Significance of waveform design to achieve bipolar electrochemical jet machining of passivating material via regulation of electrode reaction kinetics

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\section*{A B S T R A C T}

Electrochemical machining (ECM) using the bipolar pulse technique shows significant potential for the effective machining of prone-to-passivation materials. However, despite its success in machining specific materials (e.g. tungsten carbide), the underlying mechanism remains unclear. This study presents an in-depth analysis of the interplay between cathodic polarisation (CP) and anodic oxidation in bipolar pulse electrochemical jet machining (bipolar-EJM). An observational study of the structural changes in the anodic oxide film indicated that the oxide broke down by electrochemical reduction and mechanical damage when subjected to CP. The electrochemical kinetics at the electrode interface, particularly the proton transport and discharge reactions, were discussed to elucidate the mechanism. This study first discloses that the bipolar pulse waveform plays a crucial role in overcoming the oxide film and achieving machining in bipolar-EJM. Variations in waveform shape result in distinct interactions of the cathodic pulse with the anodically formed surface oxide. A principal approach of bipolar-EJM was thus developed to effectively remove or eliminate passive oxide films by controlling the bipolar pulse. The material removal mechanism of the developed method is described and the corresponding kinetic model of the electrode reactions is presented. For verification, the bipolar-EJM of the strongly passivating metal niobium (Nb) is first demonstrated in a pH-neutral NaNO\textsubscript{3} aqueous solution, demonstrating the effectiveness of the proposed method. The new insights into the bipolar pulse process established here will be believed to provide valuable guidance to advance the bipolar electrochemical process, including ECM and electrochemical polishing.

\section*{1. Introduction}

Electrochemical machining (ECM) is an unconventional near-net-shape metal-shaping process in which the shape of a tool electrode is transferred to a working electrode (workpiece) by anodic dissolution [1]. The non-contact nature of ECM enables it to form complex geometries, independent of the mechanical properties of metallic materials. ECM produces no thermal or mechanical effect on the workpiece material because the process generates almost no heat or stress [2]. Therefore, ECM exhibits unique advantages for the creation of complex structures with high surface integrity in tough and exotic materials that are difficult to machine using conventional methods such as cemented carbide, nickel alloys, and titanium alloys [3,4]. These benefits make ECM a superior manufacturing method for aviation, medical, and automotive industry applications.

In contrast, as an electrochemical process, the chemistry involved in the process, including the material type of the workpiece, electrolyte composition, and pH value, significantly influences the performance of ECM. Therefore, ECM encounters significant challenges in machining susceptible-to-passivation metals such as niobium (Nb), titanium (Ti), and tungsten (W), which worsen when a passivating neutral electrolyte solution is used. These materials are believed to form high-resistance oxide films on their surfaces, which compactly cover the material surface and hinder the progress of anodic dissolution. As described by Yerokhin et al. [5], the anodisation process in ECM can cause either material dissolution or the formation of a passivation film on the
electrode surface, depending on the electrolyte chemical activity with respect to the metal. The formed oxide film can be insoluble, thus causing passivity. When a passivation film is formed on the anode metal surface, electron migration is challenging because of the poor conductivity of the passivation film, which hinders the dissolution reaction of the working anode [6]. As stated by, Engell et al. [7] oxide films form on most corrosion-resistant materials, which can suppress corrosion to the dissolution rate of the oxide films. In ECM, an oxide film forms on the anode surface at low current densities, resulting in a considerable decrease in the current efficiency for material removal [8,9]. This principle of using a passivating electrolyte, such as sodium nitrite (NaNO$_3$) solution to induce the formation of oxide films has been widely applied in ECM to improve material dissolution localisation by avoiding stray current corrosion.

However, the ECM of passive electrodes requires a high anodic polarisation to achieve transpassive dissolution [10,11]. A passivation film in ECM provides an additional resistance $R_p$, which acts in series with the electrochemical double-layer capacity from a microscopic perspective. $R_p$ may increase the time constant and govern the charge of the double layer, leading to unlocalised dissolution [12]. Therefore, the growth of the passivation film should be minimised in ECM. For strongly passivating materials such as Nb, Ti, and W, the $R_p$ may exceed the electrolyte resistance $R_e$ in the machining gap. The compact and thick passivation film significantly inhibits material removal and poses severe problems for ECM.

