DOI 10.5162/Ultrasonic2025/P1.19

Applications of Ultrasonic Actuators for Electrochemical Deposition Processes

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Abstract: Ultrasound has been used in various actuator applications, including mixing, phase separation, and enhancing chemical reactions. Moreover, electrochemical processes have been identified as an application for acoustic actuators. Ultrasound has been demonstrated to target the depletion layer directly, thereby improving mass transport and enhancing the process. This results in a reduction of processing time, a decrease in energy consumption, and an enhancement of material properties such as hardness and surface roughness.

Keywords: Guided Acoustic Waves, Electrochemical Deposition, Acoustic Streaming, Acoustic Actuator, Sonoelectrochemistry

Introduction

Ultrasound has been used for versatile actuator technologies to assist in a wide variety of pharmaceutical or chemical processes for a long time [1, 2]. Common applications are lab-on-a-chip devices for the manipulation of liquids or particles. Typically, ultrasonic waves have been used to mix reactants or to separate different phases, but also to accelerate chemical reactions. A less commonly known but equally promising application for ultrasound are electrodeposition processes such as electroplating or electropolishing [3].

Despite the paucity of established industrial applications in this domain, it has been recognized that ultrasound can provide a beneficial effect on these processes. A review of the extant literature indicates that the predominant utilization of acoustic waves in this context is of an inefficient diffuse nature, emanated by sonotrodes [4]. However, guided acoustic waves (GAW) hold particular promise in ensuring precise mixing at the interface between the surface and the electrolyte [5].

Consequently, this study proposes a multi-stage methodology for modeling such electrochemical interface processes, utilizing the example of copper electropolishing. In addition, the impact of ultrasonic technology on electrochemical processes in experimental settings is demonstrated.

Methods and Results

Generally, gradients in ion concentration at electrochemical interface processes are known to have a negative impact on the processes [6]. In this context, the basic idea behind ultrasound technology using GAW is to overcome concentration-based limitations by utilizing acoustically induced streaming right on the interface. To understand the processes behind this, a multi-step simulation model was developed. This model was based on a simple electropolishing process of a copper electrode in a phosphoric acid electrolyte. The first step was to calculate all relevant combinations of GAW modes and the corresponding pressure fields in the electrolyte for this setup. To achieve this, a section of the electrode in contact with the electrolyte was modeled in an eigenfrequency study based on a unit cell approach [7]. The simulation provided the local plate displacement u and the electrolyte pressure field p for the existing GAW mode shapes. A standing Quasi-Scholte-platemode (QSP) with an evanescent pressure field was selected as the starting point for the next simulation step (Fig. 1a). This mode carries the sound wave's energy directly on the interface, preventing it from being lost by any decoupling parts.

In the next step, the acoustically induced flows were calculated for the corresponding modes using a perturbation approach [8]. Fig. 1b shows the resulting vortex flows, with four alternatively rotating flows per wavelength. In the final step, ion transport in the electrolyte and charge exchange at the surface were considered. The charge exchange depends on the ion concentration at the surface and can be calculated using the Butler–Volmer equation [9]. Ion transport in the electrolyte occurs via diffusion or forced streaming. In addition to other mixing methods, the acoustically induced streaming vortexes from the previous step were considered. Fig. 1c shows the concentration profile at the deformed electrode due to acoustic streaming. This acoustic-based mixing

