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Experimental Design and Response Surface Analysis as Available Tools for Statistical Modeling and Optimization of Electrodeposition Processes

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1. Introduction

Electrodeposition, also called electroplating, is one of the most commonly used methods for metal and metallic-alloy film preparation in many technological processes. This method is generally considered an economically interesting and easily controlled process to protect and enhance the functionality of parts used in diverse industries (home appliances, jewelry, automotive, aircraft/aerospace, and electronics) in both decorative and engineering applications. It promotes the appearance, extends the life, and improves the performance of materials and products in different media (Schwartz, 1994; Oriňáková et al., 2006).

Despite these applications, electrodeposition methods have, for decades, been industrially regarded as a means for the mass production of cheap materials and not for the production of advanced materials with high values. Their use has been limited to surface protection or plating of decorative metallic layers (Yoshida et al., 2009). The evolution of modern technology, however, has created increased demands on the structures and properties of deposits and directed the emphasis of electrodeposition mainly toward engineering processes and materials technology. Electrodeposition is now regarded as a state-of-the-art technology. For example, electrodeposited Cu is the material of choice for the interconnects in ultra-large-scale integrated (ULSI) circuits, and electrodeposited soft magnetic alloys are an important component of magnetic recording heads (Schwarzacher, 2004; Yoshida et al., 2009). In fact, the deposition of alloy coatings is one of the most rapidly expanding topics in the current literature (Oriňáková et al., 2006; Santana et al., 2006, 2007; Dubent, 2007; Ferreira et al., 2007; Silva et al., 2008; Brankovic et al., 2009; Gupta & Podlaha, 2010, Düzgün et al., 2010). Compared to the electrodeposition of a single metal, alloy coatings show better properties because their chemical composition can be varied to the required function. Alloy coatings are denser, harder, generally more resistant to corrosion, possess better magnetic properties and are suitable for subsequent coating by electrodeposition (Senna et al., 2003; Santana et al., 2006).

Nanostructured coatings, with their advanced properties, can also be produced by electrodeposition, where the nanoparticles are directly attached to the substrate.

Electrodeposition is considered a simple, fast, and inexpensive method and is among the most familiar binder-free techniques employed for the preparation of nanoparticles. In comparison to other techniques, the particle size, crystallographic orientation, mass, thickness, and morphology of the nanostructured materials can be controlled by adjusting the operating conditions and bath chemistry. These nanostructured coatings offer great potential for various applications because of their superior characteristics relative to those of conventional coatings (Mohanti, 2011; Lu & Tanaka, 1996; Huang. & Yang, 2005; Finot, et al., 1999; Gurrappa & Binder, 2008). In addition, recent research has been focused on demonstrating the feasibility of the co-deposition of ceramic materials with metals and polymers to create opportunities for the preparation of novel hybrid nanomaterials and nanostructures. Nanohybrid coatings result from the development of novel electrochemical strategies. These coatings exhibit advantageous properties compared with those of individual materials. The coatings also exhibit properties that cannot be obtained by other methods or with single-phase materials (Gurrappa & Binder, 2008; Tsai et al., 2010; Mosavat et al., 2011).

However, the production of the electrodeposited coatings, especially the alloys and hybrid coatings, is always a complex process. For each application, several critical parameters (chemical and operational) must be accurately controlled to fulfill the required characteristics of the produced coating. The conventional and classical methods of studying a deposition process are usually univariate methods in which most of the deposition parameters are maintained at constant values while one of them is varied in a chosen direction. The use of univariate methods means that, in practice, the best parameter values are often chosen empirically, and the coatings are then produced at "optimum conditions," which may not represent the best conditions to obtain the desired coating properties (Ferreira et al., 2007). In addition, these experiments are time consuming, requiring a large number of experiments, and also produce substantial amounts of wastewater. Moreover, the influence of the combined parameters on the studied variables is not evaluated, which confirms that the optimum levels determined by these methods are generally unreliable (San Martín et al., 1998; Rabiot et al., 1998; Santana et al., 2007a, Santana et al., 2007b). Therefore, to ensure greater reproducibility and quality, the development of a more scientific approach that leads to a better understanding of alloy deposition phenomena is important.

One way to achieve a better approach, given the complexity of the deposition processes, is to use experimental design, response surface methodology, and other statistical techniques, in which all the parameters are varied simultaneously, showing the responses of their synergic and antagonistic interactions. These methodologies both drastically reduce the number experiments needed to optimize the process and give statistical inference on the optimum deposition conditions (Rabiot et al., 1998). These methodologies also allow improvements in both process performance and reliability, thereby decreasing the cost and the volume of produced wastewater in addition to leading to the creation of new coatings systems that can fulfill industrial needs (Ferreira et al., 2007; Santana et al., 2007a). Nevertheless, these tools are not extensively used to enhance the quality of the proposed electrodeposition baths or to achieve realistic optimized conditions, and the reports found in the literature are still related to few research groups. This work presents a review concerning the statistical approach for performing one or multi-responses experiments and

its application to the electrodeposition processes of metal and alloy coatings. Therefore, the main topics covered by this review will be the following:

- An overview of the electrodeposition process and the conventional methods used in the literature to perform a study concerning the production of metallic, alloy and hybrid coatings;
- A screening concerning factorial experimental designs and how these designs can be used in electrodeposition processes;
- The surface response method for one response variable or for multi-response variables;
- The optimization of the electrodeposition process using a statistical approach;
- The main results presented in the literature concerning the above-mentioned statistical topics applied to the electrodeposition of metal, hybrid, and alloy coatings.