Several effective methods can be used to overcome the oxide layer in the state-of-the-art ECM of passive electrodes. A typical method is to enforce the dissolution of the workpiece in an active state by exploiting a strong, aggressive electrolyte, such as hydrofluoric acid (HF), to dissolve the formed oxide. However, concentrated acidic electrolytes are undesirable in terms of work safety and environmental waste treatment costs. Applying a high current density and potential can remove the oxide layer; for example, in the ECM of stainless steel with the neutral electrolyte NaNO$_3$. However, achieving high current densities in strongly passivated materials is challenging. In certain aggressive electrolytes containing halide ions, such as Cl$^-$, Br$^-$, and I$^-$, the oxide films can be locally broken down, leading to pitting corrosion [13]. Zhang et al. [14] applied transmission electron microscopy to directly observe Cl$^-$ attack on the passivation film of an FeCr$_{15}$Ni$_{15}$ alloy. From the results, chloride ions were transferred to the metal/film interfaces along the grain boundaries of the passive film. The accumulation of Cl$^-$ at the interface results in lattice expansion of the metal, undulations of the interface, and structural inhomogeneity of the film, eventually causing passivity

| Table 1 |
|---------------------------------|-------------------|
| Condition | Value |
| Nozzle material | Stainless steel 304 |
| Nozzle inner diameter | 1.11 mm |
| Workpiece | Nb plate, 0.1 mm thick |
| Inter-electrode gap | 0.5 mm |
| Electrolyte | 20 wt% NaNO$_3$ (aq.) |
| Electrolyte flow rate | 6 mL/s |
| Power supply | Constant current control |

Waveform definition:
- $I_a$ / $I_c$: anodic current / cathodic current
- $I_p$ / $I_c$: anodic on time / cathodic on time
- $Q_a$ / $Q_c$: positive charge / negative charge
- $T$: pulse period $T = t_a + t_c$
- $f$: pulse frequency $f = 1/T$

Fig. 1. Principle and experimentation for bipolar electrochemical jet machining of passivating materials. Bipolar-EJM involves alternative formation and reduction of the oxide film. Accurate waveform design of bipolar pulse, principally $f$ and $Q_a/Q_c$, is proposed here to realize machining via precise control of the kinetics of anodic oxide formation and cathodic oxide reduction.

Fig. 1. (a) Schematic of bipolar-EJM principle. (b) Experimental setup.
breakdown. However, high concentrations and high current densities are required in ECM, in addition to their corrosive characteristics. Specifically, for electrochemical jet machining (EJM), attempts have been made to overcome the anodic oxide film by selecting proper electrolytes and introducing extra energy fields. Speidel et al. [15] undertook a systematic investigation into the influence of electrolytes. They indicated that compared with NaNO$_3$ electrolyte, NaCl and NaBr electrolytes may better suppress the passivation of Ti–6Al–4V in the EJM for the formation of TiCl$_4$/TiBr$_4$ which can retard oxide growth. However, even utilizing electrolytes containing halide ions, the machining response is often still poor, especially in translating EJM of titanium alloys. This is because, as reported by Liu et al. [16], the removal of oxide film on titanium alloy necessitates a high current density and adequate attacking time. Liu et al. [17] proposed an organic electrolyte in EJM of titanium alloys, NaCl ethylene glycol-based solution, which can effectively avoid oxide layer formation and achieve satisfactory precision. As for EJM of another typical passivating metal, tungsten carbide, a mixture of NaNO$_3$ and NaOH was selected as the appropriate electrolyte by Hackert-Oschätzchen et al. [18].

Recently, hybrid ECM processes have received attention for the activation of passivated electrodes. Pajak et al. developed laser assisted EJM, which uses laser to help to break the oxide film that occurs on the surface of titanium alloy [19]. Zhan et al. proposed plasma-assisted ECM method to strengthen the capacity of ECM in machining passivating material tungsten [20]. Smith et al. [21] observed in the EJM of titanium that ultrasonic assistance can partially remove the passivation film and reactivate the machining gap, thereby enhancing the machining aspect ratio and surface quality by ultrasonic cavitation. Mechanical

Fig. 2. Phenomenological study on passivation oxide film of Nb subjected to cathodic polarisation by single-pulse experiments. (a) As-anodised spot of Nb resulting from a positive pulse; (b)–(d) Cathodic polarisation of the anodically formed oxide film with different pulse durations; (e) XRD spectra of the as-anodised oxide film; (f) Diameter of the destructed region of oxide film corresponding to cathodic polarisation time.
depassivation using abrasive particles to scrape the oxide film, such as the hybrid process of ECM with grinding [22] and abrasive-enhanced EJM [23], is under development.

Conversely, Maeda et al. [24] and Masuzawa et al. [25] demonstrated an innovative ECM approach that realises the dissolution of tungsten carbide (WC) alloy in a neutral electrolyte NaNO$_3$ by applying an alternating current. The insoluble tungsten oxide (WO$_3$) film grown on the surface of the workpiece by anodic oxidation was dissolved by alkaline NaOH generated during the negative pulse duration. However, the application of this method is limited to tungsten, as most passivation films are still insoluble in NaOH-like alkaline solutions. Meng et al. [26] applied bipolar pulses to electrochemically process nickel-based metallic glass in wire electrochemical micromachining utilizing a 0.1 M H$_2$SO$_4$ electrolyte. Bipolar pulses can effectively inhibit passivation film growth on Ni-based metallic glass in dilute acidic electrolytes, the mechanism of which is not detailed. Hall et al. [27] employed a pulse/pulse reverse approach to achieve electropolishing of the passivating material Nb like in an aqueous electrolyte of 2–10 wt% H$_2$SO$_4$. Material removal is believed to be realised by depassivation of the workpiece using reverse pulses. However, the exact mechanism of cathodic depassivation has not yet been elucidated. Moreover, a hazardous chemical species H$_2$SO$_4$ is still required as an electrolyte in their experiments, the reason for which has not been explained. Therefore, a significant gap still exists between the experimental and theoretical understanding of depassivation in bipolar processes.

