Imitating nature in building up thermodynamically stable layers on metals for protection against corrosion

A. F. Batzias[1] & G. Batis[2]

[1]*Lab. of Simulation of Industrial Processes, Dept. of Industrial Management and Technology, University of Piraeus, Greece*
[2]*Section of Materials Science and Engineering, Dept of Chemical Engineering, National Technical University of Athens, Greece*

Abstract

By imitating the way that nature builds up thermodynamically stable layers to protect certain metals against corrosion, we can enhance the qualities of these metals and keep them in good condition during service. An algorithmic procedure that we have designed/implemented to facilitate/modify the natural process of passivation, can support/improve human expertise and provide the necessary information (by means of a Knowledge Base built *ad hoc*) for increasing effectiveness. Nevertheless, it is also proved that the higher the passivation achieved by increasing protective layer thickness, the higher the breakdown probability becomes; apparently, an optimal point of passivation exists, setting an applicability limit for corrosion engineers.

1 Introduction

Most metals are found in nature in the form of chemical compounds because this is a thermodynamically stable state for them. Among these compounds, oxides form the largest category. Metals and their alloys are very useful in every day life and the process of human civilization has past through periods characterized by the introduction and wide usage of a metal for first time (copper/bronze age, iron age). The separation of a metal (Me) from its oxide is achieved by reduction: e.g. $2Me_xO_y + yC \rightarrow yCO_2 + 2xMe$, where carbon serves as the reductive agent. During its useful time, the metal exhibits a natural tendency to

come back to its thermodynamically stable condition as oxide, mainly by means of a mechanism known as electrochemical corrosion: $2xMe + yO_2 \rightarrow 2Me_xO_y$. Nevertheless, several metals, as soon as they form a relatively thin oxide film on surface, stop further natural oxidation, because this film is thermodynamically stable and acts as a passivative agent which protects the rest of the metal from further deterioration (corrosion). Man is imitating this naturally occurring process of passivation to create similar protective layers under nearly the same mechanism and in a highly uniform structure to avoid irregularities (occurring in natural layers) which set up local electrochemical cells that promote corrosion.

In this work, we present (a) the design of a methodology for imitating Nature in building up thermodynamically stable layers on valve metals (Al, Ti, Zr, Ta, Bi, etc) and (b) an implementation of this methodology by producing aluminium anodic films with a honeycomb structure based on a 'natural' compact layer, properly modified for nanotechnology and electrical/electronic applications, including also the manufacturing of magnetic recording media, optical devices, functional electrodes, electrochromic and electroluminescence display devices. We also present experimental evidence from our recent laboratory work as well as thermodynamic calculations to show the barriers/ limitations that exist in trying to copy/modify/exploit Nature.

2 Methodology

The methodological framework presented herein has been designed on the basis of (i) the information extracted from technical literature and (ii) the accumulated experience during several years of working on corrosion control in our laboratories as well as in the field. For the sake of completeness, this framework includes 16 activity stages and 6 decision nodes (see Fig. 1 for their interconnection) although we do not implement all of them in every case under consideration. Most times, when the engineer omits implementing a stage, he/she has already taken into account its contribution to the project via a subconscious mechanism that uses implicit or tacit knowledge. Nevertheless, adopting a methodological framework facilitates (i) transforming part of implicit to explicit knowledge and (ii) creating/enriching a Knowledge Base to support/improve human expertise and provide the necessary information for training neural networks that may be used in stages 8, 10, 13, 14.

1. Determination of system under consideration (metal, function, natural environment, conditions of operation).
2. Search for natural conditions (and reveal of the corresponding mechanism) that develop spontaneously a natural passive surface layer (mainly oxide, hydride, chemical compound, adsorbed substance) protecting the metal against corrosion.
3. Study of surface structure with advanced testing techniques, e.g. Scanning Electron Microscopy (SEM) with X-ray microprobe analysis, Auger Electron Spectroscopy (AES), atomic force microscopy (AFM).

Figure 1: Flow chart of the algorithmic procedure designed for imitating nature in building up thermodynamically stable layers on valve metals (Al, Ti, Zr, Ta, Bi, etc), according to given specifications as regards corrosion resistance.

