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Boundary element method applied to electroforming process

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Abstract. Elecform3D™ is a analysis and simulation tool of electroforming process, in order to facilitate design and manufacturing tasks. Electroforming is an electrolytic process that enables the manufacture of metallic parts with good mechanical properties with a high level of accuracy and reproducibility. In this process a thin metallic shell is deposited on a model part and later released from it. Distribution of deposited metal is not uniform due to current density distribution on the cathode. The results obtained with the first version of this product were very promising, and also indicated the need for a more precise analysis of electrochemical phenomena in this process.

The methodology is based on the well-known potentials model of LaPlace, it enables deposited metal distribution prediction with high grade of precision, being experimentally validated with cathodic polarization curves. These boundary conditions at the electrodes serve to combine the existing electrical and chemical effects in the process. On the active surfaces of the electrodes the current density is a function of the nonlinear laws of polarization in the electrode-electrolyte interface. Analytically the resolution of these problems is totally unworkable, at least for real geometries, so it is used for solving the employment of numerical methods. The resolution has been considered using the boundary element method (BEM), because we are only interested in obtaining the solution on the surface of the cathode.

Elecform3D™ is an important step beyond electroforming so far, and combined with almost all additive manufacturing 3D printer, is a cheaper alternative for high quality metallic parts manufacturing in comparison with other Rapid Manufacturing technologies.

Introduction

Techniques of Rapid Manufacturing (RM) have been widely developed during the last few years. It is well known that today the competitiveness in product manufacturing in general is based on three fundamentals pillars: quality, flexibility and reduction in time to market. The cost of RM technologies for metallic part manufacturing are still non-viable for many SMEs companies. Apart from this the market of 3D printers has been growing hugely in the last few years because of low cost and enhanced quality of plastic parts.

Electroforming is a manufacturing process of simple and complicated components by means of electroplating. The electrolytic bath is formed by metal salts with two submerged electrodes, an anode (nickel or copper) and a cathode (model part). Plastic model parts must be electrically conductive on the active surface, by previously applying silver paint or electroless plating. Electroforming faithfully reproduces the model surfaces exactly, thereby the quality of the metallic shell is mainly conditioned by the quality of the model. The main advantages of the process are the capability to make very complex geometries such as organic geometries, easy control of material properties changing the processing parameters or electrolytic bath composition and deposited metals. Disadvantages of the process are low deposition speed and non uniformity of thickness, due to the fact that current lines are more concentrated in some locations of cathode than in others. This research work focuses on the evolution of Elecform3D^{TM} product, applied to this well-known electroforming process. It enables better thickness uniformity as well as lower time manufacturing, obtaining High Speed Electroforming and enabling new application fields.

In general, a uniform deposit is achieved when the current density is distributed evenly over the electrode surface. The nature of the electrodeposition process itself is such that there is a strong tendency for this current density not to be uniform. Of these, the best known effect is the non-uniformity in the distribution of electrical potential resulting from the actual geometry and electrode configuration. The ability to accurately predict the distribution of current density on the surface of the cathode, and thus re-design parts to improve it, has been one of the important factors that has contributed to the technological advancement of this process [1].

Faraday's Law establishes a relationship between the operating parameters of the process and characteristics of the electrolyte, allowing the determination of the thickness of the metal layer being deposited to distribute evenly over the surface of a part. This law states that the amount of metal deposited on a metal plating process is directly proportional to the applied current density, therefore, the problem of non-uniformity in the distribution of shell thickness can be addressed by electroforming. Now there is the problem of non-uniform current density distribution over the surface of the part [2]. Current density in turn is determined by the existing electrical potential distribution inside the electrolyte, mainly due to the geometry of the electrodes and by the relative arrangement between the two.

Developing simulation models to represent, with a high grade of reliability, the process occurring into electrolytic baths is not an easy task, mainly due to complex interaction between: electrochemical kinetic, hydrodynamic flow and ionic transport and diffusion [3]. Three degrees of approximation can be set for the simulation of current density distribution on the active surfaces of the cathode.

- *Primary current density*. It takes into account only the geometric and electric factors.
- *Secondary current density*. Comes into play beside the aforementioned electrical factors, factors specific to the chemical phenomenon that takes place at the electrode-electrolyte.
- *Tertiary current density*. Other factors are taken into account in addition to the above, such as material transport due to imbalances in the chemical potential and temperature gradients present inside the electrolyte.