Zhao et al. [28] performed cathodic hydrogenation experiments on workpiece electrode niobium using the EJM technique. Based on the results, cathodic hydrogenation can prominently interact with the workpiece electrode and cause evident hydrogen embrittlement owing to the introduction and incorporation of hydrogen into the workpiece. Meanwhile, it has been reported that a surface oxide coating formed on bare metal has a considerable impact on retarding and reducing cathodic hydrogen diffusion and permeation, which assists in preventing the hydrogen embrittlement of metals [29]. Conversely, corrosion science research has often described the cathodic breakdown phenomena of the anodically formed passive oxide film. Haring [30] revealed the electrolytic rectification effect of tantalum (Ta) electrode film with Ta oxide in an electrolytic cell, showing the ability of electrons to traverse the oxide film thickness under a cathodic pulse. However, the cathodic breakdown of oxide films has not yet been discussed in detail. Schultze et al. [6] discussed electron-transfer reactions on passive oxide film of tantalum, considering its dependence on film thickness. Takahashi et al. [31, 32] revealed film breakdown and pit formation in the cathodic polarisation (CP) of aluminium covered with anodic oxide films accompanied by hydrogen evolution. They state that pits are formed by local corrosion of the substrate owing to a local increase in pH. The film structure, for example, thickness and imperfections in the oxide, influence pit formation. Hassel et al. [33] also demonstrated the cathodic breakdown of anodic oxide films on Al (3–15 nm formed by 1 V anodic polarisation) by monitoring the current transients and discussing the effect of cathodic hydrogen evolution, film thickness, and polarisation potential.

The above studies indicate a significant interplay between CP and the oxide film. However, the potential range applied in these potentiostat pulse experiments (generally +1 to −3 V) is far from the ECM conditions (high current density and high fluid flow rate). The complete removal of metal oxides insoluble in alkaline solutions has not been discussed in depth. Further, no research has investigated the effect of continuous pulses on cathodic breakdown. Therefore, the interaction behaviour and mechanism of CP with anodic oxide films in bipolar pulse electrochemical machining of passivating materials remain unclear and unexplored. This study aims to reveal the underlying mechanisms of oxide depassivation...
film removal or elimination under bipolar pulse conditions, advancing the ECM process.

2. Methodology and materials

For ECM variation, the EJM was implemented to conduct experimental research considering its flexibility and repeatability. Owing to the advantages of high surface integrity and microscale resolution, EJM technology has received extensive attention for micromachining and surface engineering. A schematic of bipolar-EJM is shown in Fig. 1 a. The electrochemical components of the tool electrode, electrolyte, and workpiece electrode were determined to be a stainless-steel nozzle tool electrode - NaNO$_3$ solution - Nb workpiece electrode. A pure Nb metal plate (99.9%) was selected as the workpiece specimen to facilitate the experimentation. Nb is a strongly susceptible-to-passivation material that can only be electrochemically dissolved in a highly concentrated acidic solution, mostly H$_2$SO$_4$–HF mixtures [34]; however, it is also prone to hydrogen embrittlement [28, 35]. To achieve eco-friendly ECM, a widely used pH-neutral NaNO$_3$ electrolyte was selected as the working fluid. In the EJM, a fine electrolyte jet stream is employed instead of a well-designed cathode tool to achieve localised polarisation of the target workpiece material. By simply reversing the workpiece polarity to negative, localised hydrogen deposition can be realised via a cathodic hydrogen evolution reaction [28].

The bipolar-EJM experiments were conducted on a homemade platform, as shown in Fig. 1 b. The system allows for an adjustable inter-electrode gap (IEG), controlled jet movement, and controlled electrolyte flow; the details can be found in a previous study [28]. The experimental method was determined as follows: In the single-pulse experiments, the workpiece specimens were first anodised by EJM to intentionally form oxide films with different thicknesses on the material surface. Next, the polarity was reversed to apply a negative pulse to implement galvanostatic CP at the jet-impinging zone, thus leading to the deposition and interaction of hydrogen with the oxide film. Changes in workpiece surface morphology were evaluated to explore the impact of CP on the oxide film. Further, we exploited a continuous bipolar pulse output, as illustrated in Fig. 1 c, to implement an alternative oxidation-reduction process. It is proposed here that, machining of passivating materials can be achieved by alternative oxidation and reduction of the workpiece with bipolar pulses. The anodic pulse enables oxide formation, while the subsequent cathodic pulse removes the oxide by cathodic breakdown.

