Hybrid electrochemical additive and subtractive manufacturing (HEASM) based on simultaneous mask electrochemical deposition and dissolution

Wentao Yang1 · Yan Zhang1 · Hantao Zhao1 · Guofeng Han2 · Kangjie Cai1

Received: 23 April 2022 / Accepted: 25 June 2022 / Published online: 4 July 2022 © The Author(s), under exclusive licence to Springer-Verlag London Ltd., part of Springer Nature 2022

Abstract
This paper proposed a method for hybrid electrochemical additive and subtractive manufacturing (HEASM) to fabricate microstructures with high-dimensional accuracy and good surface quality. Electrochemical additive manufacturing is achieved by applying positive pulses between the electrodes and then negative pulses are subsequently applied to achieve electrochemical finishing of the shape and surface. In this study, the formation of irregular surface defects was investigated, and a verification experiment was carried out. The inter-electrode pulse waveform and machining process were observed to characterize the electrochemical deposition and dissolution machining. The effects of pure electrodeposition, HEASM, and excessive electrolysis on the surface morphology were compared experimentally. The results indicate that HEASM can reduce the surface roughness by 45.5% but excessive electrolysis can cause a collapse of edge regions. Finally, Taguchi optimization experiments were carried out, and an optimized parameter combination for HEASM was obtained. A microstructure manufactured with an optimized pulse number ratio $0.6 \times 10^{-2}$, peak current ratio 0.5, and pulse width ratio 1.0 had the best surface morphology and dimensional accuracy. And its surface roughness and height were 0.343 μm and 33.563 μm, respectively.

Keywords Hybrid additive and subtractive manufacturing · Mask electrochemical deposition · Electrochemical desolution · Micro structure · Surface quality

1 Introduction
Micro-components are widely required in aerospace [1], precision mold [2], and integrated circuit [3, 4] applications due to their excellent integration properties [5, 6]. However, their application is extremely limited by manufacturing problems, especially achieving high-dimensional accuracy and good surface quality. For instance, the micro- and nano-springs used in MEMS [7, 8], high-frequency antennas [9], and high-performance sensors [10] should have a high elastic modulus and elastic energy storage, but inferior manufacturing accuracy and poor surface morphology significantly limit their performance and application. In general, prevailing quality issues with microstructures are due to nonuniform profiles and coarse surface morphology, which form during manufacture due to the size and complex shape of the micro- and nano-features of the microstructures. Until manufacturing methods with high-dimensional accuracy and good surface quality are developed for micro-components, it will be impossible to utilize fully the advantages of surface microstructures.

Mask micro-electrochemical deposition has been proven to have potential as a localized electrochemical manufacturing method for fabricating microstructures with complex 3D shapes [11, 12]. For example, LIGA and UV-LIGA technology were successful applications of mask micro-electrochemical deposition in the field of MEMS. Theoretically, the metal atoms formed by the reduction reaction were stacked in designed structure layer-by-layer; thus, the mask micro-electrochemical deposition has higher fabrication precision and aspect ratio among several candidates for micro fabrications. But mask micro-electrochemical deposition can have issues achieving the required dimensional accuracy and surface morphology. As the lithography-fabricated
mask shields are part of the cathode surface, the electric field lines converge in the designated region of cathode and resulting in intensive distribution of the electric field in the edge, the uneven distribution of electric field significantly leads to the difference deposition rate and growth rate of metal grain among variant regions, and the metal was accumulated in the boundary with the increasing deposition time; thus, the significant protrusion of the deposited layer was generated, and defective profile with bulging sides and low central region was formed. In addition, the dimensional consistency of microstructure was affected for different grain size of each layer. The surface issues will enlarge the dimensional tolerances and surface roughness of the microstructure, and the assembly process, friction, and adhesion behavior of MEMS devices were largely influenced [13] ultimately. To overcome these limitations of mask micro-electrochemical deposition, reversed pulse current is used to improve the electrodeposition processing, and several relative researches have been carried out. Fei et al. prepared Zn-Co alloy deposits by means of pulse-plating technique; the energy dispersive X-ray analyzer (EDA) and the surface morphology showed significantly improvement in grain size, surface appearance, and internal stress [14]. Awad et al. studied the effects of various pulse reversal plating parameters on the grain size and smoothness of Ni film, and the optimal parameters have been obtained, and the results showed smooth-plated surface free from defects or voids [15]. Seet et al. fabricated Ni80Fe20-deposited layer by using four methods of DC, pulse, PR electro-deposition, and PR electrodeposition with off-time respectively; the magnetic properties can be drastically improved [16]. Karslioglu et al. prepared Ni-Co/multiwalled carbon nanotube (MWCNT) composite coatings by direct current (DC), pulse current (PC), and pulse reverse current (PRC) methods; the higher hardness values and better wear resistance coatings have been fabricated in the PRC method due to increased MWCNT content [17].

