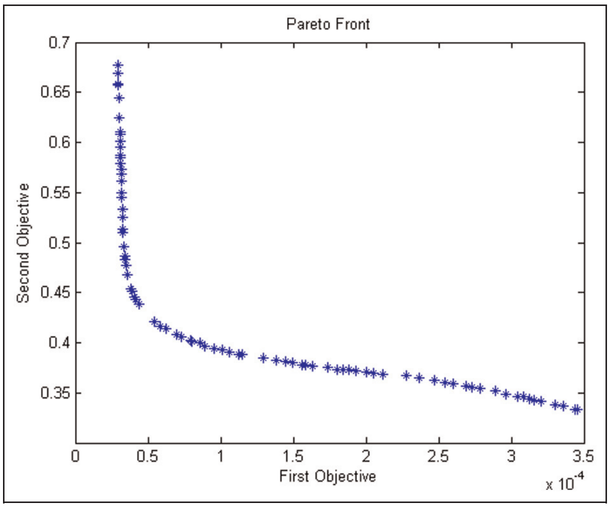

Figure 6. The Pareto front after 80 generations (population size = 100).

individual objectives (here the best of the first and second objectives found anywhere in the Pareto set). The average parameter values for such a representative solution from 10 runs of the code are presented in Table 2.

Conclusion

Recognizing the significant contribution of nanostructure coatings to the improved thermal/electrical properties of steel and their oxidation, corrosion, and wear resistance, the optimal design of a sol-gel TiO_2 coating was studied. The *dip-coating rate, heat-treatment rate, drying time*, and *number of coating layers*, as design parameters, play an important role in the corrosion behavior of nanostructure coatings deposited by sol-gel method. The corrosion resistance of samples along with a simplified measure of the practicality of the design variables was considered as objectives to be maximized. The approach uses an ANN model of the coated sample, trained and tested with experimental data by the sol-gel coating method, to estimate the corrosion resistance of the coating at significantly reduced computational cost. It also uses a multiobjective EA to find the set of Pareto-optimal solutions to the problem. The applicability and efficiency of the proposed approach was demonstrated using a case study involving a 316L stainless steel substrate. It was concluded that a model-based approach could be employed to quite affordably solve complex,

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Table 2. Representative solution (average from 10 runs).

Parameters	Dip-coating rate (mm/s)	Drying time (min)	Heat-treatment rate (°C/min)	Number of dip coatings	R_p (KΩ cm^2)
Optimal values	1.73	3.11	1.09	1.75	31910.20

computationally expensive optimal design problems provided that the underlying model is supported by a reliable experimental knowledge of the phenomenon being studied.

Finally, there is widespread interest in TiO_2 nanostructure coating for applications such as thin ceramic films for implants in orthopedics, maxillofacial surgery and dental implants, thin ceramic membranes with controlled porosity, and antireflection coatings for solar cell collectors that show the industrial application of the TiO_2 nanostructure coating and the importance of the proposed method in this research.

Funding

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

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