Prior to the experiments, the workpiece sample was degreased by sonication in ethanol for 2 min at room temperature, rinsed with deionised water, and dried in the air. The current and voltage signals were monitored during the experiments. Electrochemical measurements were conducted using a potentiogalvanostat (Corrtest, CS2350). We performed X-ray diffraction (XRD, Rigaku Smartlab), scanning electron microscopy (SEM, Hitachi TM4000Plus, and ZEISS Merlin), and atomic force microscopy (AFM, Bruker Dimension Edge) to investigate the surface of the processed samples. The surface profile was detected by laser scanning confocal microscopy (LSCM, KEYENCE VK-X1000) and stylus instrument (SURFCOM NEX 031). Unless specified otherwise, all experiments were conducted under the conditions shown in Table 1.
3. Interplay of hydrogen with passive oxide film in cathodic polarisation

3.1. Surface response of passive oxide films to cathodic polarisation in a single pulse

As shown in Fig. 2, a thin and compact film exhibiting an interference colour corresponding to its thickness was readily formed on Nb by anodising the sample material for 1 s at a current density of 31.6 A/cm$^2$. The formed niobium oxide acted as a barrier, preventing the anodic dissolution of the metal substrate. The XRD spectra of the anodised spot presented in Fig. 2e indicate that the main component of the passivation film is niobium pentoxide, resulting from the following reaction [36,37].

$$2\text{Nb} + 5\text{H}_2\text{O} = \text{Nb}_2\text{O}_5 + 10\text{H}^+ + 10\text{e}^-$$  

(1)

The oxidised spot was subjected to galvanostatic CP by reversing its polarity. Under a cathodic pulse, the hydrogen evolution reaction shown below can be inferred:

$$\text{H}_2\text{O} + \text{e}^- = \frac{1}{2}\text{H}_2 + \text{OH}^-$$  

(2)

The evolved hydrogen interacts with the oxide film-covered Nb working electrode, causing cathodic hydrogenation. At a negative current density of 63.2 A/cm$^2$, nanometric pitting appeared on the oxide film at $t = 1$ s, as seen in the SEM image (Fig. 2b). The nano-pitting increases and coalesces with prolonging cathodic polarisation time, eventually resulting in localised large-area destruction of the passivation film. Further, the centre of the oxide film underwent a noticeable colour change from blue to white, as marked by the dashed red circle, indicating that the film destruction or thickness variation likely results from

![Fig. 5. Failure modes of the oxide film as viewed in an SEM resulting from a single bipolar pulse. (a) Nano-pitting along specific orientations; (b) Large-area dissolution by cathodic corrosion; (c) Random nano-pitting and exfoliation of the oxide film; (d) Pitting, cracking, and flaking-off, accompanied by hydrogen embrittlement of substrate metal.](image)

![Fig. 6. Schematic of oxide film reduction by pitting formation and cathodic corrosion. Protons (H$^+$) discharge at the oxide surface releases H atoms, which reduce the oxide or form hydride, resulting in pit formation and cathodic reduction-induced corrosion.](image)
cathodic reduction (Fig. 2b–d). By defining the area of the colour change as the region of the passivation film damaged by cathodic polarisation, we can plot, as shown in Fig. 2f. The lighting conditions were kept the same during image acquisition for comparison purpose, and an image processing software ImageJ is applied to measure "area of colour change" objectively by considering RGB thresholds. From the results, the diameter of the damaged oxide film region increased with increasing CP time before it stabilised.

We intentionally prolonged the anodising time to produce a thicker oxide film. The interaction between the cathodic polarisation and the passivation film becomes more significant with increasing film thickness, as shown in Fig. 3. With an increase in the cathodic on time, the damage mode of the passivation film underwent the following transitions: (i) dissolution or pitting along grain boundaries (Fig. 3a and b), (ii) large-area dissolution caused by cathodic reduction corrosion and coalescence of nano-pits (Fig. 3c), and (iii) cracking, flaking-off, or exfoliation (Fig. 3d). Nano-pitting is neatly distributed along specific orientations. Cracking, flaking-off, and exfoliation of the oxide film occurred at a substantial cathodic on-time (Fig. 3d), which showed a significant lag relative to the appearance of pitting corrosion during the CP process.

Meanwhile, the resulting sample surface shows distinguished white and grey areas under a long cathodic polarisation pulse of ~0.6 A and 60 s, as shown in the SEM image in Fig. 4a. Based on EDS analysis, the grey area exhibits 15–18% oxygen, indicating a passivation film composed of niobium oxide. In contrast, much less oxygen was detected in the white region, suggesting a restored virgin metal surface of Nb (Fig. 4b). The white area appeared locally and discretely because of localised destruction and exfoliation of the oxide film. AFM measurements of the surface profile confirm a height difference of several tens of nanometres, as shown in Fig. 4c, implying that the white area is the initial sample surface exposed after the oxide film exfoliation. Fig. 4d presents exemplar evidence of local removal of the oxide film. However, the removal area exhibited an irregular shape, and the removal edge was rough, implying a cathodic corrosion-induced exfoliation mechanism. On the residual oxide film in the periphery, 50–80 nm nano-pits were observed. Further, approximately same-sized nano-bulges (protrusions) are produced on the exposed substrate surface. These results indicate that the CP process can locally destroy the passivation film and reactivate the workpiece electrode by re-exposing the substrate material surface to the electrolyte.