2. Conventional and classic methods for the study and optimization of electroplating conditions

The production of coatings using electrodeposition was developed in the 1800s and is still considered a simple, low-cost and easy operational process. At a minimum, the electrodeposition of a single metallic coating requires an electrolyte containing the reducible metal ion, a conductive substrate, a counter electrode, a power supply, and a container to hold the electrolyte and electrodes. This simplicity accounts for the appeal of electrodeposition, but may also lead to some basic controls that are needed to ensure reproducibility being neglected (Jeerage & Schwartz, 2004). Different substrate preparations, stirring speeds, applied current densities (or potentials), and deposition temperatures, for example, are some parameters that must be well controlled to produce a coating with the desired qualities and to guarantee reproducibility. When an alloy or a hybrid coating is being produced, or even when a complexant agent or additives are included in the electrolytic bath, the complexity of the electrodeposition process increases, and the control of deposition parameters becomes more critical.

The literature contains several reports that propose electrolytic baths and electrodeposition processes for the production of different kinds of coatings for numerous applications. Figure 1 shows the main parameters that usually need to be controlled in an electrodeposition process. The kind of substrate used, the finish process used to prepare the substrate, the electrolyte composition (with respect to different ions and/or ion concentrations, additives, complexant agents, etc.), the physico-chemical characteristics of the solution (e.g., pH or conductivity), the mode of current used, and other parameters such as temperature or stirring speed can, together or individually, affect the quality and the properties of the produced electrodeposits. In general, most of the reports in the literature have involved the use of conventional univariate methods to study the influence of the deposition parameters on the deposition mechanisms and the coating properties. In these studies, each of the previously discussed parameters has been investigated separately while the others have been held at constant values. The best results obtained under the given conditions were then used to study the effects of another parameter, and so on. Few works include any kind of statistical evaluation, and those that do primarily present the average value and standard deviation. However, it is important to note that the obtained responses of the studied variables are valid only for the chosen experimental conditions. Examples from the literature can be found in later sections of this text.
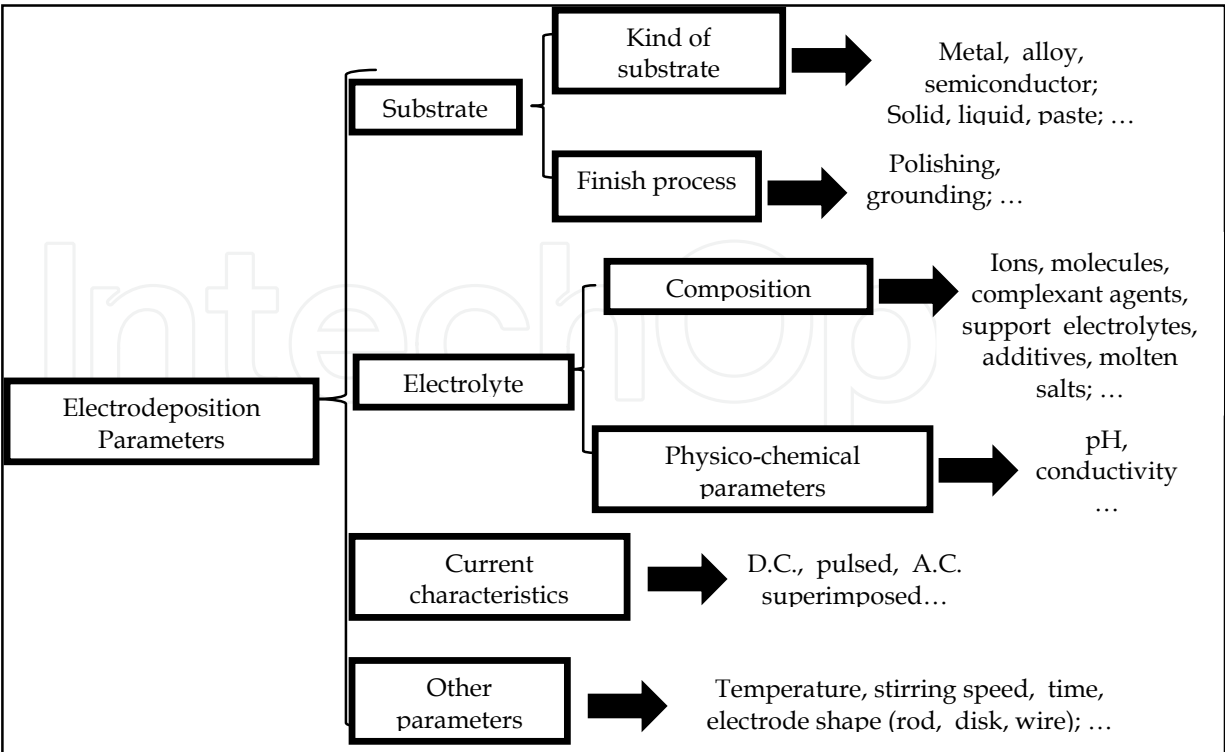
Fig. 1. Main parameters usually controlled in an electrodeposition process.