4. Reproduction of (nearly) the same 'natural' passive surface layer on the same metal in the laboratory under artificial conditions (not necessarily simulating the natural conditions but possibly having initially the natural physicochemical mechanism as a pilot).
5. Study of surface structure (like in stage 3) and processing of results to reveal the thermodynamically most stable pattern.
6. Laboratory testing under accelerated corrosion conditions; e.g. in a salt spray chamber or within experiments of stress corrosion cracking where the corrosive solution concentration and the anodic current density take values adequately high to reveal in a limited number of days or weeks what is expected to occur in several years of real service.
7. Search for artificial conditions that produce a structure which is not observed to build up under 'natural' conditions.
8. Search for combinations of other 'natural' conditions, which give certain similar structure, but significantly more uniform/ controlled and without defects.
9. Selection of other similar structures met in other domains in Nature.
10. Optimization of structure with functional criteria.
11. Dynamic mathematical modelling of the structure and evaluation of its stability as regard the main functional independent variables.
12. Production of surface layers that deviate from structural uniformity (first kind of order) to investigate their qualities/characteristics and function/behaviour under special conditions (e.g. semiconductive layers under weak electric or electromagnetic field or solar radiation).
13. Design of exogenous/endogenous measures of deviation.
14. Correlation of quality/functionality measures with the measures of deviation, to optimize characteristics/behaviour.
15. Parameter identification, incorporation to existing Physical Theory, checking for advancement in explainability/predictability.
16. Creation/Enrichment of Knowledge Base.
 P. Is the final surface structure adequately uniform?
 Q. Are the test results satisfactory?
 R. Have such artificial conditions been determined?
 S. Has such a combination of 'natural' conditions been determined?
 T. Is there a possibility for building a dynamic mathematical model?
 U. Is the correlation significant at a predetermined confidence level?

3   Implementation

The above described methodology has been successfully implemented in the case of building up thermodynamically stable anodic oxide layers on aluminium, primarily for protection against corrosion and secondarily for nanotechnology applications. The implementation of the first ten stages of methodology are described subsequently in some detail, as their content is of common interest for most purposes/applications of anodized aluminium.

1. The system under consideration is aluminium in natural and artificial environments, met during its surface treatment and useful life service. Consequently, the environment may be dry, wet or/and contaminated atmosphere, pure or salt or contaminated water, viscous liquids and detergents, oxide-solvent and oxide-nonsolvent electrolytes under strong agitation by mechanical stirring or bubbling, conductivity increasing additives, dying and sealing solutions at temperature levels up to the boiling point. The latter solutions contain $(CH_3COO)_2Ni$ or $Na_2Cr_2O_7$ (plain or with either Na_2CO_3 or $NaOH$).

2. The natural passive layer, which protects the metal against corrosion, is a hydrated aluminium oxide. Such hydrates are the α- and β-monohydrates and the corresponding trihydrates. The thickness of this natural layer is usually between and $5 - 15$ nm and does not exceed 30 nm, under normal conditions. In case that a breakdown of this film takes place, a differential aeration cell is setup according to electrochemical thermodynamics to repair the damage. The corresponding electrochemical semi-reactions are $3O_2 + 12e \rightarrow 6O^{2-}$ and $4Al - 12e \rightarrow 4Al^{3+}$, for cathode and anode, respectively; the two products are then combined to reform the natural passive layer: $4Al^{3+} + 6O^{2-} \rightarrow 2Al_2O_3$. The kinetics of the natural film formation follows in the long run the exponential law, with diminishing rate of oxidation over time. In the short run (about 2 hours exposition of fresh cleaned surface to atmosphere), a logarithmic kinetic equation fits better the data but this model is not taken into account as the time course to reach almost complete passivation is 100 hours, approximately.

3. Scanning Electron Miscroscopy (SEM) in combination with X-ray microanalysis is used to examine the topography of both, the outer surface and the inner interface between the natural oxide and the metallic substrate. In the latter case, the coating is stripped in a boiling solution of chromic acid and phosphoric acid. Carbon replicas and metallic shadows applied on surface in high vacuum increase resolution. Spatial mapping (using energy filtered imaging or high angle annular dark field microscopy) may provide additional information.