3.2. Cathodic breakdown mechanism of the oxide film: electrochemical and mechanical aspects

As described above, the CP process damages the oxide film in four distinct ways: 1) nano-pitting, 2) dissolution, 3) cracking, and 4) flaking-off or exfoliation, as shown in Fig. 5. This observation suggests that both electrochemical and mechanical breakdowns are involved in oxide removal. Because the cathode reaction involves reducing protons and precipitation of hydrogen gas, we infer that hydrogen (H⁺, H, and H₂) plays a vital role in the process. A detailed discussion of both mechanisms is presented below.

(I) Electrochemical breakdown. The oxide film exhibited an evident failure mode of nanometric pitting and cathodic corrosion, as observed in Fig. 5a and b. Many nano-pits appeared in the oxide film, which, in most cases, were distributed locally along specific crystal orientations. Protons (H⁺) are discharged directly at the oxide surface by increased...
Fig. 9. Influence of cathodic polarisation on oxide film failure in terms of cracks and exfoliation. (a–d) shows a significant aggravation of oxide film cracking and exfoliation with an increase in current amplitude and ON time of the cathodic pulse. The error bars represent the highest and lowest values in the repeated experiments.

Fig. 10. Effect of oxide film thickness on the impact of cathodic hydrogenation: (a) shows evident hydrogen embrittlement of a bare Nb metal resulting from cathodic polarisation; (b) shows the retard of hydrogen embrittlement owing to the presence of anodic oxide film on Nb; (c) and (d) shows the failure degree of the oxide film under different anodisation conditions. The thicker the oxide film, the more pronounced the hindering effect on hydrogen. The error bars represent the highest and lowest values in the repeated experiments.
conductivity at the weak spots of the oxide film or by electron tunneling, as shown in Fig. 6. The released hydrogen can modify the oxide structure, reduce the oxide to metal, or form hydrides, resulting in pit formation and cathodic reduction-induced corrosion \[32, 38\]. Several possible hydrogen reactions, based on the E-pH diagram of the Nb–H\(_2\)O system \[39\], are presented in Fig. 6. In many cases, nano-pits exhibit specific orientations, indicating preferred proton discharge at grain boundaries or specific crystal orientations owing to a weaker oxide strength. The nano-pits further caused local exfoliation of the oxide film, as observed in Fig. 5c.

(II) Mechanical breakdown. In most cases, nanoscale cracks formed in the oxide film were rather straight and exhibited evident orientations, as shown in Fig. 5d. Most of the cracks formed were distributed locally and aligned in parallel. The propagation, intersection, and convergence of crevices led to the local flaking-off of the oxide film. The cracks in specific orientations are considered to result from the increased interaction (transportation, reaction) of protons with the oxide film and the metal substrate occurring at intergranular regions and upon grains with preferred orientations \[14, 28\]. Notably, the flaking-off area of the oxide film exhibits a polygonal shape with specific angles close to 90° and 120°. Further, the formation of cracks in the exposed Nb substrate was observed. The crack locations in the metal substrate overlap with those in the oxide film, indicating that hydrogen enters the passive film and diffuses into the substrate material, causing hydrogen embrittlement of Nb. The penetration of hydrogen into the substrate material suggests that protons arrive at the oxide/metal interface through diffusion and obtain electrons from the metal to discharge. Consequently, tiny bubbles are generated and accumulated at the interface, causing cracking and flaking of the oxide film. The schematic of the cathodic process is shown in Fig. 7. According to the diffusion theory in solids, small-sized protons (H\(^+\)) or hydrogen atoms (H) preferentially diffuse along the substrate/passivation film interface, grain boundaries, and dislocations in the oxide film and substrate material at a higher diffusion rate than lattice diffusion. Considering the high diffusion coefficient of H \[40\], a diffusion length of about several tens \(\mu\)m can be achieved within 1 s. Hydrogen diffusion along these fast channels (i.e. channelling) causes a significant local increase in the hydrogen content, leading to hydrogen-rich regions and further formation of hydrides or minute

![Fig. 11. Electrochemical impedance spectroscopy of sample surfaces subjected to a bipolar pulse. (a) Illustration of the EIS characterisation area; (b) Bode plot of as-jet-anodised sample; (c) Bode plot of anodised sample further subjected to cathodic polarisation; (d) Nyquist plot.](image1)

![Fig. 12. Equivalent electrical circuits to model/fit the EIS spectra. (a) As-obtained oxide film resulting from jet anodisation; (b) The oxide film further subjected to cathodic polarisation. Notations: \(R_{sol}\) refers to the solution resistance; \(R_{ox}\), CPE is the resistance and pseudocapacitance of the oxide film, respectively.](image2)
hydrogen bubbles ($H_2$). The existence of hydrogen in solid solutions causes lattice expansion, interface undulation, structural in-homogeneity, and eventually, cracks [14, 28, 41].