Relevant researches mentioned above have demonstrated the superior capability of reversed pulse on enhancement of electrochemical deposition, but insulated mask with high aspect ratio results in excessive deposition rate in the boundary region, and redundant metals were formed; thus, the height of boundary region was much higher than the center, and deep mask also leads to difficulties of mass transfer in the solution [18]. The combination of electrochemical dissolution as subtractive manufacturing process with mask electrodeposition can effectively level the morphology of microstructure, electrochemical dissolution is a promising method that removes metallic material through electrochemical reaction on anodic, and the burr and deformation of micro structures were avoided. Moreover, the localized distribution of electrolyte and electric field can be used to fabricate the complex microstructure. Chen et al. proposed a method of masked jet electrochemical machining (jet-ECM) to fabricate micro channels, and the ECM model were experimentally validated by manufacturing a micro through-slit array with different moving speeds of workpiece [19]. However, there are seldom researches combining electrochemical dissolution as subtractive manufacturing process with mask electrodeposition. For example, Li et al. compared the effects of pulse (PC) and pulse-reverse current (PRC) on the mechanical responses of the electrodeposited micro-pillars [20], but the anodic current was only used to block the growth of coarser columnar grains, and the capacity of subtractive manufacturing of reversed pulse has not been noted. Zhao et al. has combined electrolysis and electro-plating as hybrid electrochemical technique for fabricating inkjet printing nozzle [21], but the electrochemical dissolution was only used to fabricate the initial profile of the micro nozzle. Therefore, the hybrid manufacturing process combining the cathodic electrochemical deposition and anodic electrochemical dissolution based on mask has been proposed in this paper, which named hybrid electrochemical additive and subtractive manufacturing (HEASM). In HEASM, electrochemical deposition is used to form a layer of a complex microstructure, and then the electrochemical dissolution is used to smooth the irregularities on its surface. Chandrasekar has summarized a review on pulse and pulse reverse techniques for electrodeposition and its applications, and previous studies have proved that pulse electrodeposition (PED) significantly raises the limiting current density by replenishing metal ions in the diffusion layer during pulse interval and reverse pulse, and thus, appropriate composition can be obtained [22]. However, the researches mentioned above just using electrochemical dissolution as an auxiliary means to improve electrochemical deposition. Moreover, the difference between the mask electrochemical deposition and Chandrasekar’s summarized researches lies in a more significant growth rate of metal in the edge region due to the convergence of electric field lines, which results in the accumulation of surface defects. The formed surface defects are hardly leveling during the reversed pulse period and thus ultimately affect the dimensional accuracy and surface morphology of the microstructures. Rather than the mentioned methods in Chandrasekar’s paper, this hybrid manufacturing process can not only level the surface or alleviate electrochemical polarization but also sufficiently remove redundancy metal by applying appropriate ratios of positive and negative pulses inter electrodes and obtain atomic thickness microstructure. In addition, by applying positive and negative pulses alternately, microstructures with well surface morphology could be obtained layer-by-layer, and the accumulation of surface defects can be avoided.

In this study, HEASM was studied by observing the reactions and the machining waveform, and electrochemical analysis was also carried out. Furthermore, the numerical simulation and comparison experiments were carried
The surface morphology and dimensional uniformity of microstructure arrays were characterized to verify the performance of HEASM in high-quality microstructure fabrication. The core element is the relation between the positive and negative pulses. Taguchi experiments were used to investigate the effects of pulse number ratio, peak current ratio, and pulse width ratio on the surface roughness and microstructure height. Optimal parameter values were obtained to minimize the surface roughness and maximize the height. A surface microstructure array was fabricated using these optimized parameters.

2 Hybrid electrochemical additive and subtractive manufacturing

Figure 1a is a schematic of the mechanism of HEASM. A microstructure was prepared by lithography with an insulating photoresist, which acts as a mask to shield designated areas on the workpiece surface from the electric field, so that electrochemical reactions take place only in the unmasked regions. A metal structure is deposited at the micro-scale atom-by-atom. Moreover, any convex defects are leveled by the subsequent electrochemical dissolution. Positive and negative pulses were applied between the two electrodes, and the same composite working solution was used in the two processes.

2.1 Electrochemical deposition stage

Figure 1c shows the electrochemical additive manufacturing process during the positive pulse period. In this process, metal ions from the anode are reduced and converted to atoms. These metal atoms are then stacked in layers on the cathode surface and finally form a metal structure with micro-scale thickness. However, due to the concentration of the electric field near the edge of the mask cavity, the metal is deposited far more quickly at the edge areas than at the center. This results in an uneven profile like a valley with bulging sides and a low central region, as shown in Fig. 1b. Furthermore, ions are transported into the micro-hole more slowly than the bulk solution, so the rapid deposition of the edge region also leads to a significant consumption of metal ions. The nonuniform distribution of the ion concentration causes metal ions to deposit in areas with a high ion concentration, resulting in different electrochemical deposition and subtractive manufacturing process. b Deposited microstructure and irregular surface defects. c Positive pulse and deposited layer. d Negative pulse and electrolytic polishing.
rates in different regions. Thus, surface humps form, which reduces the accuracy of the profile and increases the surface roughness of the workpiece.

The formation of defects can be better understood by considering the electrochemical deposition reactions on the cathode. There is a proton transfer reaction and also electron transfer reactions:

\[ \text{Ni}^{2+} + \text{OH}^- \rightarrow \text{NiOH}^- (aq) \]  

(1)

\[ \text{NiOH}^- (aq) + 2e^- \rightarrow \text{Ni(s)} + \text{OH}^- \]  

(2)

Nickel belongs to the iron group of elements. Its salt solution has a high degree of polarization. The standard electrode potential of nickel (−0.25 V) is lower than that of hydrogen (0 V). Hence, hydrogen ions are liberated at the cathode because the hydrogen evolution reaction occurs at the cathode:

\[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2(g) \]  

(3)

The side reaction of hydrogen evolution given by Eq. 3 increases the pH. Therefore, boric acid is used as a pH buffer to maintain the stability of the pH near the cathode:

\[ \text{H}_3\text{BO}_3(s) \rightleftharpoons \text{H}_2\text{BO}_3^- + \text{H}^+ \]  

(4)

### 2.2 Electrochemical dissolution stage

The irregular surface defects formed in the mask electrochemical deposition can be flattened by electrochemical dissolution, which occurs when a negative pulse is applied, as shown in Fig. 1d. The electric field lines in the electrolytic process are constrained in the same way by the insulating mask. Furthermore, the edge of the deposited layer is more prominent and there is an obvious point-effect compared to other regions. Thus, any bulges or humps deposited on the surface are quickly leveled off, which clearly improves the dimensional accuracy. In addition, the excess metallic materials dissolve into the bulk solution, preventing any increase in the differences in the concentration of metal ions.