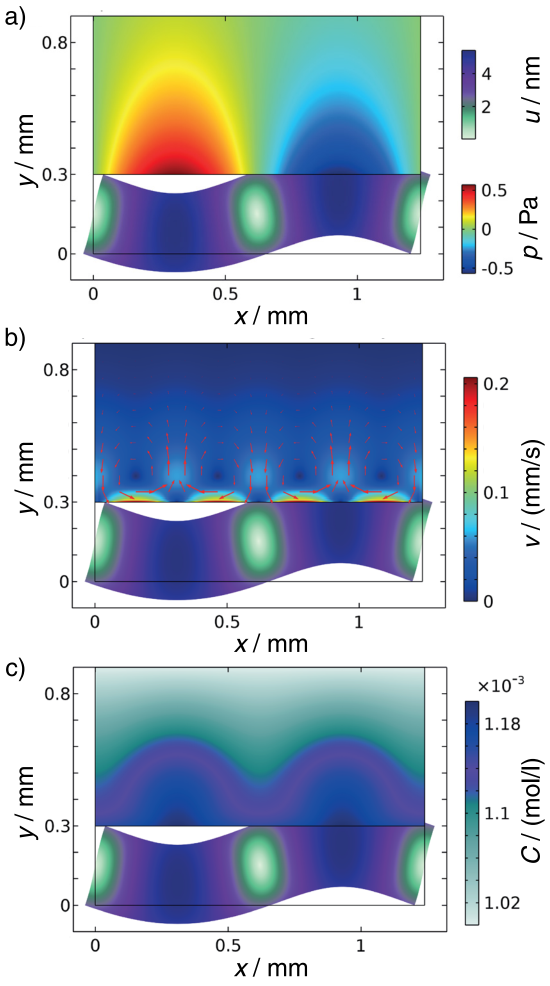

Fig. 1: Multi-stage simulation for the evaluation of different relevant aspects of electrochemical processes with GAW-based enhancement: (a) sound field, (b) streaming profile and (c) ion concentration distribution.

ensured that fresh electrolyte was transported to the electrode while exhausted electrolyte was removed. Comparative calculations have shown reduced processing time using ultrasonic technology.

In order to evaluate the multi-step model, the data from an experiment was compared with the simulations. In the experiment, a copper plate was subjected to potentiostatic polishing for a duration of 20 minutes in two phases. The initial phase was performed without acoustic enhancement. In the second phase ($t > 11$ min) the acoustic excitation was activated. The measured current profile is shown in Fig. 2a. At the beginning of the experiment, the polishing current exhibits an initial high value. This phenomenon can be attributed to the fact that, at this particular stage, fresh electrolyte is present at the surface. During the initial phase of the polishing process an inhibition layer was formed gradually as a result of the progressive presence of dissolved copper ions. The trend of the curves shows that, after a period of $t > 4$ min, a state of equilibrium was achieved. Here, only the amount of copper is dissolved which can be removed by diffusion and convection effects. In the second phase of the experiment, the polishing current was raised to a higher level by switching on the GAWs. This level was kept until the end of the experiment. So, the corresponding process efficiency was increased by 10 % to 20 %. The corresponding transient simulation of the polishing process is shown in Fig. 2b. It is evident that the two processes were performing highly analogous. The findings from simulation and experiment have demonstrated the initial formation of an inhibitory diffusion layer, in addition to the subsequent escalation of the polishing current attributable to acoustically induced mixing.