2.1 Evaluation of the kind of substrate and/or the finish process in the electrodeposition process

Both the kind of substrate used and its finish process may cause differences in the electrodeposition process by influencing the morphology, the growth process, and other properties of the coatings. The substrate and finish process are particularly important when alloys and nanomaterials are produced or when a mechanism is developed. For example, Gomez & Vallés (1999) have noted that the initial stages of the electrodeposition of Co–Ni alloys were influenced by the kind of substrate used. The nucleation and three-dimensional growth, which resulted in compact, fine-grained and homogeneous deposition, occurred in all substrates, with preferential deposition of cobalt and anomalous co-deposition. Concerning the electrodeposition of Zn–Co alloys, Roventi et al. (2006) have observed no significant changes in the polarization curves and the composition of the coatings when the mild steel substrate was changed to platinum. On the contrary, when the substrate tested was glassy carbon, a strong decrease in current density was noted, which started to increase only when the electrode surface was completely covered by the alloy. This behavior was related to a strong inhibition of the deposition process on the glassy carbon cathode.

The properties of the substrate can also influence the coating characteristics. Kim et al. (2009) have shown that the substrate conductivity greatly affected the structural and optical properties of ZnO nanorods produced by cathodic electrodeposition: more conductive substrates favored the growth of high-quality ZnO nanorods at low temperature (80 °C). In addition, studying the effects of Zn substrate finish on the production of ZnO nanoplates, Illy et al. (2005) have observed that the as-received or mechanically polished Zn substrate was the most suitable substrate finish and allowed more highly aligned, dense structures to

be grown, whereas electropolished substrates formed inhomogeneous deposits. The investigations concerning this topic are generally performed by changing the substrate and/or its finish treatment while keeping all other parameters constant.

2.2 The effects of other deposition parameters on the coating properties

Because each system substrate/coating may exhibit a different behavior for each electrolyte used, the electrolyte composition, pH and (less often) conductivity are also important and typically studied parameters that can affect the electrodeposition process. Changes in the electrodeposition process occur if only one cation, several cations, or even dispersed particles are present in the electrolyte. Moreover, the solution pH and conductivity, as well as the presence of complexant agents and/or additives, are parameters considered when a new system is under investigation. Other parameters, such as current density, deposition potential, deposition temperature, and stirring speed are also studied. Several works may be used as examples to demonstrate the methodologies usually found in the literature to evaluate these parameters and attempt to find optimum conditions to produce the metallic/alloy/hybrid coatings.

The effects of additives and complexant agents on electrodeposition baths for deposition of metallic and alloy coatings has been investigated by a number of authors. For example, Healy & Pletcher (1998a, 1998b) have shown that the studied additives (Cl-, polyethylene glycol, and 4,5-dithiaoctane-l,8-disulfonic acid) adsorbed on the electrode at different deposition potentials and stirring speeds influences in the copper reduction mechanism. Similar results were observed by Bozzini et al. (2006) and Tantavichet & Pritzker (2006), who studied the effects of polyethylene glycol and benzotriazole, respectively. Nayana et al. (2011) have investigated the influence of additives on the morphology and brightness of nanocrystalline zinc electrodeposited from an acid sulfate bath. The mechanism of zinc deposition also changed in the presence of the additives. Drissi-Daoudi et al. (2003) have studied the influence of several complexant agents on the copper deposition mechanism and showed that the kind of complex formed (strong- or weak-field complex) affected the reduction potential of the metallic ion. The electrodeposition of Cu–Zn alloy on carbon steel from pyrophosphate-base baths in the presence of additives has been investigated by Senna et al. (2003) and Senna et al. (2005). The authors chose one stirring speed and pH value, whereas the bath composition and the current density were varied. Their results have shown that the alloy coating composition, the coating morphology, hardness and corrosion resistance were dependent on these two parameters. Coating compositions similar to that of bulk brass (70 % m/m Cu and 30 % m/m Zn) were obtained from baths that contained allyl alcohol as an additive.

The composition of the electrodeposition bath has been widely studied, in combination with the effects of pH, current density (or applied potential), temperature and stirring speed, as a means of controlling the coating composition and properties. Takata & Sumodjo (2007) have observed the effects of pH and the $[Co^{2+}]/[Pd^{2+}]$ ratio on the composition, morphology and magnetic properties of electrodeposited Co–Pd thin films from a glycine bath. Initially, the pH was kept constant while the $[Co^{2+}]/[Pd^{2+}]$ ratio was varied. As a result, the current efficiency was not affected, whereas the alloy composition changed, which resulted in an increase in the Pd content in the coating. Under these conditions, cracks were always observed, and increasing palladium content in the Co–Pd alloy resulted in deposits with

more cracks. The magnetic properties also changed with the increase in Pd content in the coating. Then, the authors maintained the bath composition and varied the pH between 6.5 and 9.4, which did not change the current efficiency or coating composition. All morphological and magnetic changes were related to other parameters (in this case, current density). While investigating the electrodeposition of hybrid coatings, Wu et al. (2004) have demonstrated the influence of the plating parameters on the electrodeposition of a Co–Ni–Al$_2$O$_3$ composite from a sulfamate electrolyte. Similar to the methods in previously discussed investigations, certain parameters were kept constant (such as the solution pH, deposition temperature, and current density) while others were varied separately (the cobalt concentration and the alumina concentration in the bath, for example). The authors were able to determine the best conditions to produce composite coatings with the maximum alumina content.