Unlike the deposition process, when a negative pulse is applied, the nickel in the deposited layer dissolves into the water due to desorption:

\[ \text{Ni} + \text{H}_2\text{O} \rightarrow \text{NiOH} + \text{H}^+ + e^- \]  

(5)

\[ \text{NiOH} \rightarrow \text{Ni}^{2+} + \text{OH}^- + e^- \]  

(6)

In addition, nickel chloride—a surface active agent—is used to generate new activation sites on the deposited layer, blocking the formation of a passivation coating and prompting pitting corrosion of the oxide film, thus accelerating the dissolution of the nickel:

\[ \text{Ni} + \text{H}_2\text{O} + \text{Cl}^- \rightarrow \text{NiClOH}^- (aq) + \text{H}^+ + e^- \]  

(7)

Variations in the pH caused by related reactions can also be managed with boric acid, as in electrochemical dissolution, as given by Eq. 4.

In summary, HEASM, which is based on simultaneous mask micro-electrochemical deposition and dissolution, exploits the advantages of both processes to realize efficient and precise manufacturing of surface microstructure arrays.

### 3 Experimental

#### 3.1 HEASM machining system

Figure 2 shows the processing setup for HEASM. The system consisted of a pulsed power supply (YS9000DDB, China), electrochemical processing system, thermostatic...
electrolyte circulation system, and hydraulic control system. The power supply was programmable and could be used to apply a pulse current between the electrodes with different parameters. It allowed accurate control of the electrodeposition and electrolysis reactions. The electrochemical processing system had a hydraulic rod, motion system, and a marble base. The lower fixture was stationary whereas the upper fixture was connected to the hydraulic rod. The upper fixture was tightly fitted to the hydraulic rod during electrochemical machining to prevent leakage of the electrolyte and to ensure the anode and cathode surfaces remained parallel. The circulation system consisted of a cylinder, vane pump, filter, and thermostatic system. The electrolyte was delivered to the fixture through the vane pump. The temperature sensor and heating coil ensured the electroforming solution had a constant temperature.

4 Materials and measurements

A nickel sulfamate electroforming solution was used for its high limiting current density and efficiency. It has gradually replaced Watts’ bath electroforming solution and is now widely used in electrodeposition. The solution consisted of nickel sulfamate, nickel chloride, boric acid, sodium dodecyl sulfate, and saccharin. Nickel sulfamate was the main electrodeposition salt, and it provided metal ions for the electrochemical reactions. Nickel chloride was the anode activator, ensuring the normal dissolution of the anode. Boric acid was used as a pH buffer. It stabilized the pH value and reduced the evolution of hydrogen or oxygen by decreasing or increasing the pH value. Sodium dodecyl sulfate is a wetting agent. It reduced the surface stress of the deposited layer and thus decreased the number of pores and other surface defects. Saccharin is a brightener. It helped to refine the layer and thus decreased the number of pores and other surface defects. Saccharin is a brightener. It helped to refine the layer and thus decreased the number of pores and other surface defects. Saccharin is a brightener. It helped to refine the layer and thus decreased the number of pores and other surface defects.

Table 1 Parameter values for the numerical simulation

| Parameter                     | Value    |
|-------------------------------|----------|
| Nickel sulfamate (Ni(NH₄SO₄)₂·4H₂O) | 300 g L⁻¹ |
| Nickel chloride (NiCl₂·6H₂O)     | 20 g L⁻¹  |
| Boric acid (H₃BO₃)              | 30 g L⁻¹  |
| Sodium dodecyl sulfate (SDS)    | 0.4 g L⁻¹ |
| Saccharin (C₃H₅O₃NS)            | 2.5 g L⁻¹ |
| Maximum voltage                | 5 V      |

Table 2 Parameter values for the numerical simulation

| Parameter                          | Value     |
|-----------------------------------|-----------|
| Ion concentration, c              | 500 mol/m³|
| Diffusion coefficient for Ni²⁺, D_{Ni²⁺} | 4.89 × 10⁻¹⁰ m²/s |
| Diffusion coefficient for NH₄SO₄⁻, D_{NH₄SO₄⁻} | 4.89 × 10⁻¹⁰ m²/s |
| Anodic transfer coefficient, a_u  | 1.5       |
| Charge number for Ni²⁺, z_{Ni²⁺}  | 2         |
| Charge number for NH₄SO₄⁻, z_{NH₄SO₄⁻} | −2 |
| Temperature, T                    | 298 K     |
| Conductivity, σ                   | 64.3 mS/cm|
| Faraday constant, F               | 96485 A·s·mol⁻¹ |
move and deposit onto the cathode. $T^{d}_{OFF}$ is the relaxation period for the pulse, which was helpful in alleviating the polarization of the ion concentration. The sum of $T^{d}_{ON}$ and $T^{d}_{OFF}$ is the positive pulse period $T$. The ratio of the conduction period to the pulse period is the duty cycle ($W_d$). The total deposition time is the product of the number of pulses $N_d$ and the period $T$. Figure 3b shows the pulse waveform applied in hybrid machining.

Appropriate negative pulses were applied after a certain number of positive pulses, so as to polish the microstructure surface. $I_e$, $T^{e}_{ON}$, and $T^{e}_{OFF}$ are the peak current, conduction period, and relaxation period for the negative pulses, respectively. $W_e$ is the duty cycle of the negative pulses. Similarly, the total electrolytic time is the product of the number of negative pulses $N_e$ and their period $T$. Figure 3c shows pulse waveforms for excessive electrolysis between the electrodes. It can be seen that both the negative peak current $I_e$ and number of pulses $N_e$ were greater than the corresponding values in the hybrid process, which may result in over-corrosion of the microstructure.

The differences in microstructure height and surface morphology of the workpieces prepared by the above processing methods were characterized to assess whether hybrid manufacturing improved the profile precision and surface quality. Table 3 lists the parameter values used in the comparative experiments.