4. Reproduction of passive compact oxide surface layer on pure aluminium in the laboratory under artificial conditions: anodic oxidation in 3% tartaric acid plus ammonium hydroxide to bring the pH to $5.0 - 5.5$ (current density 2 A/dm^2, processing time 1 min, film thickness up to 500 nm, approximately) or 10% boric acid plus 0.1% borax.

5. Examination of surface structure (like in stage 3) and processing of results obtained by anodizing in different conditions to determine the thermodynamically most stable pattern and the economically most beneficial layer. These tasks can be achieved by determining optimal thickness either by means of thermodynamics under economic constraints or by means of economics under thermodynamic constraints. The latter method is dominant in industrial production of external and indoor building components made of aluminium (e.g. windows, double-glazing frames, patio doors, curtain walling, canopies, partition systems, grilles, fascias and shop fronts), as the

client or/and the market in general demand a low price product under certain technical specifications. Nevertheless, the former method is preferable for higher added value (measured as monetary units per anodizing area) components, like dry capacitors, where even minute defects should be avoided.

6. Performance of accelerated corrosion tests that can be correlated with long-term exposure under real service conditions. For very thin compact films, developed on alloys of poor corrosion resistance, such as the Duralumin – type alloys, the salt spray test (5 – 10% NaCl) is adequate. For thicker films, the breakdown of the passive coating by pitting, used as a measure of corrosion susceptibility, can be accelerated by the addition of acetic acid to a 3% NaCl solution to give a pH of 3.2 – 3.5. For thick corrosion resistant sealed porous films, the copper-accelerated acetic acid salt-spray (CASS) test should be applied (5% NaCl, 0.026% $CuCl_2$). Other tests can also be used, like (i) the cathodic dissolution (developed by the Ford Motor Co. of Detroit) by placing a drop of CASS solution over a small area of anodized surface which is made the cathode and applying a high DC potential between a Pt anode and the test panel and (ii) the electric charge passing through the film during a 5 minute test period under 40 V potential within a 5% formic acid bath.

7. The artificial conditions that can produce by anodic oxidation at small scale thicker layers of higher corrosion resistance are 12 – 24 mean voltage V, 1.5 – 4.5 A/dm^2 mean current density I, 2400 – 5700 Cb/dm^2 cumulative electric charge Q, resulting to 12 – 24 μm film thickness L. Theoretically, L is directly proportional to Q, but in practice a parabolic relation $L = f(Q)$ is valid with $dL/dQ < 0$ because of the dissolution of Al_2O_3 in the acid bath (sulphuric, chromic, oxalic, phosphoric). In artificial layer construction, the acid electrolyte and the electric current are the means through which the anodic oxide is formed, i.e. they play the role of the atmosphere and the spontaneous electric micro-cells when the natural layer construction is considered. The structure of the artificial anodic porous aluminium oxide can be described as a hexagonal close-packed array of columnar cells. The base of these cells consists of compact (non-porous) oxide, called generally 'barrier layer', with its thickness depended on the forming voltage and the kind of electrolyte (about 1.05 nm/V and 13.00 nm/V, for oxide-solvent and oxide-nonsolvent electrolyte, respectively). In large, industrial scale, a voltage of 80 – 100 is common while the bath temperature should be kept in the vicinity of 0°C if thick and hard oxide coatings are desirable. Under these conditions, the similar-to-natural compact layer may exceed 100 nm. To obtain thicker artificial layers that imitate the natural ones, oxide-nonsolvent electrolytes must be used (see stage 4).

8. Such combinations can be achieved by establishing homogeneity either in the anodizing means or/and on the metallic surface. In the first case, strict bath and operational control is necessary: for temperature ±1°C, for current density ±0.15 A/dm^2, for acid concentration ±0.2%; the corresponding ranges and the conditions for metallic substrate cleaning by means of alkaline

etching before anodizing can be determined through neurofuzzy estimation/control [1], as there are not explicit relations interconnecting these variables/parameters; the data set and the empirical rules used for training the neural network should come from the same etching and anodizing tanks as their geometry, agitation/cooling system and arrangement of anodes/cathodes are unique. In the second case, i.e. achieving homogeneity on the metallic surface, the initiation sites of pores can be laid out in lattice patterns of desired geometry by using an imprinting process. If square lattice patterns are used, instead of the 'natural' thermodynamically stable hexagonal ones, the shape of the pore remains square at the bottom (near the 'natural' compact layer) but becomes circular at the surface [2]. This means that Nature finds out the way to reach thermodynamic stability according to its original plan by keeping also the man-made origin unchanged.