Most of the time the design of the selection of the correct cell configuration and process conditions is subject to extensive trial and error, involving huge human resources and considerable time. In order to ensure high efficiency and low cost of this process, a quantified model that describes the physics of the process, combined to a powerful software that allows to simulate these electrochemical processes is necessary. These simulations enable the design of proper cells, hence avoiding a lot of “trial and error” cycles.

State of art

As commented before the first numerical simulations for the prediction of metal deposition in the electrochemical process were based on current density distributions obtained using the potential model. Several authors applied the potential model to compute the current density distribution and electrode shape change as a function of time, comparing the obtained results with experiments. Some of these applied the finite element method (FEM) to solve the resulting Laplace equation, with non-linear boundary conditions to account for the electrode charge transfer reaction [4]. Others used the finite difference method (FDM) to solve a changing electrode profile with primary, secondary and tertiary current density distribution [5]. And finally others had chosen discretized the equations of the potential model using the boundary element method (BEM) in order to compute the changes of the electrode profile for primary and secondary current density distribution [6]. Only a limited number of publications deal with 3D current density distribution simulations in electrochemical reactors. Applications that consider current density distributions for more complex 3D geometries can be found in the field of cathodic protection and wafer plating, but in the field of 3D electroplating or even in the electroforming process they are very scarce.

Some electroforming equipment include some sort of cathode or anode movement but there isn't anyone positioning the part in optimal orientations, at different periods of time and controlled by computer. These devices are usually focused on specific applications for specific problems. As far as software is concerned there are some packages for electrodeposition processes analysis and simulation. These software consider approximately physical and chemical processes involved into electrodeposition, under various operative parameters. Some of them allow the option to simulate the effect of auxiliary elements (i.e. barriers) on final thicknesses distribution, pulsatile currents and multiple parts. Elsyca plating master [7], L-Cell design [8] or Accuplate 3D (Stewart Technologies, Inc.) are three computer aided engineering software equipped with 3D analysis capacities and are good examples of these. Most of these programs have been developed for surfaces coating (electroplating), where the thickness of deposit is quite a bit lower than in electroforming. Some commercial CAD programs integrate a module of analysis and facilitate the geometry design. Nevertheless all the referenced packages work under static conditions and configurations [9].

One of the most important problems to solve in this model of analysis is the determination of the polarization curves of the solution. These experimental curves show the interdependence between the electrode potential and current (i vs. E), and they are essential in the model to obtain reliable results in the determination of thickness deposited Druesne et all [10].

Analysis model

This tool is formed by the automatic device of cathodic orientation (ADCO) inside electrolytic baths, and a software to control this device and to analyze the process. Through ADCO the electric flow lines distribution change and the current density can be more uniform in all active surfaces of the model. This analysis consists of evaluating the part geometry and components of the electrolytic cell and calculates the sequence of optimal positions of the model part, to achieve uniform thickness for and the period of time of each one. There is a simulation module that has a friendly interface to show the thickness distribution in active surfaces of parts. A high quality of the part is obtained, taking advantage of electroforming properties and improving manufacturing speed because it could have applied a higher current density.

The first step was to consider a simplified method, in which the thickness distribution on the cathode could be approximately calculated starting only from geometric factors. Otherwise potentials influence is negligible and only electrical effects are involved. In consequence current density and thickness distribution are established by considering cathode relative position with regard to anode. Taking into consideration the previous hypothesis if relative position between cathode and anode are modified one sequence should exist or relative positions group where the thickness uniformity is maximum. With the aim of define these movements or positions sequence, it is necessary to approximately evaluate thickness of deposit on each position of the study in order to select from them those which deviate in thickness related to an average value as minimum. In this simplified method the calculation time is quite fast although the final accuracy is worse [11]. The results obtained with this first version were very promising, and also indicated the need for a more precise analysis of electrochemical phenomena in the process of electroforming.

The well known—potentials model of LaPlace enables deposited metal distribution prediction, and it allow a high grade of precision, being experimentally validated. To be applicable, electrolyte must have uniform conductivity. The experience gained in the field of metal electrodeposition can ignore those effects which under certain conditions have been found to have little influence. For example, if you have a good system of agitation of the bath and proper renewal of the electrolyte, the gas accumulations on the surfaces of the electrodes and high gradients of temperature and concentration in the electrolyte and at the interface between it and the electrodes can be avoided. In this case the hydrodynamic flow effects can be neglected and the ion transport is governed mainly by the diffusion mechanism.