HEASM hybrid the electrochemical deposition caused by positive pulse and the electrochemical dissolution caused by negative pulse, so the ratios of the numbers of pulses, peak currents, and pulse widths for the positive and negative pulses had the most significant effect on the surface roughness and structural dimensional accuracy among the numerous pulse parameters. Using appropriate values of the ratios can smooth bulges and humps in the deposited layer and improve the uniformity of the microstructure. Inappropriate ratios can cause over-corrosion, bubbles, cracks, and other defects.

The volume of material deposited or dissolved can be calculated by Faraday’s law. Here, the volume of the fabricated micro-column was $V_1$, the number of applied positive pulses was $N_d$, the peak current was $I_d$, and the pulse width was $W_d$. After that, $N_e$ negative pulses with peak current $I_e$ and pulse width $W_e$ were applied to remove a bulge of volume $V_2$ from the edge by electrolysis. Thus, an expression for the matching coefficient $S$ for the positive and negative pulses can be obtained:

$$S = V_2/V_1 = N_e I_e W_e/N_d I_d W_d$$

Replacing the corresponding parameters with the pulse number ratio $S_N = N_e/N_d$, ratio of peak currents $S_I = I_e/I_d$, and ratio of pulse widths $S_W = W_e/W_d$, a simplified expression can be obtained:

$$S = S_N \cdot S_I \cdot S_W$$

The effects of different values of the above ratios were studied by the orthogonal optimization method. Orthogonal table $L_{16}(4^3)$ was adopted and the parameter values are shown in Table 4. The parameter values for the positive pulses were the same as those in Table 2. The height $H$ and surface roughness $S_q$ were characterized by morphometry and SEM.

### Table 3 Parameter values for the comparative experiments

| Parameter                  | Pure electrodeposition | HEASM       | Excessive electrolytic |
|----------------------------|------------------------|-------------|------------------------|
| Positive pulse number/k    | 3600                   | 45          | 45                     |
| Positive peak current/mA   | 70                     | 80          | 80                     |
| Positive pulse width/ms    | 0.5                    | 0.6         | 0.6                    |
| Positive frequency/Hz      | 1000                   | 1000        | 1000                   |
| Negative pulse number/k    | 0                      | 18          | 45                     |
| Negative peak current/mA   | 0                      | 60          | 80                     |
| Negative pulse width/ms    | 0                      | 0.4         | 0.6                    |
| Negative frequency/Hz      | 0                      | 1000        | 1000                   |
Table 4. Table 4 shows the hybrid waveform, which has an electrochemical deposition period and a dissolution period. The pulse period was 1 ms. In the electrochemical deposition, the electrons moved to form a positive current, and metal ions near the workpiece surface captured electrons and were deposited. The pulse current was approximately 80 mA. Correspondingly, during dissolution, the electrons in the circuit accumulated in the nickel plate to induce electrochemical dissolution of the microstructure. The negative pulse current was 40 mA. Figure 4b and c are amplifications of the pulse waveform. The current waveform illustrated in Fig. 4 proves that pulse currents in different directions can be formed between the anode and cathode by controlling the pulse parameters applied between the electrodes. Thus, electrochemical deposition and dissolution reactions can be triggered on the workpiece surface to manufacture a microstructure.

The inter-electrode reactions on the workpiece surface during HEASM were observed, as shown in Fig. 5. A brass substrate was used as the workpiece. Electrochemical deposition and dissolution were carried out with the same composite electrolyte. The switching of electrochemical processes was realized by applying positive and negative pulsed currents between the two electrodes. The reactions were observed simultaneously.

Figure 5a–c show the inter-electrode reaction and the workpiece surface after applying a positive pulse. The brass was the cathode, and a nickel plate was the anode. Electrodeposition and hydrogen evolution occurred simultaneously. There is an obvious edge effect around the electrode, so the hydrogen evolution was relatively more significant than in the central region and numerous bubbles appeared in that area. The workpiece gradually developed a silvery surface of nickel, indicating the electrochemical deposition of nickel metal.

Figure 5d–f shows the reaction and workpiece surface after the negative pulses. The nickel deposited onto the brass workpiece turns to the anode and electrochemical dissolution occurred. In some regions, the base metal was exposed. Obvious hydrogen bubbles can be observed around the nickel plate. Figure 5g–i show the reaction and workpiece surface in the second cycle. Electrochemical deposition occurred again on the workpiece surface. Because the concentration of metal ions near the workpiece was higher

| Factor | Parameter | Level |
|--------|-----------|-------|
| A      | Ratio of pulse number, \( S_{\text{p}}/\times 10^{-2} \) | 0.3 0.6 0.9 1.2 |
| B      | Ratio of peak current, \( S_{\text{i}} \) | 0.5 0.75 1 1.25 |
| C      | Ratio of pulse width, \( S_{\text{w}} \) | 0.6 1 1.4 1.8 |

Table 4. Parameter values for the orthogonal experiments

![Fig. 4](link-to-figure) Fig. 4. Current waveform applied between electrodes. a Hybrid machining. b Amplification of positive pulses. c Amplification of negative pulses.
Fig. 5 Inter-electrode reactions in hybrid manufacturing: a–c electrodeposition after the positive pulses. d–f Electrolysis after the negative pulses. g–i Electrodeposition after the secondary positive pulses.
than in the previous dissolution stage, the deposited layer of nickel is smoother than after the initial cycle.

According to the electrochemical reactions in Eqs. (1)–(4), hydrogen evolution occurred synchronously with the electrodeposition, which resulted in morphological defects and increased pH near the electrode. Moreover, due to the limited volume of electrolyte, the lack of metal ions is significant. The electrochemical dissolution reactions that occurred during the negative pulses can effectively solve this problem. From Eqs. (5)–(7), the excess metal deposited in the bulge re-entered the solution in the form of metal ions, which obviously, subsequently alleviated the shortage of metal ions near the workpiece surface. In addition, oxygen evolution side reactions inhibited the continuous rise of the pH. However, excessive electrochemical dissolution may break the metal layers of the surface and even introduce metallic elements from the substrate into the solution. The observations of the inter-electrode reactions demonstrated that electrochemical deposition and dissolution occurred during the positive and negative pulse periods, respectively, accompanied with hydrogen and oxygen evolution side reactions. A layer of nickel was deposited and dissolved consecutively on the workpiece surface.