9. Other similar structures based on the hexagonal pattern and caused by natural forces or created by living organisms include uniform corrosion of metals/ alloys (e.g. mild steel), and liquid-air foam and honeycomb. In the last case, it has been proved that the hexagonal shape is the most economical on beeswax; as the cells have to be the right size for the bee larvae, the volume and the length of each cell is fixed, leaving only the cross section to be optimized; according to a proof given only recently by Hales [3], regular hexagons provide the least-perimeter way to enclose infinitely many unit areas in a cross-section, implying directly least beeswax consumption. Similarly, bubble shapes evolve in a way that is most economical on energy, and this turns out to be the shape with the least surface area for a given bubble volume; therefore, an almost perfect liquid-air foam is expected to be an array of hexagons in a two dimensions domain, just like the cross-section of the honeycomb. Since energy and mass (i.e. wax) economy leads to the same spatial configuration, we conclude that thermodynamics can be used for modeling/examining these layers (see also Appendix II, for natural-type compact layers).

10. Optimization of structural characteristics (like thickness and porosity of the oxide film), can be achieved by fuzzy mapping of processing conditions on product qualities coupled with the inverse procedure which connects a product quality vector with all possible combinations of production condition vectors. The clustering/filtering of these combinations gives the alternatives among which a fuzzy multicriteria method can select the best [4].

The modeling of the porous anodic oxide (stage 11) is based on linear dependence of cell diameter D on voltage: $D = a_o + a_1V$, where a_o is the pore diameter and $a_1/2$ the wall thickness (according to [5], a_o = 12nm and $a_1/2 = 0.8$ nm/V for electrolyte of 15% sulphuric acid at 10°C, but linear regression on our results gives 9% and 24% higher values, respectively). Deviations from uniformity (stage 12) may result due to variations in the inclination of the pores above different crystal orientations in the aluminium substrate; a measure of deviation (stage 13) is obtained by counting number of pores appearing by tilting a stripped oxide film in relation to incident beam when an electron microscope is used in transmission mode; as optical examination of the original anodized

aluminium under polarized light gives a similar effect when the specimen is rotated [6], we can make correlations to obtain a measure of surface anisotropy (stage 14). For parameter identification and advancement in explainability/ predictability (stage 15) electronoptical, gravimetric and adsorption measurements (for such a combination, see [7]) should be combined within a KB (stage 16) which can be continually enriched endogenously via the interactive information lines depicted in Fig. 1 and exogenously via an intelligent agent [8]. Explainability can be also improved at a deeper knowledge level by examining the role of natural driving forces to the construction of the artificial-type film [9].

4   Discussion

The combination of stages 4, 7, 8 of the algorithmic procedure described above may result in the design of composite passivation layers with a uniform distribution of characteristics that can be easily measured directly or indirectly. Fig. 2 in Appendix I shows the dependence of current density I on anodizing time t, according to the new model $I = g / t + I_\infty [1 - \exp(-kt)]$, we have designed by synthesizing two simple laws, the hyperbolic and the declining exponential (the values of parameters g, I_∞, k have been estimated by means of nonlinear regression). Initially, a steep decrease of I is observed, indicating the development of the barrier layer, which is the compact oxide film corresponding to the natural passivation layer, formed under artificial conditions instead. I passes through a minimum and subsequently increases with a diminishing rate towards the asymptote I_∞ (which can be predetermined experimentally), representing the steady state of the artificial porous film growth. Consequently, this model depicts the transition from the natural-type to the artificial-type passivation which results in obtaining a uniform surface of a high thickness oxide (see Fig. 3) with enhanced properties. If natural-type passivation is required over all layer thickness L, then an oxide-nonsolvent electrolyte should be used. It is worthwhile noting that, as layer thickness L increases, the probability for film breakdown also increases, as it is shown through thermodynamic reasoning in the Appendix II, where a generalized model involving the impact of L on film pressure p is presented (for simplified modelling see [10-12]). This means that by imitating Nature we can improve certain qualities to a certain degree, after which we have to pay a price by undertaking an increasing risk.