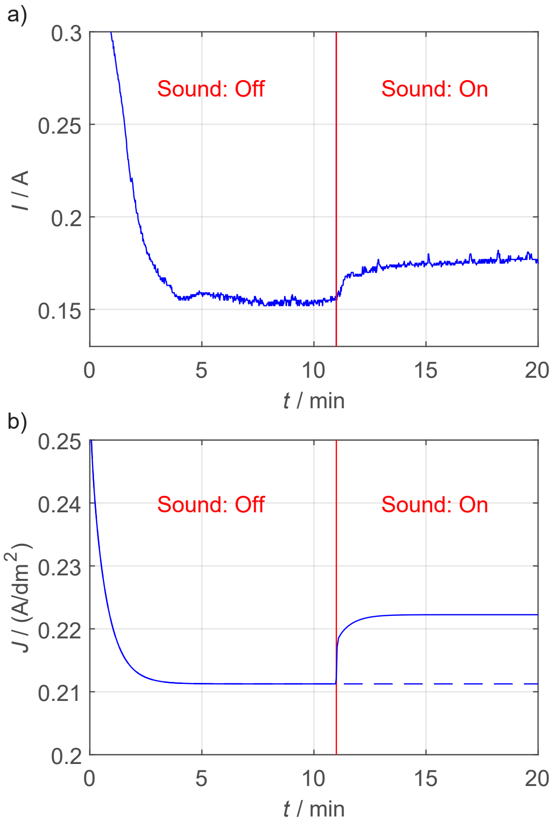

Fig. 2: Current profiles for an electro-polishing process of a copper plate in phosphoric acid with temporary GAW-based enhancement: (a) experimental data and (b) transient simulation.

It is evident that the model presented is capable of being readily transferred from anodic to cathodic

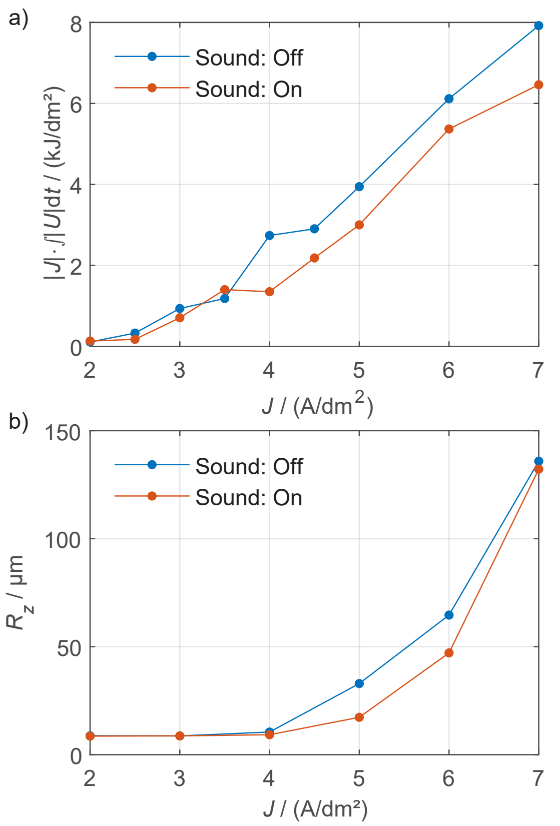

Fig. 3: Influence of ultrasound on the (a) energy efficiency of the plating process and (b) the resulting surface roughness for a additive-free Cu-Eletrolyte.

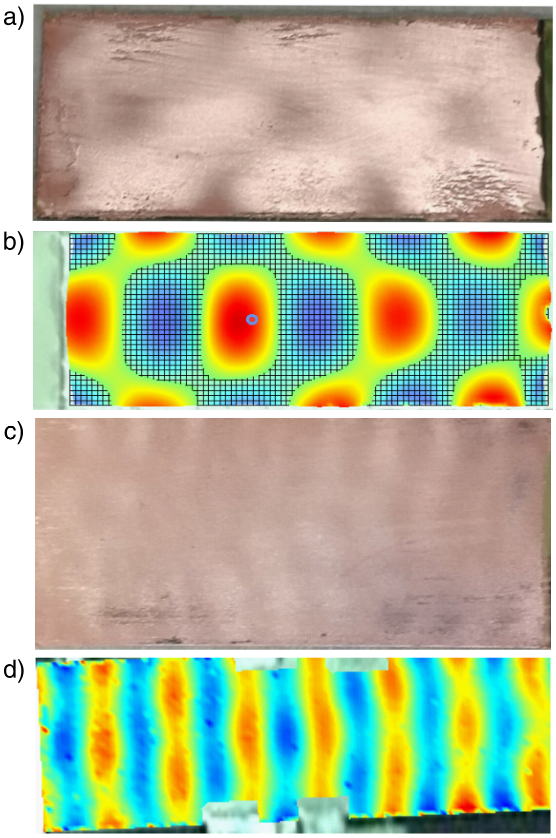

Fig. 4: Probes show a visible pattern on the sample surface (a,c) after acoustic enhanced plating. This pattern matches the related standing waves visualized by LDV measurements (b,d).

processes. For typical coating process, the electrolyte generally contains a higher concentration of dissolved ions from the outset. It is imperative to ensure the availability of sufficient free ions at the component surface throughout the process. Consequently, the occurrence of depletion effects would be able to inhibit the process.