The current characteristics also affect the coating composition and morphology and need to be controlled to produce coatings with the desired properties. Vicenzo et al. (2010) have compared the tin deposition process from a commercial bath using direct and pulsed current. The authors noted several differences in the microstructure and in the properties of the coating after the application of pulsed current. Moreover, changes in the duty cycle and in the frequency of the pulsed current deposition mode also affected the cathodic efficiency and the coating microstructure. Ramanauskas et al. (2008) have studied the deposition of Zn–Ni, Zn–Co, and Zn–Fe alloys using pulsed current mode. The authors performed the electrodeposition experiments by varying one parameter at a time, with the other parameters being fixed at standard levels. The plating parameters studied included the peak cathodic current, i_p, the time of current on, t_{on}, and the time of current off, t_{off}. The coating compositions—mainly the zinc content in the studied alloy coatings—were strongly affected by these parameters. Topographic and phase changes were also noted. The best parameters for each alloy coating deposition were determined, and the coatings were produced on a steel substrate under their respective optimum conditions. The polarization curves of these coating/substrate systems were obtained in a naturally aerated NaCl + NaHCO$_3$ solution at pH = 6.8. The lowest i_{corr} values under all deposition conditions were exhibited by Zn–Ni coatings, whereas Zn–Co and Zn–Fe, except for t_{off} variation, exhibited similar corrosion resistance.

The previously discussed works and several other studies found in the literature produced valid and consistent results that can contribute to a better comprehension of the electrodeposition process and the mechanisms involved in the reduction of one or more ions in an aqueous bath. However, the use of univariate methods cannot allow the evaluation of simultaneous effects of more than one deposition parameter on the same variable. This limitation means that the joint effects of simultaneous variations in bath composition, current density, and temperature, for example, cannot be obtained by these methods. Consequently, the optimum conditions determined by variation of one of these parameters at time may not always represent the real process.

3. Optimization strategies and multivariate approach as a means for enhancing electrodeposition processes

Optimization strategies are procedures followed when, for instance, a product or a process is to be optimized. In an optimization, one tries to determine the optimal settings or conditions for a number of factors. Factors are parameters than can be set and reset at given

levels, e.g., temperature, pH, reagent concentrations, reaction time, etc., and that affect the responses of a product or process. The factors and their level ranges form the experimental domain within which the global optimum is sought. Factors also might "interact." For instance, a two-factor interaction occurs when the influence of one factor on the response is different at different levels of the second factor.

When only one factor needs to be optimized, a simple univariate procedure is performed. Nonetheless, two or more factors are typically studied using either univariate or multivariate optimization strategies (Massart et al., 1997).

An applied univariate procedure, as previously discussed, is the one-variable-at-a-time (OVAT) approach, where only one factor at a time is varied and optimized. The OVAT procedure, however, has some disadvantages: interactions between factors are not taken into consideration; many experiments are needed when the number of factors increases; only a small part of the experimental domain is analyzed; the global optimum might not be found; and the found optimal conditions might depend on the starting conditions (Massart et al., 1997).

However, a multivariate approach varies several factors simultaneously. Multivariate approaches are subdivided into sequential and simultaneous procedures (Massart et al., 1997). Sequential procedures involve a few initial experiments and use their results to define the subsequent experiment (s) (Dejaegher & Vander Heyden, 2009). Sequential approaches can be applied when the experimental domain containing the optimum is *a priori* unknown, but are limited to the optimization of only one response. Simultaneous procedures perform a predefined number of experiments according to a well-defined experimental set-up, e.g., an experimental design (Massart et al., 1997).

An experimental design is an experimental setup to simultaneously evaluate numerous factors at given number of levels in a predefined number of experiments. Rigorously, experimental designs can be divided into screening designs and response surface designs. Screening designs involve screening a relatively large number of factors in a relatively small number of experiments. They are used to identify the factors with the strongest influence. Typically, the factors are evaluated at two levels in these designs. Response surface designs are used to find the optimal levels of the most important factors (which are sometimes selected from a screening design approach). In these designs, factors are examined at a minimum of three levels. The optimal conditions are usually derived from response surfaces build with the design results.

The optimization of a method is often divided into screening and optimization phases. During the screening phase, all factors that potentially influence the responses of interest are tested to indicate those with the largest effects. These most important factors are then further explored in the optimization phase, where their best settings, i.e., the optimum conditions, are determined. Screening and response surface designs, respectively, are applied in these steps (Massart et al., 1997).

After optimization, the method should be validated, i.e., evaluated whether it can be applied for its intended purpose (s). One of the method validation items is robustness testing, which evaluates the effects of small changes in the factors on the considered responses and which applies screening designs for this purpose (Dejaegher & Vander Heyden, 2009; Montgomery, 2005).

The classic screening and response surface designs are now presented. Some applications in electroplating processes will be further discussed in the context of process optimization.