Figure 6 presents the polarization curves of the hybrid electrochemical process. The polarization curves for deposition and electrolysis were measured by an electrochemical workstation. The working electrode (WE) was made of pure brass and had an effective area of 1 cm². It was attached by phenolic resin in a cylindrical mold. Before each measurement, the fabricated electrode was consecutively ground by SiC sandpaper of 200, 400, and 800 mesh, and polished with diamond paste. The reference electrode (RE) was a saturated calomel electrode (SCE) connected to a glass salt bridge filled with KCl and coupled with a Luggin capillary. The counter electrode (CE) was a platinum plate. In the electrodeposition stage, the scanning range was from 0.4 V to −1.5 V while in the electrolysis stage, it was reversed. The scanning rate was 5 mV/s.

Figure 6a shows the polarization curve during electrodeposition. The polarization region surrounded by the box marked with a dashed line has a linear section, a low-polarization region, and a Tafel region. The cathodic and anodic Tafel slopes can be determined by drawing tangent lines in the Tafel region. Thus, the potential can be obtained from the Tafel formula:

\[ \eta = a + b \log i \]

where \( \eta \) is the overpotential. \( a \) and \( b \) are related to the size, properties, materials, and surface state of electrode. They also account for the composition and temperature of the solution. The exchange current density \( i_c \) can be obtained by extrapolating the cathodic and anodic Tafel curves to the equilibrium potential \( E_{Ni^{2+}/Ni}^0 \). The equilibrium potential was more negative than the Nernst equation suggests, which indicates that overpotential deposition occurred between the electrodes. Moreover, the standard electrode potential of \( Ni^{2+}/Ni \) was less than 0 V, so that bubbles were observed on the workpiece surface during the deposition process. As the current density log \( i \) increased, the potential in the polarization curve tended to decrease. The equilibrium potential is given by the Nernst–Planck equation:

\[ E_{Ni^{2+}/Ni} = E_{Ni^{2+}/Ni}^0 + \frac{RT}{zF} \ln \frac{a_{Ni^{2+}}}{a_{Ni}} \]

where \( E_{Ni^{2+}/Ni}^0 \) is the standard electrode potential of \( Ni^{2+}/Ni \) (−0.25 V), \( a_{Ni^{2+}} \) is the activity of an \( Ni^{2+} \) ion, and \( a_{Ni} \) is the activity of \( Ni \). Since the activity of the metallic element was equal to 1, then the activity of \( Ni^{2+} \) ions decreased with a
reduction of the potential, which indicates that electrodeposition reactions occurred.

Figure 6b shows polarization curves during electrolysis. The two curves are for whether activator NiCl₂ was or was not added to the solution. As shown by the curve within the box marked by a dashed line, the current density increased with an increase of the potential, which means the activity of the metallic Ni²⁺ ions was higher so that electrochemical dissolution occurred. However, there is a passivation zone in the polarization curve, whether or not NiCl₂ was added. The passivation zone without activator was more obvious and the corresponding current density was lower, indicating that dissolution of the deposited layer was difficult.

The polarization curves characterize the inter-electrode electrochemical deposition and dissolution reactions in HEASM, respectively. The ion activity and deposit potential in the positive pulse period indicates that there was overpotential deposition on the workpiece surface. The increase in the metal ion activity during the negative pulses indicates the occurrence of metal dissolution. Moreover, the polarization curves also illustrate the hydrogen and oxygen evolution side reactions.

5.2 Comparative analysis of HEASM with pure electrodeposition and excessive electrochemical corrosion

A multi-physics comparative simulation was carried out for three methods: pure electrodeposition, hybrid processing, and excessive electrolysis. The results are shown in Fig. 7. Figure 7a shows the governing equations and boundary settings of the multi-physics simulation, the current density in the electrolyte can be described as the multiplication of ion flux and its charge, as shown in equation:

\[ j = F \cdot \sum_{i=1}^{n} z_i \cdot N_i \]  \hspace{1cm} (12)

where \( j \) is the current density, \( F \) is the Faraday constant, \( z_i \) is the number of charge, and \( N_i \) is the flux of the species \( i \). The flux of species \( i \) can be written by the Nernst–Planck equation:

\[ N_i = -z_i u_i F c_i \cdot \nabla \phi_i - D_i \cdot \nabla c_i + c_i \nu \]  \hspace{1cm} (13)

The equation consists of different terms: the electro migration term (\( z_i u_i F c_i \cdot \nabla \phi_i \)), the diffusion term (\( D_i \cdot \nabla c_i \)), and the convection term (\( c_i \nu \)). Where \( u_i \) is the ionic mobility, \( c_i \) is the concentration, \( \phi_i \) is the electrolyte potential, \( D_i \) is the diffusion coefficient of the species \( i \), and \( \nu \) is the flow rate. The accumulation of each species in the electrolyte should also satisfy the mass balance equation, as shown in the equation:

\[ R_{tot} = \frac{\partial c_i}{\partial t} + \nabla \cdot N_i \]  \hspace{1cm} (14)

where \( R_{tot} \) is the total number. The concentration gradient can be ignored for well convection conditions in the bulk solution; therefore, the current density and mass transport can be simplified as Laplace’s equation:

\[ j_i = -\kappa \nabla \cdot \phi_i \]  \hspace{1cm} (15)

\[ \nabla^2 \phi_i = 0 \]  \hspace{1cm} (16)

where \( j_i \) is the total current density in electrolyte. Electrode reactions resulting in local current \( j_{loc} \) can be described by the Butler-Vollmer equation:

\[ j = F \cdot \sum_{i=1}^{n} z_i \cdot N_i \]  \hspace{1cm} (12)