For industrial applications, often mechanically generated flows are employed for active mixing. Therefore, nozzles or continuous sample movement are typically used for such applications. However, most of the circulation occurs far away from the component with minimal impact on the boundary layer close to the surface. This is equally applicable to sonotrode-based acoustic applications. In this instance, too, there is a lack of power in the areas where it is required. In addition, chemical additives are frequently used to ensure the uniform distribution of layers or to produce glossy surfaces. These substances frequently require analytical monitoring and online dosing. To this end, the potential of ultrasound technology in this field was investigated.

In order to address this topic, experiments were carried out with an industrial electrolyte free of additives. The samples were subjected to galvanostatic plating at varying current densities. In all cases, one sample was coated with sound, while a reference sample was coated without sound. The evaluation process involved the calculation of the energy requirements for each sample, which are displayed in Fig. 3a. As demonstrated in Fig. 3a, the two curves match within the low current density range up to $J \leq 3.5\text{A/dm}^2$. This is also specified in the datasheet as the normal operating range. In contrast, the two curves exhibit a divergence at this point. Thereby, the ultrasonic curve is consistently lower than the other curve. This phenomenon can be attributed to the active reduction of inhibitions by ultrasonic technology, thereby decreasing bath resistance. In addition, the roughness values on the coated samples were determined (Fig. 3b). Here, the values for low current densities are also congruent. Beyond the conventional operational parameters, there is a pronounced increase in surface roughness, which can be considered as a reduction in surface quality. Again, the values with sound perform out those without.

In experiments in which samples were subjected to high acoustic amplitudes during the plating process, irregularities were observed on the surface of the resulting coating. Fig. 4a,c illustrates two examples. The observation of these patterns clearly shows the impact of ultrasonic excitation on the process. These phenomena bear a striking resemblance to wave patterns, particularly standing waves, which are known to occur on finite samples. One sample displays a "checkerboard pattern" (Fig. 4a), while the other exhibits a "parallel waves" (Fig. 4c) configuration. A subsequent analysis of the excited oscillations using laser Doppler vibrometry (LDV) corroborates this initial supposition (Fig. 4b,d) [10]. In both specimens, there is an observable congruence between the surface pattern and the oscillation pattern. The distinction between the various types can be attributed to the utilization of varying frequencies in combination with different piezoelectric transducers used for the GAW excitation. Consequently, such patterns can also be avoided by slightly varying the frequencies during the plating process.

Discussion and Outlook

In summary, the ultrasonic technology based on GAWs promises to enhance the efficiency of electrochemical processes. The results presented demonstrate that processes can be accelerated, inhibitions reduced, the range of applications extended, and material properties improved. The imprinted wave patterns further substantiate the hypothesis that the crystal structure is influenced by the GAWs. Our preliminary research on electroplated nickel coatings has yielded initial evidence suggesting that ultrasonic waves may enhance the hardness of the coatings. This phenomenon is further substantiated by the observations made by the use of a scanning electron microscope. The images reveal a more sophisticated columnar growth in the presence of sonication as compared to its absence. These observations must be further investigated and confirmed in future experiments.

Funding

This research was funded by: Technologie Allianz Oberfranken TAO; Bayerisches Staatsministerium für Wirtschaft, Landsentwicklung und Energie; Bayerisches Staatsministerium für Wissenschaft und Kunst; Bundesministerium für Bildung und Forschung and Gemeinsame Wissenschaftskonferenz GWK

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