3.3. Process parameters influencing the breakdown of oxide films in a single bipolar pulse

We attempted to exploit the cathodic breakdown phenomenon to completely remove the oxide film and reactivate the working electrode surface in the ECM. Therefore, the fundamental process parameters; that is, the polarisation time and current, were systematically investigated to clarify their effects on oxide removal. To determine the degree of removal, the area percentage of oxide exfoliation and the density of cracks in the oxide film viewed in the SEM were quantitatively evaluated. In particular, the SEM image was analysed using the image processing software Image J and separated into exfoliation areas, cracks, and oxide areas by adjusting the threshold of the grey scale. Fig. 8 shows an example in which the white areas representing oxide exfoliation in the left SEM image are converted to black after image processing.

In a single bipolar pulse, the samples were subjected to a positive pulse, followed by a negative pulse. The positive pulse was maintained constant to ensure identical anodisation conditions. Repeated experiments revealed that with the prolongation of the CP time or increase in the cathodic current, both the crack density and the exfoliation area of the oxide film showed an approximately linear growth, as shown in Fig. 9. However, despite the evident oxide breakdown, the CP process could not completely remove the passive oxide film. Further, the increase in the removal of the oxide film was accompanied by an increase in the degree of hydrogen embrittlement of the metal substrate Nb, indicating the increased presence of reduced hydrogen in the substrate material resulting from cathodic polarisation. Because the hydrogen damage exerted on the substrate material is not desired for precision
machining, the use of an excessively long cathodic pulse should be avoided.

However, the presence of a passive oxide film on the workpiece surface can significantly reduce the hydrogen embrittlement effect of the substrate material by retarding hydrogen deposition. We proved this by changing the anodising conditions of the samples during the pre-oxidisation process while maintaining the same cathode polarisation process. As shown in Fig. 6, the impact of hydrogen on the Nb substrate differed significantly with and without the oxide film. The surface covered with the oxide film exhibited fewer cracks. Increasing the anodising current or time resulted in a linear decrease in the exfoliation area of the oxide film and the surface crack density of the substrate. Based on the results, a thicker oxide film results in a more significant hindering effect on cathodic hydrogen deposition. However, increasing the thickness of the oxide film cannot completely prevent hydrogen from destroying the substrate material during the cathodic process. In addition, no apparent correlation existed between the crack position and the exfoliation area. Therefore, we infer that despite the significant presence of the oxide film, protons can still diffuse through the film and arrive at the metal interface, causing hydrogen embrittlement of the substrate material. When the oxide film is thinner, a larger exfoliation area is achieved during the cathodic process, suggesting a high potential for the oxide film to be completely removed in the bipolar process by controlling its formation of the oxide film.

4. EIS analysis of passive oxide film subjected to cathodic polarisation

On a reduced current pulse for CP, the destruction phenomena of the surface oxide film were relatively weak to observe using a microscope. To verify the impact of CP on the oxide breakdown at a reduced cathodic pulse, EIS measurements were conducted using an electrochemical workstation (Corrtest, CS2350) connected to a three-electrode electrochemical cell [42]. The measured impedance spectra over a wide frequency range were used to study the changes in the passive oxide film on Nb. Particularly, EIS was performed on oxide film-covered Nb samples in an electrolyte solution similar to that used in the EJM experiments, 20% wt. NaNO₃ at room temperature under static conditions. The oxide films formed by electrochemical jet anodisation with and without CP were investigated. The current pulse for anodisation and CP was 0.1 A for 60 s and −0.1 A for 60 s, respectively. Experiments were conducted using a three-electrode cell consisting of a working electrode (WE, sample), an Ag/AgCl reference electrode with saturated KCl, and a counter electrode (CE, platinum mesh). The exposure area of the working electrode was a circle with a diameter of 0.5 cm, comparable to the CP-influenced area. Impedance spectra were recorded with an AC amplitude of ±10 mV vs. open-circuit potential in the frequency range of 10 kHz - 0.1 Hz and a density of 10 points/decade. The fitting and interpretation of the EIS results were performed using ZView® software. An illustration of the characterisation area and the measurement results are shown in Fig. 11.