3.1 Screening designs

Screening designs are used to indicate the most important factors from those that potentially influence the considered responses. Screening designs are applied in the context of optimizing separation techniques during screening and in robustness testing, and in the context of optimizing processes. Most often, two-level screening designs, such as fractional factorial design, are used (Montgomery, 2005), which allow the examination of a relatively large number of factors f at L = 2 levels in a relatively small number of experiments (N ≥ f + 1). When f is small, two-level full factorial designs might also be applied for screening purposes (Montgomery, 2005). These designs allow the simultaneous investigation of qualitative and quantitative factors.

3.2 Two-level full factorial designs

A two-level full factorial design contains all possible combinations between the f factors and their L = 2 levels, leading to N = L^f = 2^f experiments to be performed. Suppose that three factors, A, B, and C, each at two levels, are of interest. The design is called a 2^3 factorial design, and the eight treatment combinations are shown in Table 1. Using the "-1 and 1" notation to represent the low and high levels of the factors, we list the eight runs in the 2^3 design as in Table 1. This is sometimes called the design matrix. These designs allow the estimation of all main (i.e., of the factors) and interaction effects between the considered factors (Montgomery, 2005). The interaction effects are calculated from the columns of contrast coefficients (Table 2).

Run no.	Factors		
	A	B	C
1	-1	-1	-1
2	1	-1	-1
3	-1	1	-1
4	1	1	-1
5	-1	-1	1
6	1	-1	1
7	-1	1	1
8	1	1	1

Table 1. The 2^3 two-level full factorial design for 3 factors

3.3 Two-level fractional factorial designs

A two-level fractional factorial 2^{f-v} design contains a fraction of the full factorial design, and allows examining f factors at two levels in N = 2^{f-v} runs, with $1/2^v$ representing the fraction of the full factorial (v = 1, 2, 3, . . .) (Table 3) (Montgomery, 2005). For fractional factorial designs, N is a power of (N = 8, 16, 32, . . .). Because only a fraction of a full factorial design is carried out, some information is lost.

Run no.	Contrast coefficients			
	AB	AC	BC	ABC
1	1	1	1	-1
2	-1	-1	1	1
3	-1	1	-1	1
4	1	-1	-1	-1
5	1	-1	-1	1
6	-1	1	-1	-1
7	-1	-1	1	-1
8	1	1	1	1

Table 2. The columns of contrast coefficients for the interactions

It is important to note that not all main and interaction effects can be estimated separately anymore. Some effects are confounded, meaning that they are estimated together (Table 3). For instance, in a half-fraction factorial design, each estimated effect is a confounding of two effects.

Run no.	Factors				Contrast coefficients		
	A	B	C	D	l_1	l_2	l_3
1	-1	-1	-1	-1	1	1	1
2	1	-1	-1	1	-1	-1	1
3	-1	1	-1	1	-1	1	-1
4	1	1	-1	-1	1	-1	-1
5	-1	-1	1	1	1	-1	-1
6	1	-1	1	-1	-1	1	-1
7	-1	1	1	-1	-1	-1	1
8	1	1	1	1	1	1	1

Table 3. The 2^{4-1} fractional factorial design for 4 factors, and the columns of contrast coefficients that can still be constructed. A = BCD, B = ACD, C = ABD, D = ABC, I_1 = AB + CD, I_2 = AC + BD, I_3 = AD + BC.

3.4 Supersaturated designs as screening designs

A saturated design is defined as a fractional factorial in which the number of factors or design variables k is given by $k = N – 1$, where N is the number of runs. Recently, considerable interest has been shown in the development and use of a supersaturated design for factor screening experiments. In this design, the number of variables k is $k > N – 1$, and these designs usually contain more variables than runs (Montgomery, 2005).

Supersaturated designs have not found popular use. They are, however, an interesting and potentially useful method for experimentation with systems that involve many variables and where only a very few of these variables are expected to produce large effects (Montgomery, 2005). Their application in the screening design for electroplating processes has not yet been reported.

3.5 Response surface designs

The most important factors—either found from screening or known from experience—are investigated in more detail using response surface designs. These, in fact, are used to determine the optimal conditions for the factors. In these designs, only quantitative and mixture-related factors are examined because the responses considered are modeled as a function of the factors. The response surfaces are then visualized. Most often, only two or three factors are further explored. For more than two factors, only fractions of the entire response surface are visualized (Massart et al., 1997; Montgomery, 2005).

Response surface methodology, by definition, is a collection of mathematical and statistical techniques that are useful for the modeling and analysis of problems in which a response of interest is influenced by many variables; the aim is to optimize this response (Montgomery, 2005). For example, suppose that a plating engineer wishes to find the levels of current density (x_1) and stirring rate (x_2) that maximize the yield (Y) of a process. The process yield is a function of the levels of current density and stirring rate, such as (Equation 1)

$$y = f(x_1, x_2) + \varepsilon \tag{1}$$

where ε represents the error observed in the response y. If we denote the expected response by (Equation 2)

$$E(y) = f(x_1, x_2) = \eta \tag{2}$$

then the surface represented by $\eta = f(x_1, x_2)$ is called a response surface.