Under these conditions the potential model predicts the distribution of weld metal with a high degree of accuracy. This model will be completed including the boundary conditions at the electrodes, these conditions serve to combine the existing electrical and chemical effects in the process, working accordingly with secondary current density. In this case thickness distribution could be studied through the following steps:

- Potentials distribution in bath determination for a certain potential difference applied between electrodes.
- Current density distribution starting from the potentials distribution.
- Thickness distribution on cathode applying Faraday´s Law

The problem domain (Ω) provided by the electrolyte is limited by the surfaces of the electrodes, anode (ΓA) and cathode (ΓC), in addition to the limits of the basin (ΓR), Fig. 1.

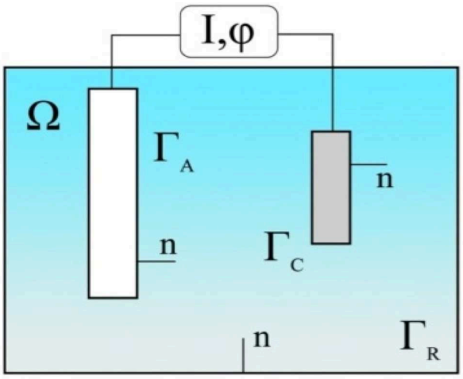

Figure 1. Scheme of the analysis system

The electric potential at each point of the electrolyte is determined from Laplace's equation Eq. 1, which describes the phenomenon of ion migration (movement of ions) due to the presence of an electric field.

$$-\nabla^2 u = 0 \qquad \text{in } \Omega \qquad (1)$$

The system is completed with the boundary conditions at the edge of the tank and non-conductive surfaces Eq. 2, where the current density must be zero.

$$\sigma \frac{\partial u}{\partial n} = 0 \qquad \text{relates to } \Gamma R \qquad (2)$$

On the active surfaces of the electrodes the current density is a function of the laws of polarization in the electrode-electrolyte interface. These intensity-potential difference relationships are nonlinear, so that the whole problem is nonlinear Eq. 3 & 4.

$$\sigma \frac{\partial u}{\partial n} = f(u) \qquad \text{relates to } \Gamma C \qquad (3)$$

$$\sigma \frac{\partial u}{\partial n} = g(u - \varphi) \qquad \text{relates to } \Gamma A \qquad (4)$$

The current density vector is determined by the potential gradient in the electrolyte. This relationship is described through Ohm's law Eq. 5, and at every point of the domain is given by the expression Eq. 6.

$$\vec{J} = -\sigma \cdot \vec{\nabla} u \tag{5}$$

$$J_n = \vec{J} \cdot \vec{n} = -\sigma \frac{\partial u}{\partial n} \tag{6}$$

Consider the effects of polarization to determine the total current density J_{Tot}, and the cathodic current efficiency of $\theta(J_{Tot})$. All the deposited metal thickness δ is calculated by applying Faraday's law Eq. 7.

$$\delta = \frac{M}{nF\rho} \cdot \theta(J_{tot}) \cdot J_{tot} \cdot t \tag{7}$$

Analytically the resolution of these problems is totally unworkable, at least for real geometries, so it is used for solving the employment of numerical methods. Since your resolution has been considered using the boundary element method (BEM), it is not necessary to discretize the entire domain of the problem. Simply divide the boundaries or contours of the same, so that surface elements are used rather than volume. As this discretization is achieved by significantly reducing the number of nodes processed, which makes them the most attractive method for solving problems where the domain is large and we are only interested in obtaining the solution of the problem on the surface or the contours of it. This method is combined with Newton-Raphson to treat non-linearity imposed by the boundary conditions on the surfaces of the electrodes. [5]. Based on this mathematical model, an analysis module was developed by Continuum Mechanics and Structures research division of Institute of Intelligent Systems and Numerical Applications in Engineering (SIANI) of the ULPGC. This analysis module can be used for other potential problems, and it has been tested and validated for the simulation of metal electroplating by using reference solutions of problems in the literature.