The relationship between frequency and impedance is described as:

\[ |Z| = \frac{1}{\omega C} + \frac{1}{\omega^{2} L} \]

where \( \omega \) is the angular frequency of the test signal, \( Re(Z) \) is the real part of the impedance, represents the resistance characteristic of the interface, \( Im(Z) \) is the imaginary part that refers to the capacitance and inductance characteristics of the interface. In Fig. 11b, the EIS spectra of the as-anodised surface show a near-capacitive response, as evidenced by the nearly constant phase angle close to 90° over a wide frequency range. Further, the phase angle decreases linearly at high frequencies from \( 10^{3} \) to \( 10^{5} \) Hz, indicating a typical thin oxide film on Nb, which exhibits predominantly capacitive behaviour. In contrast, when the oxide film was subjected to CP, the EIS spectra in Fig. 11c present two evident time constants (i.e. two symmetrical peaks in the phase angle curve), representing the number of surface state variables that influence the output current signals. Further, the sample subjected to CP exhibited a lower impedance modulus, indicating a defective oxide film resulting from the CP.

It is inferred that CP results in pitting corrosion on the surface oxide film, leading to a porous outer layer in the oxide film. The different oxide structures influenced the output signal, producing two peaks. The Nyquist diagram in Fig. 11d also confirms the impedance decrease of the passive film after CP treatment. Further, the impedance decrease in the imaginary part is more significant than that in the real part, indicating that CP causes more severe damage to the capacitance characteristics of the oxide film than the resistance characteristics. The Nyquist diagram exhibits a more depressed curve after CP, indicating that the capacitor in the equivalent circuit can be replaced by a constant phase element (CPE) [43]. Fig. 12 shows the equivalent electrical circuits, which agree with the EIS spectra. The equivalent electrical circuit model combined with the EIS spectra indicated that the as-anodised sample surface exhibited a typical nonhomogeneous oxide film. When the oxide film is further subjected to CP, the superficial oxide is partially damaged by cathodic reduction (e.g. nano-pitting and corrosion), leading to the formation of a porous outer layer in the oxide film.
5. Mechanism of material removal and design of bipolar pulse waveform

5.1. Influence of bipolar pulse frequency on oxide elimination

The single-pulse experiments above provide evidence that CP of the oxide film-covered working electrode effectively breaks down the oxide by electrochemical or mechanical means via proton incorporation and reaction. Moreover, the failure of the oxide film increased as its thickness decreased. However, the oxide film could not be completely eliminated. Further, despite the existence of an oxide film, hydrogen embrittlement of the substrate material occurs at excessive negative potentials. However, pitting corrosion in the oxide film, which initiates earlier than cracking in CP, electrochemically removes the oxide film without causing damage to the substrate material. Therefore, we infer that it is possible to thoroughly remove the oxide film by accurate modulation of the anodic oxide formation and cathodic breakdown process at the electrode interface through a dedicated design of the current pulse waveform while avoiding damage to the substrate material (e.g., hydrogen embrittlement).

Based on the above discussion, we performed bipolar-EJM experiments with continuous pulses. To modulate the kinetics of oxide formation and proton diffusion and reaction, we intentionally varied the pulse duration by changing the bipolar pulse frequency. The duty cycle was 50% and the other fundamental parameters were maintained constant. A unipolar pulse was also conducted for comparison. The experimental results are shown in Fig. 13. Compared with the unipolar pulse, the bipolar pulse at a low frequency of 5 Hz causes damage to the oxide film in the central area. However, the oxide removal was insignificant because of the relatively large oxide film thickness resulting from the long anodic pulse duration, as shown in Fig. 13a and b. An increase in the pulse frequency to 1000 Hz led to a reduced oxide film on the workpiece surface under a unipolar pulse owing to the reduced oxide growth efficiency, as shown in Fig. 13d. However, the bipolar pulse
significantly overcomes the anodic oxide film, resulting in cavity-like material removal of the Nb substrate material (Fig. 13c). The resulting cavity was 20 μm deep and was free of hydrogen embrittlement. Further, no oxide film can be observed by the naked eye, demonstrating significant success in machining the workpiece material Nb.

However, a further increase in the bipolar pulse frequency to 5000 Hz rarely resulted in material removal. Moreover, no oxide film formed on the material surface at the centre of the jet-impinging spot. Rather, the base material was severely damaged by significant hydrogen embrittlement (Fig. 13e), indicating the incorporation of H into the substrate material. However, the unipolar pulse at the same frequency produced a rather obvious oxide film (Fig. 13f), strongly indicating that the cathodic process inhibits oxide formation under bipolar conditions. The effect of the pulse frequency on bipolar-EJM is summarised in Fig. 14 through experiments. From the results, the optimum frequency range is found near 1000 Hz–1400 Hz. It is worth noting that, a good agreement is found between our and others’ research which all show that frequency behaviour can be exploited to control electrochemical machining performance [44], or even allow measurement [45].