The response surface designs can be divided into symmetrical and asymmetrical designs, depending on their appropriateness for use in an asymmetrical domain (Massart et al., 1997; Montgomery, 2005).

3.6 Symmetrical designs

Symmetrical designs cover a symmetrical experimental domain. They contain, for example, three-level full factorial and central composite designs. Often, in these designs, the central point is replicated 3–5 times, usually to estimate the experimental error. A three-level full factorial design contains all possible combinations between the f factors and their $L = 3$ levels, which leads to $N = L^f = 3^f$ runs, including one central point. Thus, for two factors, 9 runs are needed, whereas the inclusion of three factors requires 27 runs (Montgomery, 2005).

A central composite design (CCD) contains a two-level full factorial design (2^f runs), a star design ($2f$ experiments) and a central point, which requires $N = 2^f + 2f + 1$ runs to investigate f factors (Massart et al., 1997; Montgomery, 2005). Thus, for two factors, 9 runs are needed, whereas for three factors, 15 are needed. The points of the full factorial design are situated at the factor levels −1 and +1, those of the star design are situated at the factor levels 0, −α and + α, and the central point at the factor levels is situated at 0. Depending on the α value, two CCDs exist, i.e., a face-centered CCD (FCCD) with $|\alpha| = 1$, which examines the factors at three levels, and a circumscribed CCD (CCCD) with $|\alpha| > 1$, which examines the factors at five levels. For a so-called rotatable CCCD, the α level should be $|\alpha| = (2^f)^{1/4}$, i.e., 1.41 and 1.68 for 2 and 3 factors, respectively (Massart et al., 1997; Montgomery, 2005).

A Box–Behnken design contains N = (2f (f − 1)) + 1 runs, of which one is the center point (Montgomery, 2005). For two factors, no design is described. For three factors, 13 runs are described to be performed (Table 4).

Run no.	Factors		
	A	B	C
1	1	1	0
2	1	-1	0
3	-1	1	0
4	-1	-1	0
5	1	0	1
6	1	0	-1
7	-1	0	1
8	-1	0	-1
9	0	1	1
10	0	1	-1
11	0	-1	1
12	0	-1	-1
13	0	0	0

Table 4. Box–Behnken design for 3 factors

A Doehlert (uniform shell) design has equal distances between all neighboring runs (Doehlert, 1970). The Doehlert design for two factors consists of the six vertices of a hexagon with a center point, which requires N = 7 experiments. The design for three factors consists of a centered dodecahedron, which requires N = 13 runs (Table 5). Contrary to the aforementioned response surface designs, the factors are varied at different numbers of levels, e.g., one at three and one at five levels in the two-factor design, and one at three, one at five, and one at seven levels in the three-factor design.

Run no.	Factors		
	A	B	C
1	1	0	0
2	0.5	0.866	0
3	0.5	0.289	0.816
4	-1	0	0
5	-0.5	-0.866	0
6	-0.5	-0.289	-0.816
7	0.5	-0.866	0
8	0.5	-0.289	-0.816
9	0	0.577	-0.816
10	-0.5	0.866	0
11	-0.5	0.289	0.816
12	0	0.577	0.816
13	0	0	0

Table 5. Doehlert designs for three factors

3.7 Asymmetrical designs

When an asymmetrical domain should be investigated, asymmetrical designs, such as designs constructed with the uniform mapping algorithm of Kennard and Stone, can be applied (Massart et al., 1997; Kennard, 1969). These designs are called asymmetrical because when their experiments are plotted, they result in an asymmetrical shape when an asymmetrical domain is studied. These designs can also be used in a symmetrical domain, and then a symmetric shape may be obtained. Asymmetric designs are used because symmetric designs in an asymmetric domain are problematic: either they are too large and require experiments in an impossible area, or they are too small and a considerable part of the domain is not covered (Massart et al., 1997; Montgomery, 2005).

Most often, from a response surface design, the general model build for *f* factors is (Equation 3)

$$y = \beta_0 + \sum_{i=1}^{f} \beta_i x_i + \sum_{i=1}^{f} \beta_{ij} x_i x_j + \sum_{i=1}^{f} \beta_{ii} x_i^2 \qquad (3)$$

where y is the response, β_0 is the intercept, β_i are the main coefficients, β_{ij} are the two-factor interaction coefficients, and β_{ii} are the quadratic coefficients. Occasionally, the interaction terms are restricted to two-factor interactions ($x_i x_j$) and the higher-order interactions are neglected, as in Equation 3. Occasionally, the non-significant terms of the model are deleted after a statistical analysis.

3.8 Data interpretation

3.8.1 Screening designs

From the results of a full factorial or fractional factorial design, the effect of each factor *X* on each response *Y* is estimated as shown in Equation 4:

$$E_X = \frac{contrast}{n2^{k-1}} \qquad (4)$$

where E_x represents the effect or interaction, *n* is the number of replicates and *k* is the number of variables or factors.

Generally, a regression model estimates the relation between *N x 1* response vector **y**, and the *N x t* model matrix **X**, where *N* is the number of design runs, and *t* is the numbers of terms included in the model. The model matrix is obtained by adding a column of ones before the *t – 1* design matrix columns, which consists of coded factor levels and the column of contrast coefficients, as defined by the experimental design (Equation 5):

$$y = (X\beta) + \varepsilon \qquad (5)$$

where **β** is the t x 1 vector regression coefficients and **ε** is an error vector. The regression coefficients, **b**, are calculated using least squares regression (Equation 6):

$$b = (X^T X)^{-1} X^T y \qquad (6)$$

where $\mathbf{X^T}$ is the transposed matrix of $\mathbf{X}$.