Polarization curves

The polarization during electrodeposition of the metal depends on the types of metals, the nature and composition of the bath, the presence of additional agents, temperature and current density. When no potential is applied to an electrolytic cell, the anode and cathode potentials are equal, or at least the order of mV. Thus, if the electrodes are connected externally, there will be no current flow. To produce current flow, an external electric potential must be applied. In each of the electrodes of the cell that is not polarized anodic and cathodic reactions occur at equal speeds, and therefore there is no net flow of currents for this exchange. The application of the polarization potential reduces the cathode potential, thereby accelerating the deposition reaction (cathodic reaction) and also slows the dissolution reaction (anodic reaction), so there is a net cathodic current flow and therefore the corresponding deposition of metal. At the anode potential increases with the opposite consequences. The change in the potential of both electrodes is what is called polarization.

To obtain a high accuracy depositing thickness is essential to know the behaviour of electrochemical laws on the electrodes. The polarization laws measurements describe the potential gap at the electrode/electrolyte interface in an electrolytic cell. There is no possibility to measure the potential gap on the electrodes, so it is necessary to use a working electrode and also a reference electrode.

To validate the polarisation curve mathematically determined, several experimental deposition tests must be done, which helps to prove the effectiveness of the BEM method with the calculated boundary conditions and its correlation with experimental results. Druesne et all [10,12] proposed a new procedure where polarisation laws are measured using a practical geometric point (calculated by linear interpolation between the anode and the cathode). Then, a numerical model is designed in order to determine the real experimental polarisation law by correlating the distance between the working electrode and the reference electrode with the polarisation curve. As it is shown in [10], it is more convenient to measure with accuracy a polarisation law at a point that is not disturbed, and then approximate by numerical tools the polarisation law on the electrode, due to the impossibility to measure the potential gap on the interface of the deposition and the bath, where the chemical reaction takes place.

Then, the polarization law must be approximate to the geometrical point of the bath where it is necessary to know: the interface. Two different numerical procedures have being used by the authors mentioned above to finally determine the polarisation laws in each case: the Adjoint State Method and a Newton-Rapson iterative technique.

Finally, Panayiotis Miltiadou and Luiz. C Wrob [13] applied an inverse BEM formulation to estimate the polarisation curves as a result of the algorithm by using genetic algorithms. These robust search techniques facilitate to obtain optimal values that minimize the difference between experimental and calculated thicknesses. Always related to these methods of analysis for determining the polarization curves, an important laboratory work is necessary to create a useful and reliable tool that will give greater potential to this product.

Meshing

Elecform3DTM requires that all the geometrical information, which is necessary for the adequate definition of the problem, will be put through a mesh. On the first versions this mesh was only a modification of a standard STL file which represent the original geometry of the problem by way of a list of linear triangular elements with three nodes on each one. The modification introduced consist only in the division of these initial elements in two, three or more elements in order to obtain a new mesh which have elements with a better formal factor or uniformity grade, than it has before. With this simple operation we obtain new meshes with a quality grade higher than the mesh has in the initial STL file. But the evolution of Elecform3D^{TM} with the adoption of the new analysis subroutine for solving the problem of current density distribution using the boundary elements method brought about the need to seek meshes with a degree of sophistication greater than previously required. The first change came with the definition of the elements. It has evolved from simple 3-node linear elements, a mesh consisting of triangular parabolic elements of 6 nodes and quadrilaterals of 9 nodes, or a combination of them. Those are accepting the application in the stage of development, mainly due to the optimization of computer resources. These new meshes are now built using CAD software and converting it in a mesh in the adequate format, which is accepted by the developed module.

At the time of writing this paper, we are completing the final validation stages of the analysis model. For the first test has been used copper sulfate bath, with electrolytic copper anode in a square plate with dimensions of 50x50x12 mm. The cathode geometry has been tasted with a spherical surface with 20 mm of diameter, to avoid edge effects. This simple experimental test is shown in Fig. 2.

