Simplified cellular automata model of aluminum anodization

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Abstract—Recently we have shown that the pore formation in anodized alumina passive layers can be modeled in a cellular automata approach taking into account the oxygen anion formed at the layer-solution interface and drifting towards metal-layer interface where it oxidizes the metal. Here we present an alternative, simpler anodization model. The simplification amounts to reducing the number of states by eliminating the state considered to represent the anion and its drift across the passive layer. The aim of this paper is to show that the simpler model can reproduce at least qualitatively the results of the more complex model. The anion drift effect can be viewed as similar to hole conductivity where holes are layer states free of walkers that simulate the effect of the electric field. By the known symmetry argument the drift of walkers from high to low density region incurs an equivalent and opposite drift of holes. We also modify our approach to random walker generation and metal oxidation at the metal-oxide interface to conform better to electrostatic condition implying that the metal surface is equipotential. We compare the results obtained for both of these models. The essential feature of the original model, obtaining a hexagonally ordered, porous oxide layer is preserved in the simplified model.

Keywords: Cellular automata, Parallel programming, Anodization, Corrosion

1. Introduction

Anodization is a process extensively used in corrosion protection and staining of metallic parts for about a century. It can be applied to valve metals in a simple way enhancing the protective and decorative functions of the passive layer obtained particularly on aluminum. A successful anodization of a given metallic surface requires only a specific electrolyte bath and external voltage to polarize the system. In such conditions anodic oxidation and related phenomena occur. The structure formation of anodic films on aluminum was first observed in 1953 by Keller et. al[1] using transition electron microscopy. Unexpectedly, a well organized lattice of hexagonally arranged pores appeared to form in the layer. This discovery did not attract a particular attention at first. Recent interest in anodic aluminum oxide has been renewed due to its potential applications in nanotechnology as scaffolds for other nanostructure synthesis[2]. The experimental procedures for preparation of the hexagonal alumina layers are described by Masuda et. al.[3] and further developed by Li[4] and Jessensky[5].

Theoretical work on anodization lags behind the experimental development and cannot describe all aspects of the process to help design and rationalize the experimental procedures. There are two most often considered theoretical approaches to the process, namely Field Assisted Dissolution(FAD)[6] and Field Assisted Flow(FAF)[7]. The approaches have some basic features in common but differ widely in defining the fundamental cause of the emergence of an organized porous structure. In the case of the Field Assisted Flow approach the driving force of the process is assumed to be mechanical stress generated due to the Peeling-Bedworth factor associated with forming oxide on the metal oxide interface. This mechanical stress causes movement of the quasi fluid oxide layer and as consequence repulsive interactions between individual pores. The result of these repulsive interactions is a hexagonally ordered layer of pores. However the stability of the asymptotic solutions of the Field Assisted Flow model proposed by Singh, et. al[8] is put to question by the work of Gomez and Paris[9]. This model and our previous model assume the Field Assisted Dissolution approach. The main principle of the Field Assisted Dissolution is that reaction rates during anodization depend on the electric field across the layer and particularly at the metal oxide and oxide solution interface. The electric field is stronger at the bottom of a pore than at its top due to the difference in oxide thickness while the potential difference is constant. Hence a dynamic equilibrium between metal oxidation and oxide dissolution can be achieved.

2. Methods

To model the process of anodization we employ a probabilistic, three dimensional, asynchronous cellular automaton approach with periodic boundary conditions along two axes and fixed boundary conditions along the third axis. We use the 3D Moore neighborhood for a given cell. For the cell update however we select at random a pair of neighbors and update them according to a formal reaction scheme depending on their state. The basic implementation of this model is the same as our former model[10]. We employ 4 cell states: M the state corresponding to the metal, OX - to the oxide, EF - to the walker representation for electric field in the oxide that will be detailed further, S - to solvent. The
rules we use are as follows:

\[
M + S = OX + OX \quad (1) \\
EF + S = S + S \quad (2) \\
EF + S = OX + S \quad (3) \\
M + OX = EF + EF \quad (4) \\
M + OX = M + EF \quad (5) \\
EF + OX = OX + EF \quad (6) \\
S + OX = OX + S \quad (7) \\
S + EF = EF + S \quad (8) \\
\]