Because effects estimate the change in response when the factor levels are changed from -1 to $+1$ and the coefficients are between levels 0 and $+1$, both are related as follows (Equation 7):

$$E_X = 2b_X \qquad (7)$$

Usually, a graphical and/or statistical interpretation of the estimated effects is performed to determine their significance. Graphically, normal probability or half-normal probability plots can be drawn (Montgomery, 2005). In these plots, the unimportant effects are found on a straight line through zero, whereas the important effects deviate from this line.

The statistical interpretations usually involve a calculation of a *t-test* statistic for the factors (Equation 8) and a comparison between this *t-value* and a limit value, $t_{critical}$, or between the effect E_X and a critical effect, $E_{critical}$, respectively. All effects that are greater than or equal to this $E_{critical}$ in absolute value are then considered significant (Montgomery, 2005):

$$t = \frac{\left|E_X\right|}{(SE)_e} \Leftrightarrow t_{critical} \qquad (8)$$

with $(SE)_e$ being the standard error of an effect. The critical t-value, $t_{critical}$, depends on the number of degrees of freedom associated with $(SE)_e$ and on the significance level, usually $p = 0.05$. The critical effect, $E_{critical}$, is then obtained as follows (Equation 9):

$$E_{critical} = t_{critical}(SE)_e \leftrightarrow \left|E_X\right| \qquad (9)$$

The standard error of an effect, $(SE)_e$, can be estimated from different data: from the variance of replicated runs, from *a priori* declared negligible effects, or from *a posteriori* defined negligible effects. We consider the last two approaches the most appropriate for the proper estimation of $(SE)_e$.

3.8.2 Optimization using the desirability function

Many response surfaces imply the analysis of several responses. The simultaneous consideration of multiple responses involves first building an appropriate response surface model for each response and then attempting to find a set of operating conditions that, in some sense, optimizes all responses or at least keeps them within desired ranges. A useful approach to the optimization of multiple responses is the use of the simultaneous optimization technique popularized by Derringer and Suich (Derringer & Suich, 1980). Their procedure makes use of desirability functions. The general approach is to first convert each response Y_i, into an individual desirability function d_i that varies over the range $0 \le d_i \le 1$, where if response Y_i is at its goal or target, then $d_i = 1$, and if the response is outside an acceptable region, $d_i = 0$. Next, the design variables are chosen to maximize the overall desirability, $D = (d_1 \times d_2 \times ... \times d_m)^{1/m}$, where there are *m* responses (Ferreira et al., 2007).

4. The main results presented in the literature concerning the use of statistic methods in electrodeposition

In the 1990s, optimization started to be essential for development of cheap and rapid process technologies. The need for more refined and functional materials, led by the electronics industry, increased the requirements for process control in electrodeposition and stimulated the use of statistical approaches for the optimization of deposition parameters. Furthermore, experimental designs had already found widespread applications in the physical sciences, mainly because of the development of sophisticated and dedicated software for statistical analyses and numerical simulations. Another factor that contributed to the increase in research using experimental design was the extensive and world-wide use of personal computers with Internet access, mainly at the end of the 1990s. Since then, the number of works found in the literature concerning experimental design, response surface methodology, and other statistical evaluations in electrodeposition processes increased considerably. These works include the evaluation of several deposition parameters in the coatings' properties and/or in their formation mechanisms. The statistical packages of well-known software and dedicated statistics programs are now used, which also enhance the presentation of the results and the response surface designs diagrams.

In the context of optimizing electrodeposition processes, the application of screening and response surface designs has already been discussed and reviewed frequently (Bezerra et al., 2008; Ferreira et al., 2004). For screening, primarily two-level full factorial (Santana et al., 2006; 2007a; 2007b; Souza e Silva et al., 2006) and fractional factorial designs (Wery et al., 1999; Hu & Bay, 2001a; 2001b; Tsay & Hu, 2002; Hu et al., 2003; Bai & Hu, 2005; Hu et al., 2006; Dubent et al., 2007) have been applied. For the actual optimization of important factors, response surface designs, such as central composite (San Martín et al., 1998; Hu & Bay, 2001a; 2001b; Tsay & Hu, 2002; Hu et al., 2003; Bai & Hu, 2005; Hu et al., 2006; Silva et al., 2008; Musa et al., 2008; Poroch-Seritana et al., 2011), Box–Behnken (Morawej et al., 2006), and Doehlert (Chalumeau et al., 2004; 2006], have been used.