\[ N_i = -z_i u_i F c_i \cdot \nabla \phi_i - D_i \cdot \nabla c_i + c_i \nu \]  \hspace{1cm} (13)

\[ R_{tot} = \frac{\partial c_i}{\partial t} + \nabla \cdot N_i \]  \hspace{1cm} (14)

\[ j_i = -\kappa \nabla \cdot \phi_i \]  \hspace{1cm} (15)

\[ \nabla^2 \phi_i = 0 \]  \hspace{1cm} (16)
where \( j_0 \) is the exchange current density, \( R \) is the molar gas constant, \( T \) is the temperature, \( \eta \) is the overpotential, and \( a_e \) and \( a_a \) are cathodic and anodic charge transfer coefficient, respectively. The remaining boundaries can be considered insulators and its current density is zero:

\[
\nabla \phi_s = 0
\]

And Faraday’s law is used to calculate the deposition rate:

\[
\frac{dh}{dt} = -\frac{M_i}{\varepsilon F \rho_i} \Phi
\]

where \( h \) is the microstructure thickness, \( M_i \) is the molar mass of the species \( i \).

Figure 7b–d and e–g show the current density clouds and corresponding line graphs after 1000 s of electrodeposition and after 18 s or 21 s of subsequent electrochemical dissolution. Figure 7b and e indicate that the electric field was concentrated at the boundary region of the mask hole, so the current density was significantly higher than in the central area in the deposited structure. The amount of metal deposited at the edge was remarkably more than at the center, and a bulge and hump formed. Figure 7c and f illustrate the changes in the profile and current density distribution after a negative pulse had been applied. The metal electrolytic rate at the edge significantly exceeded that in the center region, and the deposited layer with the surface bulge and excess metal was rapidly flattened. After electrolysis for 18 s, the profile became smoother and the distribution of the current density was more stable. However, the mask hole will still significantly restrict the electric field, even if the deposited layer is completely finished. This is likely to cause corrosion if redundant negative pulses are applied. Figure 7d and g, respectively, show the surface profile and current density distribution after excessive electrolysis. It can be seen that the height of the micro-column decreased significantly and that the border was lower than in the center area. After 21 s of electrolysis, the height of the deposited micro-column was 0.694 \( \mu m \) lower than that of the axis region, indicating that excessive corrosion had occurred.

After the numerical simulations, comparative experiments of pure electrodeposition, hybrid processing, and excessive electrolysis were carried out. The differences in the surface roughness \( S_a \) and height \( H \) of the microstructures manufactured by the three methods were characterized by morphometry, as shown in Fig. 8. The diameter of the microstructures was 200 \( \mu m \); since the height of the deposited metal does not exceed the thickness of the photoresist mask, the roundness and dimensional accuracy of the microstructure were directly related to the lithography. The roundness of the microstructures was no more than 1 \( \mu m \), depending on the resolution of lithography. The height of the fabricated micro-column was lower after excessive electrolysis than after hybrid processing. After excessive electrolysis, the height was 24.867 \( \mu m \), which was 33.5% lower than the 37.412 \( \mu m \) for a micro-column prepared by pure electrodeposition. The surface roughness \( S_a \) was lower after hybrid processing but increased after excessive electrolysis. The \( S_a \) of the microstructure prepared by the hybrid process was 0.319 \( \mu m \), which was 45.2% less than after electrodeposition, indicating that the hybrid manufacturing method improved the surface quality. However, excessive electrolysis seriously degraded the morphology of the microstructure. The micro-column surface prepared after excessive electrolysis had quadruple the roughness than after pure electrodeposition, reaching 1.946 \( \mu m \).

SEM and laser scanning confocal microscopy were used to observe the deposition morphology and micro-column profile. The results are shown in Fig. 9. Figure 9a shows the nickel micro-column fabricated by pure electrodeposition; the distinct redundant metals were deposited at the boundary region, which resulted in rough surface morphology of the nickel microcolumn, which was consistent with the numerical simulation of pure electrodeposition. The coherent grains can be observed, mainly concentrated at the border of the column. The sectional profile indicates that the deposited metal is prominent in this area, which proves that there was rapid grain growth in this region. Figure 9b shows the micro-column prepared by hybrid processing. Compared with pure electrodeposition, the surface of the micro-column is relatively smooth. In general, there are no coarse grains or an obvious bulge, and the sectional profile is relatively flat. Hybrid processing can remove the redundant metals in the edge region efficiently to obtain smooth topography; the
The difference of height between the boundary and the center region of micro column was 1.48 μm after electrolysis for 18 s in the numerical simulations, while in the comparison experiments, the difference of height reached 1.314 μm, and HEASM greatly reduced the surface roughness of nickel micro column. Figure 9c shows the column manufactured by excessive electrolysis. Due to over-corrosion, the surface of the micro-column is rough around the boundary region and an apparent collapse can be observed. In the sectional profile, the height is lower at the edge than at the center, indicating that the excess negative pulses have impaired the flatness of the micro-column. As demonstrated by the numerical simulations, the electric field in the boundary region was still dense in the electrochemical dissolution period even the surface has been leveled, therefore the edge collapse was formed and effected the surface quality.

The numerical simulation and comparison experiments for the three different methods suggest that, because the insulating mask partially shielded the surface of the cathode, the electric field was concentrated around the edge. Thus, a valley profile was produced, which significantly reduced the dimensional accuracy and surface quality of the microstructure. By combining electrochemical dissolution with deposition, the quality of microstructure was effectively improved. The comparative experiments and simulation verified the apparent decrease of the surface roughness $S_a$ of the microstructure fabricated by HEASM. Figure 10 illustrates the micro-scale mechanism of HEASM. Because of the constraint imposed on the electric field by the mask, there was faster deposition and dissolution at the edge region. Moreover, the intense electrochemical dissolution gradually flattened the surface of the microstructure. However, the comparison experiments and simulation also indicate that applying excess negative pulses may deteriorate the surface morphology and dimensional accuracy of the microstructure because the electrochemical dissolution rate was still high around the boundary after the surface has been flattened, resulting in excessive corrosion. Therefore, the key factor in HEASM is identifying the best ratios between the positive and negative pulse parameters.