The differences between the two models can be described as the anion state \(A\) is discarded and unified with the \(OX\) state. The functionality of the discarded state is emulated by rule 4 and the drift of \(A\) is modeled by the drift of \(OX\). The rules 1-8 reflect chemical reaction-like behavior (1 to 5), model the electric field (6) and perform surface reorganization (7 and 8). The coding of the rules is the same as in [10] and explained in a greater detail here.

Reaction-like rules can be viewed as descriptions of the well-known electrochemical processes taking place during anodization. These are:

1) Passivation of the active metal (rule 1)
2) Dissolution of the oxide in high electric field (rule 2)
3) The potential vanishes in the solution thus electric field walkers disappear when stepping into the solution (rule 3). This can be viewed as hole regeneration equivalent in a sense to anion incorporation in our previous model [10].
4) Oxidation of the active metal in contact with oxide side (rule 4).

The final reaction-like rule creates electric field walkers that we use to model the presence of electric field in the oxide layer without oxidizing the metal itself. All of the reaction-like rules have a fixed probability during simulations. Additionally the probabilities of rules 2 and 3 sum to 1 as do the probabilities of reactions 4 and 5.

We base our simulations on the Field Assisted Dissolution model presented by Parkhutik and Shershulsky[11]. Assuming the same boundary conditions apply the Poisson equation which describes the electric field is reduced to a Laplace equation. The steady state diffusion equation with similar boundary conditions is also reduced to the Laplace equation. The diffusion equation can be solved by the random walk of particles. Hence we use the random walk approach of electric field particles to model the influence of the electric field in the oxide layer. A detailed explanation of how we account for the electric field presence is given in detail in our previous work[10]. The diffusion-like rule 6 governs the random walk of electric field walkers and therefore the effective displacement of holes inside the oxide layer.

This rule differs from reaction-like rules in the sense that it conserves the species involved leading to their redistribution. Its probability is set to 1 if the correct particles encounter one another. Let us emphasize again that the hole movement viewed as a free oxide transport in walker medium is a dual phenomenon to walker movement. The electric field represented by walker concentration gradient is both related by 1st Fick equation to walker flux and opposite hole flux. During anodization the electric field arises from the onset of the voltage between the metal and the solution. It is strongest at the thinnest metal-solution separation by the oxide layer and becomes weaker as the oxide layers get thicker. The concentration gradient of the electric field walker is balanced in quasistationary conditions by the electric walker flux and then both can be thought to mimic the presence of electric field.

Rules 7 and 8 describe surface reorganization. They introduce surface tension and prevent excessive branching of the developing pores. Oxide particles are kept in place by bonds to other oxide particles. Let us recall that “oxide particles” means both oxide (hole) and electric field (walker) states. These rules remind diffusion but there is a difference with the diffusion rules mentioned previously. The decision if a swap of particles occurs is based on two factors: the neighborhoods of the locations chosen for the swap and a predefined probability, \(P_{BOND}\), called “unbounding” probability. If the solvent site has more oxide neighbors then the oxide or electric field site a swap occurs. Conversely a swap may still occur but its probability is given by the power law:

\[
P = P_{BOND}^N \quad (10)
\]

where \(P_{BOND}\) is the “unbounding” probability and \(N\) is the difference of the number of neighbors between the sites. If an oxide site has no oxide neighbors it dissolves into a solvent site. The relative frequency of reaction-like, diffusion-like and surface reorganization events can be set at the beginning of the simulations.

In our simulations we use Nvidia Tesla GPGPU to decrease the time needed to complete them. The parallel CUDA architecture is a perfect match to the cellular automaton formalism. Individual threads can be assigned to portions of the grid of cells greatly increasing efficiency. The application of parallel techniques came with its own set of challenges and problems that are discussed in our previous paper[10]. Without going into much detail we can assure that there are no spurious correlations are aphysical behaviors introduced into the simulated system compared to a sequential code.