5   Conclusions

We have designed an algorithmic procedure designed for imitating Nature in building up thermodynamically stable layers on valve metals (Al, Ti, Zr, Ta, Bi, etc), according to given specifications as regards corrosion resistance. The applicability of this procedure is proved by successful implementation in the case of passive films production on aluminium by means of anodic oxidation. A new specific model was designed/applied to show quantitatively the transition from

the natural-type to the artificial-type passivation. A generalized model was also used to prove, in thermodynamic terms, that by increasing the artificial-type film thickness, in order to improve corrosion resistance, the probability of layer breakdown increases. This means that by imitating Nature we can improve certain qualities to a certain degree, after which we have to pay a price by undertaking an increasing risk.
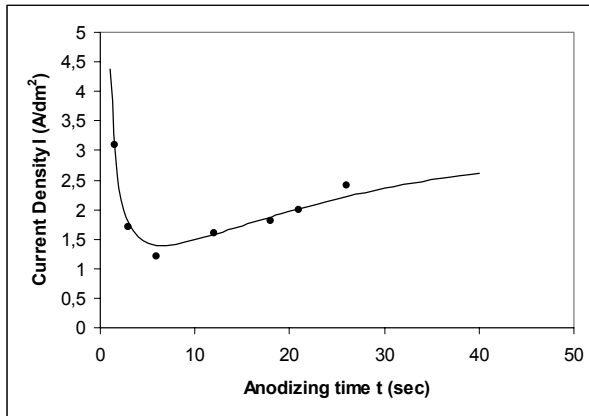
Appendix I

Figure 2: Dependence of I on t, depicting the transition from the natural-type to the artificial-type passivation; estimated parameter values $a = 4.243$, $k = 0.04181$ (st. dev. 0.1845, 0.002618, respectively), $R^2 = 0.9490$, standard error = 0.1348; $I_\infty = 3.10$ A/dm^2, experimentally determined.
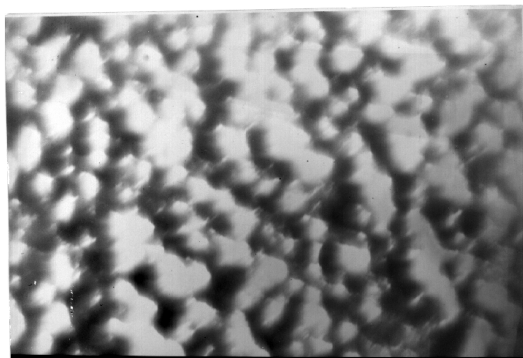

Figure 3: SEM image of outer surface of a thick artificial-type film based on a natural-type thin barrier-layer (carbon replica shadowed with gold in high vacuum); anodizing conditions: 15.2 V, 3.1 A/dm^2, 5600 Cb/dm^2, electrolyte H_2SO_4 15%, 20°C.

Appendix II

By exceeding the limits set by Nature as regards maximum thickness of passive layer, improvement of corrosion resistance is observed. Nevertheless, the rate of such an improvement decreases as thickness increases and breakdown of the passive layer may take place in higher thickness values. To establish the corresponding relation, we can start from the following thermodynamic equation [1,2]

$$dU' = TdS - p'dV - PVdE + \mu dN - Ad\gamma \tag{1}$$

where

$$U' = U + 2\pi P^2 V - \gamma A \tag{2}$$

$$p' = p - 2\pi P^2 \tag{3}$$

U = internal energy S = entropy
P = polarization of the film p = film pressure
V = volume of the film E = electric field
γ = film surface tension μ = chemical potential
A = area of the film N = number of molecules
T = absolute temperature   in the film

By taking the differential of the Gibbs-type function

$$G' = U' - TS + p'V = \mu N - \gamma A = \hat{\mu} N \tag{4}$$

and substituting it into (1), we obtain:

$$dp' = (S/V)dT + PdE + (A/V)d\gamma + \rho d\hat{\mu} + (\hat{\mu} - \mu)dN/V \tag{5}$$

where $\hat{\mu}$ is the integral chemical potential of molecules in the film, $\hat{\mu} - (\gamma A / N)$, and ρ the number density of the film, $\rho = N/V$.