4.1 Classic applications concerning the use of screening and optimization in electrodeposition

The group of Chi-Chang Hu has presented some electrodeposition experiments. To optimize the hydrogen evolution activity of Zn–Ni and Ni–P deposits, respectively, different experimental strategies, including the fractional factorial design (FFD), the path of the steepest ascent study, and the central composite design (CCD) coupled with the response surface methodology (RSM), were adopted (Hu & Bay, 2001a; 2001b; Hu et al., 2003). The same experimental strategies were used to find the optimal plating conditions in the pulse-reverse electroplating mode for non-anomalous plating of Co–Ni and Fe–Ni deposits, from chloride solutions (Bai & Hu, 2005; Tsay & Hu, 2002). The same group again reported the aforementioned strategies to study the electroplating conditions of a direct-current (DC) plating mode for the co-deposition of Sn–Zn deposits, and their composition close to the eutectic point were achieved from chloride solutions. The temperature of the plating bath, pH, and the metallic ion ratio (i.e., Sn^{4+}/Zn^{2+} ratio) were found to be the key factors that affect the composition of Sn–Zn deposits in the fractional factorial design study. The effects of pH and the temperature of the plating solution on the composition of Sn–Zn deposits

were examined using a regression model in the central composite design study (Hu et al., 2006).

Concerning the electrodeposition of ternary alloys, the Prasad group has reported some studies. Ternary alloys Ni–W–B, Ni–Fe–Mo, and Ni–W–Co were electrodeposited, and operational parameters related to their corrosion resistance and deposition efficiency were optimized (Santana et al., 2006; Santana et al., 2007a; Santana et al., 2007b). The Doehlert experimental design was applied to study Au–Co electroplating optimization, and validation was performed by means of statistical analysis (Chalumeau et al., 2004; 2006). Fractional factorial design was used to analyze the influence of plating conditions on the cathode efficiency of zinc barrel electroplating and on the quality of deposited layers for low-cyanide electrolytes (Wery et al., 1999), as well as to study the determination of the suitable electroplating conditions (i.e., electrolyte composition and cathode current density) to produce 70Sn–30Zn electrodeposits (Dubent et al., 2007).

Experimental design has been applied to study the influence of several parameters on the electroplating of Cu–Zn alloy in cyanide medium (Musa et al., 2008), and response surface modeling and optimization has been used by the Senna group to study the influence of deposition parameters on the electrodeposition of both Cu–Zn and Cu–Co alloys from in citrate medium (Ferreira et al., 2007; Silva et al., 2008). Cembero & Busquets-Mataix (2009) have also used experimental design to study the most important parameters in the production of ZnO crystals by electrodeposition.

The central composite experimental design and response surface methodology have been employed for statistical modeling and analysis of results dealing with nickel electroplating process. The empirical models developed in terms of design variables (current density J (A/dm²), temperature T (∘C) and pH) have been found to be statistically adequate to describe the process responses, i.e., cathode efficiency Y (%), coating thickness U (μm), brightness V (%) and hardness W (HV). The multi-response optimization of the nickel electroplating process has been performed using the desirability function approach (Poroch-Seritana et al., 2011). Ferreira et al. (2007), studying the electrodeposition process of Cu-Zn alloys from citrate bath, also used multi-response optimization and the desirability function approach to determine the best conditions (stirring speed and current density values) to deposit a Cu-Zn alloy coating with the best anticorrosive performance. Silva et al. (2007) were also able to obtain the best conditions to produce Cu-Co alloys from citrate baths, using the desirability function approach. Unfortunately, there are still few works concerning this topic in the literature.

5. Conclusions

This chapter has provided an overview of both classic and advanced experimental design setups and their data interpretation. Statistical methods, such as experimental design and response surface methodology, could be used to help the plating engineer find a better relationship among all the parameters that might simultaneously influence the properties and performance of metallic/alloy or hybrid coatings. Rather uncommon experimental setups, such as the Doehlert design as screening design, were also considered. This was followed by a discussion of the applications using fractional factorial designs as screening designs and also of the application of desirability functions to solve problems of multi-

responses. This last topic may be very useful for plating engineers to produce more adequate coatings for desired applications.

6. Acknowledgements

7. References

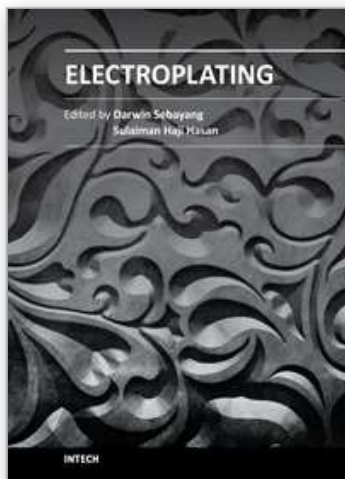Bai, A. & Hu, C. C. (2005) Composition controlling of Co–Ni and Fe–Co alloys using pulse-Bai, A. & Hu, C. C. (2005) Composition controlling of Co–Ni and Fe–Co alloys using pulse-reverse electroplating through means of experimental strategies. *Electrochimica Acta*, Vol. 50, No. 6, (January 2005), pp. 1335–1345, ISSN: 0013-4686.

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Electroplating

Edited by Prof. Darwin Sebayang

This book emphasizes on new applications of electroplating with consideration for environmental aspect and experimental design. Written by experienced expert from various countries, the authors come from academia and electroplating industrial players. Here, a very detailed explanation to the new application of the electroplating is followed by a solution of the environmental issue caused by the electroplating process and concluded by experimental design for optimization of electro deposition processes.

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- Resistant fungal biodiversity of electroplating effluent and their metal tolerance index
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