3. Results and Discussion

We present our results as a comparison between our previous model and the simpler one currently employed. We must stressed that the presented results were not selected to give layers of the same qualities. The two models do
not translate directly into one another due to the different treatment of EF particle generation. This comparison serves only to compare the two model results on a qualitative level. First let us analyze the profiles of oxide-like particles in both models presented in figure 1. The simulations were conducted in systems of size 100 by 100 by 200 in case of both models. A difference in the method of presenting the results is also made. Previous model side views and cross sections present only the interfacial oxide-like particles while the new model results portrait all oxide-like particles in the specified ranges. Both distributions of oxide-like particles

![Fig. 1: Comparison of profiles of particles in respective simulations](image)

have similar shapes with peaks appearing at both ends of the oxide layer and a large uniform area between the peaks. We have previously established that this shape of the oxide-like particle profile corresponds well to the shape of pores in a layer. The significant difference between the two profiles is the absolute amount of oxide-like particles present which indicates the two layers differ in porosity.

![Fig. 2: Side view of the previous model simulation.](image)

![Fig. 3: Side view of the current model simulation.](image)

In figures 2 and 3 side views of the simulated layers are presented. The layers are similar in their general appearance both having features of an organized porous structure. As expected from the particle profiles in figure 1 the current model exhibits a larger porosity manifesting in larger empty areas and a slightly more rugged structure compared to the previous simulations. The differences in structure are further examined in figures 4 and 5.

![Fig. 4: Cross section of previous model simulated layer at half of the simulation box](image)

A porous structure is clearly visible in both cross sections. The difference in the structures can be attributed to two factors. The first factor is lesser porosity of the layer obtained via the new model. This means that more space is filled with the solvent in comparison to the previous model layer. The second factor is the way the layers are presented. The tube-like appearance of pores in figure 4 is caused by picturing only interfacial oxide-like sites. In reality the "empty" spaces between individual pores also contain oxide material. To
better analyze these layers we made Fourier transforms of the cross sections to find what, if any, symmetry these structures poses.

Both Fourier transforms show evidence of an organized structure. However the hexagonal pattern is much more clearly visible in the case of our previous work pictured in the center of figure 6. The transform of our current model also shows a organized structure but the symmetry is less pronounced. This behavior may be caused by the relatively little amount of simulation work done up to date. The regime for organized porous growth of the oxide layer may still not be properly explored. As a final way to analyze the structure we calculate the Fourier transform modulus with respect to the wave vector modulus. The results for both simulations visible in figure 8 are similar with a broad maximum of the Fourier transform modulus. The maximum is slightly shifted to the right for the new model, which signifies the distance between pores is smaller than in the case of simulations of the previous model. This result is in line with previous result as increased porosity requires a larger pore diameter, less distance between pores or a combination of the aforementioned factors.

4. Conclusions

We conclude that abandoning the Anion state of our previous model did not significantly alter the qualitative properties of layers obtained in simulations. This study finds that hole diffusion is a viable modeling alternative to actual species diffusion. The currently used model is less computationally costly than its predecessor and offers the
same capabilities in terms of obtained layer morphology. We acknowledge the slightly lower quality of our current results in comparison to our previously reported work. We believe this lowered quality is the result of not fully exploring model parameters and that quality will improve along with the works progress. We are aware however of the limitations of this approach. Its implementation was only possible because of the relatively simple nature of Anion interactions. The usage if such simplifications may be impossible in case of more complex interactions reflecting more complex chemical interactions such as reactions between anions and oxide in the layers that were discarded in both of the analyzed models. Many of the qualitative features of the layers show a dependency on only a handful of model parameters. This makes analysis and relating the model parameters to real life parameters difficult and potentially limits the number of parameter combinations that may be simulated.

References