For solving this differential equation, we use the empirical relation

$$P = bE^\alpha \tag{6}$$

and the assumptions referred in [2] to obtain by integration

$$p' = p'_o + bE^{\alpha+1}/(\alpha + 1) - \gamma/L \tag{7}$$

where p'_o is the integral constant and L the film thickness, $L = V/A$.

By combining (3) and (6) we obtain

$$p = p' + 2\pi(bE^\alpha)^2 \tag{8}$$

By combining (7) and (8) we obtain

$$p = p'_o + 2\pi(bE^\alpha)^2 + bE^{\alpha+1}/(\alpha + 1) - \gamma/L \tag{9}$$

For $\alpha=1$, eqn (9) is reduced to the model

$$p = p'_o + bE^2(1 + 4\pi b)/2 - \gamma/L \tag{10}$$

where $b = (\varepsilon - 1)/(4\pi)$ is now the electric susceptibility and ε the dielectric constant. This model has been cited for predictive modeling [3] although its derivation is heavily based on the rough approximation $P = (\varepsilon - 1)E/(4\pi)$, which might be considered only as a limiting case [4]. In both models, the generalized (9) and the simplified (10), the terms including E represent the electrostriction

effect while the last term represents the interfacial tension ant the layer thickness effects: by imitating Nature, we can increase layer thickness L, and consequently passivity, to increase general corrosion resistance but at the same time film pressure p increases implying decrease of specific corrosion resistance as the probability of layer breakdown at certain sites of the oxide film (where some kind of structural imperfection exists) increases.

References

[1] Batzias, A.F., Batzias, F.A., Computer aided neuro-fuzzy control in anodizing of aluminium, *Computer-Aided Chem. Engineering*, **10**, pp. 433-438, 2002.

[2] Hidetaka, A., Sachiko, O., Tomohito, H., Masashi, N., Hideki, M., "Growth of anodic porous alumina with square cells, *Electrochimica Acta*, **48(2-22)**, pp. 3171-3174, 2003.

[3] Hales, T.C., "The honeycomb conjecture", *Disc. Comp. Geom.* **25**, pp. 1-22, 2001.

[4] Batzias, A.F., Batzias, F.A., Computational and experimental process control by combining neurofuzzy approximation with multicriteria optimization, *Proc. 11th Intern. Conf. on Comput. Methods and Experimental Measurements* by C.A. Brebbia, et al (Eds.), WIT Press, 2003, pp. 107-118.

[5] Keller, F., Hunter, M.S., Robinson, D.L., "Structural features of oxide coatings on aluminium", *J. Electrochem. Soc.*, **100**, pp. 411-419, 1953.

[6] Franklin, R.W., Stirland, D.J., Studies on the structure of anodic oxide films on aluminium, II, *J. Electrochem. Soc.*, **110(4)**, pp. 262-267, 1963.

[7] Paolini, G., Masoero, M., Sacchi, F., Paganelli, M., An investigation of porous anodic oxide films on aluminium by comparative adsorption, gravimetric and electronoptical measurements, *J. Electrochem. Soc.*, **112(1)**, pp. 32-38, 1965.

[8] Batzias, F.A., Marcoulaki, E.C., Restructuring the keywords interface to enhance computer aided process engineering knowledge acquisition via an intelligent agent, *Computer-Aided Chem. Engineering*, **10**, pp.829-834, 2002.

[9] Jessensky, O., Muller, F., Gosele U., "Shelf-organized formation of hexagonal pore arrays in anodic alumina", *Applied Physics Letters*, **72(10)**, pp. 1173-1175, 1998.

[10] Sato, N., A theory for breakdown of anodic oxide films on metals, *Electrochimica Acta*, **16**, pp. 1683-1692, 1971.

[11] Hill, T.L., *An introduction to Statistical Thermodynamics*, Addison Wesley: London, p. 201, 1960.

[12] Hoeppner, D.W., Chandrasekaran, V., Corrosion and Corrosion Fatigue Predictive Modelling – State of the Art Review, (Research Program "Modelling Corrosion Growth on Aircraft Structure" USAF) FASIDE Intern. Inc. Salt Lake City UT, 1998, p.35.