For meshing this test it has been taken into account the symmetry which is present in the geometry of the problem and the possibilities that the boundary elements method gives us in this regard to make the first simplifications. So finally it has been necessary to model only half of this, using only triangular elements and distinguishing the non-active and active surfaces, Fig. 2. The first ones are formed by the middle of the tank, the free surface in the electrolyte and the elements, which support the active surfaces during the electrodeposition process. The boundary condition on this type of surface will be zero flow. Active surfaces are formed by the anodic element, which in this case is the copper plate, which provides the metal for the electrodeposition process, and the cathodic element formed by the spherical surface on which will be made the electrodeposition of metal. In this case, the boundary conditions to assign on each one will be anodic and cathodic polarization curves. First experimental results may be found at Hernández et all [14,15].

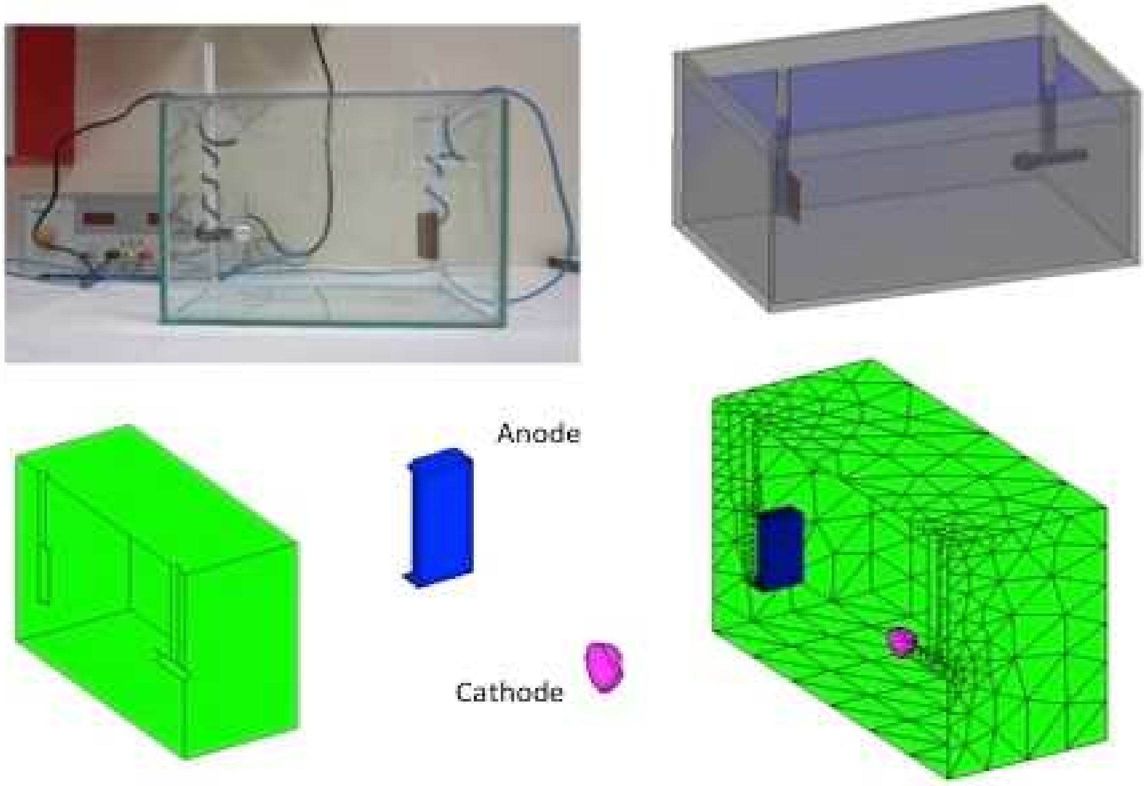

Figure 2. Experimental test and analysis model, non-active and active surfaces, and meshing

Conclusions

Electroforming process is considered as a manual activity and little widespread but with great potential and capabilities in Rapid manufacturing applications. Elecform3D^{TM} is presently potentially a step beyond electroforming, where the quality of metallic shell is improved and the processing time is reduced.

After the first results, it was considered necessary to implement an advanced model of analysis that considers the most important electrochemical Phenomena of the process.

The experimental validation has been essential to obtain a reliable analysis tool, and to identify critical process variables, but requires great effort and dedication.

Therefore Elecform3DTM and electroforming are low cost technologies for metallic part production and can be combined with almost all additive manufacturing technologies, even 3D printers. This work enable new application fields for this process. And although it has many applications the proposal is mainly addressed to rapid tooling technologies: injection and rotational moulds, EDM electrodes, and others.

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