5.3 Taguchi optimization experiments of pulse parameters

Taguchi optimization experiments were carried out to study the effects of electrical parameters (ratios of the numbers of pulses, peak currents, and pulse widths on the surface roughness $S_a$ and microstructure height $H$, as shown in Fig. 11a–c. With an increase of these ratios, the surface roughness $S_a$ of the deposited layer first decreased and then increased. Thus, there are optimum values that give the minimum surface roughness: pulse number ratio $0.6 \times 10^{-2}$, peak current ratio 1, and pulse width ratio 1.4. Moreover, the height of the microstructure decreased as the ratios increased. The microstructure fabricated with a pulse number ratio $0.3 \times 10^{-2}$, peak current ratio 0.5, and pulse width ratio 0.6 had the maximum height.

If the positive pulse parameters are kept constant, then larger ratios of the positive and negative pulse parameters indicate that there were more negative pulses with a larger...
peak current and a longer pulse width. Hence, more electricity was used for electrochemical dissolution and more metal was removed, resulting in a decrease in the height as the ratios increased. Unlike the height, the microstructural surface quality first improved and then deteriorated with an increase of the ratios. This trend for the microstructure surface roughness occurred because of the very high dissolution rate near the edge due to the concentrated electric field. The surface was leveled by the electricity applied during the negative pulse period. However, overlarge ratios caused over-corrosion, leading to an increase of $S_a$.

To achieve the minimum surface roughness $S_a$ and maximum height $H$, we need to determine the optimal ratios of the positive and negative pulse parameters. When the pulse number ratio was $0.6 \times 10^{-2}$, the corresponding surface roughness $S_a$ was a minimum, whereas when the ratio was $0.3 \times 10^{-2}$, the height $H$ was highest. In addition, the differentials of the surface roughness and height for the pulse number ratio are 0.483 and 8.012, respectively, which are both maximums. This indicates that the pulse number ratio has the most significant effect on the morphology and dimensional accuracy. The maximum value of $S_a$ is more than twice the minimum, whereas the difference for $H$ is only 18.2% of the maximum height. Therefore, the surface quality can be considered the determining factor, and so the optimal ratio selected in this work is $0.6 \times 10^{-2}$.

For the peak current ratio, the differentials for surface roughness $S_a$ and height $H$ are not the largest values, which demonstrates that the peak current ratio has less effect on the surface quality and microstructure height. The peak current ratios with the best surface quality and the highest microstructure height were 1.0 and 0.5, respectively. However, for the first three values of the ratio, the differences in the surface roughness $S_a$ are small, which is different from the microstructure height. Accordingly, the optimal value should be selected based on the height $H$ as the determining factor. Thus, the optimal peak current ratio is 0.5.

![Fig. 10](image) Schematic of electrolytic polishing and excessive electrolysis

![Fig. 11](image) Surface roughness and height in the orthogonal experiment. a) Pulse number ratio. b) Peak current ratio. c) Pulse width ratio
For the pulse width ratio, the differentials for both the surface roughness $S_a$ and height $H$ are again small, which means that this ratio is not a significant factor affecting the surface morphology or microstructure contour precision. The ratio with the minimum surface roughness was 1.4, but this ratio did not produce the highest column. The highest column was for a ratio of 0.6. Consequently, the intermediate value of the pulse width ratio, 1.0, was adopted as the optimal value.

Figure 12a–p are images of the micro-columns obtained in the orthogonal experiment. It can be seen that the edge area of the microstructure collapsed in various degrees when the ratios exceeded the optimal values.

In conclusion, to fabricate a micro-column with the best morphology and contour precision, the following ratios should be used: pulse number ratio of $0.6 \times 10^{-2}$, peak current ratio of 0.5, and pulse width ratio of 1.0. Figure 13a is an SEM image of a surface microstructure array prepared with the optimized ratios, and Fig. 13b is a 3D profile diagram of a single column between poles. The surface roughness $S_a$ of the microstructure is 0.343 $\mu$m, and the height is 33.563 $\mu$m. The SEM images demonstrate the smooth surface morphology of the microstructure array. Any irregular surface defects, such as a bulge or a collapse in the edge region, have been removed, indicating that HEASM
can effectively improve the surface quality and dimensional accuracy. In addition, using the appropriate ratios of the parameters for the positive and negative pulses can prevent excessive corrosion.

6 Conclusions

In this paper, a novel electrochemical manufacturing method—Hybrid Electrochemical Additive and Subtractive Manufacturing (HEASM) has been proposed for fabrication of microstructure with good surface quality and dimensional accuracy. The inter-electrode pulse waveform detection, machining process observation, and electrochemical analysis were carried out to characterize the inter-electrode electrochemical reaction. And the numerical simulation and comparison experiment of pure electrodeposition, hybrid process, and excessive electrolytic were carried out to verify the improvement on dimensional accuracy and surface morphology by HEASM. Taguchi experiments were carried out to study the effects of the pulse number ratio, peak current ratio, and pulse width ratio on surface roughness and microcolumn height, and the optimal ratio of parameters was obtained. The relevant conclusions are as follows:

1. The process monitoring showed that the equilibrium potential was lower than the standard electrode potential of Ni$^{2+}$/Ni during the electrodeposition, which means over-potential deposition occurred. The ion activity decreased when positive pulse applied while it increased in negative pulse period, indicating that electrodeposition and electrolysis occur during positive and negative pulse respectively.

2. Numerical simulation and comparison experiments show that proper amount of negative pulse can quickly flatten the microstructure surface, while redundant pulse may lead to collapse of edge. The simulation results present microstructure profile approach uniform when the deposition time is 1000 s and electrolysis applied for 18 s. But after 21 s of excessive electrolysis, the deposited microcolumn height of the boundary was 0.694 μm lower than the center region.

3. Taguchi optimization experiments show that with the ascension of pulse number ratio, peak current ratio, and pulse width ratio, the surface roughness $S_a$ decreases first and then increases, while the height continues to decrease. The parameters of pulse number ratio $0.6 \times 10^{-2}$, peak current ratio 0.5, and pulse width ratio 1.0 have been adopted, the microstructure with the lowest surface roughness and the highest height fabricated by such ratios was obtained, and its $S_a$ and height are 0.343 μm and 33.563 μm respectively.

Author contribution Wentao Yang was responsible for the experiment, simulation, and original draft preparation. Yan Zhang was responsible for supervision, methodology, and editing. Hantao Zhao was responsible for the validation and data curation. Guofeng Han and Kangjie Cai were involved in the discussion and contributed to making the final draft of the article.

Funding This project is supported by the Jiangsu Provincial Six Talent Peaks (JXQC-009) and Jiangsu Provincial Graduate Practical Innovation Program (SJCX21_0494).

Data availability The authors confirm that the data supporting the findings of this study are available within the article.

Declarations

Ethics approval The article involves no studies on human or animal subjects.

Competing interests The authors declare no competing interests.

References

1. Chernyshev A, Apisarov A, Shmygalev A, Pershin P, Kosov A, Grishenkova O, Isakov A, Zaikov Y (2021) Electrodeposition of niobium from the CsBr-KBr-NbBr 3 Melt. J Electrochem Soc 168(7):072501

2. Kondo T, Yoshida M, Yanagishita T, Masuda H (2021) Communication—fabrication of Li nanohole array by replication
process using anodic porous alumina template. J Electrochem Soc 168(3):032508

3. Wu C, Zhao H, Wu X, Xu B, Lei J, Zhu L, Gao C, Xiao Y (2021) The wettability of metal-based composite foils with hierarchical structure prepared by ultrasonic-assisted composite electrodeposition. Int J Adv Manuf Technol 116(7):2359–2371

4. Kim H, Kim JG, Park JW, Chu CN (2018) Selective copper metalization of nonconductive materials using jet-circulating electrodeposition. Precis Eng 51:153–159

5. Chen YL, Wang Y, Wang Y, Ju BF (2021) Meniscus-confined electrodeposition of metallic microstructures with in-process monitoring of surface qualities. Precis Eng 70:34–43

6. Ito S, Chen YL, Shimizu Y, Kikuchi H, Gao W, Takahashi K, Kanayama T, Arakawa K, Hayashi A (2016) Uncertainty analysis of slot die coater gap width measurement by using a shear mode micro-probing system. Precis Eng 43:525–529

7. Yi Z, Lei Y, Zhang X, Chen Y, Guo J, Xu G, Yu MF, Cui P (2017) Ultralow flexural properties of copper microhelices fabricated via electrodeposition-based three-dimensional direct-writing technology. Nanoscale 9(34):12524–12532

8. Carraro C, Magagnin L, Maboudian R (2002) Selective metalization of silicon micromechanical devices. Electrochim Acta 47:2583–2588

9. Dean RN Jr, Nordine PC, Christodoulou CG (2000) 3-D helical THz antennas. Microw Opt Technol Lett 24(2):106–111

10. Fang A, Haataja M (2017) Modeling and analysis of electrodeposition in porous templates. J Electrochem Soc 164(13):D875–D887

11. Zhang H, Zhang N, Fang F (2021) Study of ion transportation and electrodeposition under hybrid agitation for electroforming of variable aspect ratios micro structures. Precis Eng 72:122–143

12. Yang H, Chein R, Tsai T, Chang J, Wu J (2006) High-aspect-ratio microstructural posts electroforming modeling and fabrication in LIGA process. Microsyst Technol 12:187–192

13. Hall AC, Dugger MT, Prasad SV, Christensen T (2005) Sidewall morphology of electroformed LIGA parts-implications for friction, adhesion, and wear control. J Microelectromech S 14(2):326–334

14. Fei JY, Wilcox GD (2005) Electrodeposition of Zn–Co alloys with pulse containing reverse current. Electrochim Acta 50(13):2693–2698

15. Awad Y, Lavallee E, Beausvais J, Drum D, Mun LK, Yang P, Cloutier M, Turcotte D (2007) Nickel pulse reversal plating for image reversal of ultrathin electron beam resist. Thin Solid Films 515(5):3040–3045

16. Seet HL, Li XP, Lee KS, Chia HY (2007) Nanocrystalline grain size control for Ni80Fe20/Cu micro-composite wires by different electrodeposition methods. J Mater Process Technol 192–193:225–228

17. Karslioglu A, Akbulut H (2015) Comparison microstructure and sliding wear properties of nickel–cobalt/CNT composite coatings by DC, PC and PRC current electrodeposition. Appl Surf Sci 353:615–627

18. Nilson RH, Griffiths SK (2003) Natural convection in trenches of high aspect ratio. J Electrochem Soc 150:C401–C412

19. Chen X, Zhu J, Xu Z, Su G (2021) Modeling and experimental research on the evolution process of micro through-slit array generated with masked jet electrochemical machining. J Mater Process Technol 298:117304

20. Li M, Luo W, Chen Y, Cheng X (2021) Nickel micro-pillar mold produced by pulse and pulse-reverse current electrodeposition for nanoimprint lithography. Mater Lett 301:130310

21. Zhao X, Jia Z, Li W, Li Y, Kong Q (2018) Fabrication of optimized streamlined micro nozzles by hybrid electrochemical techniques. J Micromech Microeng 28(12):125006

22. Chandrasekar MS, Pushpavanam M (2008) Pulse and pulse reverse plating—Conceptual, advantages and applications. Electrochim Acta 53(8):3313–3322

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.