5.2. Material removal mechanism of bipolar-EJM and the role of proton

Under the application of positive potential, an oxide forms on the anodically polarised metal surface according to the high-field mechanism [46]. The oxide film grows through an ion-transfer mechanism enabled and driven by the strong field gradient through the oxide layer. Because of ion migration, the formation current is an exponential function of the electric field in the oxide film, \( E \), as described by the following equation:

\[
j = A \exp(\beta E)
\]

(4)

where \( j \) is the current density related to oxide growth and \( A \) and \( \beta \) are temperature-dependent parameters characteristic of the oxide. Assuming that all faradaic currents contribute to oxide growth, the anodising time \( t_a \) and current density \( j \) determine the growth thickness of the oxide film. Therefore, the variation in pulse frequency results in different oxide film thicknesses in every positive pulse owing to the changed pulse duration. Further, the anodisation by unipolar pulses in Fig. 13 shows that the overall oxidation decreases with the pulse frequency, implying a reduced efficiency of oxide formation at high-pulse frequencies owing to the incorporation of the pulse interval. Under continuous bipolar pulse conditions, the variation in the transiently formed film thickness at each positive pulse influences the kinetics of ion and electron-transfer reactions at the oxide/electrolyte interface. This influences the subsequent hydrogen-oxide interaction in the succeeding negative pulse. Consequently, the process responses exhibited a significant difference.

The schematic of the detailed mechanism is shown in Fig. 15. In the negative cycle of the bipolar pulse, the primary electron-transfer reaction at the oxide-covered metal electrode is considered to be the proton discharge reaction at the oxide/electrolyte interface. Proton discharge can weaken the oxide structure, reduce it to the metal, and eventually eliminate the oxide, thereby achieving material removal. However, because the oxide film is highly resistant, the electron-transfer reaction is most likely to result from electron tunnelling between the substrate metal and the electrolyte, or electron transfer at weak film spots of enhanced conductivity. Heusler et al. [47] reported that the tunnelling probability of electrons decreases exponentially with barrier thickness in semiconducting anodic niobium oxide films. The oxide grew sufficiently in the positive pulse at a low frequency, forming a thick oxide film. The considerable thickness significantly limits electron-transfer reactions at the oxide surface by suppressing electron tunnelling. Therefore, the oxide film remained intact after the process, and no material removal was observed. However, protons possibly arrive at the metal-oxide interface and are discharged by the metal via migration and diffusion, resulting in the formation of tiny hydrogen bubbles or niobium hydrides. The bubbles damage the oxide film by cracking or flaking-off.

On increasing the bipolar pulse frequency, complete elimination of the oxide film was achieved, accompanied by an evident bulk removal of the substrate metal material (Fig. 13c). The material removal indicates that the electron-transfer reaction (e.g. proton discharge and hydrogen reduction) is enhanced at increased pulse frequencies, likely resulting from the reduced oxide film thickness. SEM observation of the machined surface confirmed that the cathodic reactions in the negative pulse removed the oxide film without inducing hydrogen embrittlement in the substrate material. Therefore, it is reasonable to infer a simultaneous growth (anodic oxidation) and dissolution process of the oxide (cathodic reduction) during the bipolar process, thus achieving bulk removal.

However, if the increase in frequency exceeds a threshold value, neither oxide film growth nor bulk removal of the substrate material can occur. Instead, cracks appear on the metal surface, as shown in Fig. 13e. Combining the results of the evident oxidation by unipolar pulses (Fig. 13f), we infer that a higher frequency results in thinner oxide growth, leading to an easier electron-transfer reaction. Meanwhile, the reduction of protons in H₂O results in the hydrogenation of the metal surface as follows:

\[
\text{H}_2\text{O} + e^- \rightarrow \text{H}_ad + \text{OH}^-
\]

(5)

The reduced hydrogen atom (Hₐd) adsorbs onto the metal surface, causing hydrogen passivation of the electrode and inhibiting the oxidation reaction process. Meanwhile, hydrogen can dissolve in the substrate metal, resulting in hydrogen embrittlement (cracks).
5.3. Regulation of electrode reaction kinetics by waveform design of bipolar pulses

In addition to the pulse frequency, the waveform shape played a crucial role in determining the machining process by influencing the cathodic oxide breakdown. For example, at an appropriate pulse frequency of 500 Hz, the complete prevention of oxide film formation at the periphery of the machining spot can only succeed at a duty cycle of less than 60%, as shown in Fig. 16. We can reasonably infer that a shorter anodic pulse produces a thinner oxide film and results in an easier breakdown of the oxide, leading to successful machining.

Based on the above results, the material removal in the EJM is ascribed to alternative anodic oxidisation and cathodic reduction processes, as shown in Fig. 17a. The positive pulse oxidises the workpiece material, producing a thin and confined oxide film on the material surface. The subsequent negative pulse rapidly removes the oxide formed via cathodic breakdown. However, the thickness of the oxide film formed during the positive pulse plays a critical role in determining the machining process. In particular, it must be emphasised that removing the oxide requires precise regulation of the amount of charge transfer in both the anodic \( Q_a \) and cathodic pulse \( Q_c \), which is defined as the product of the current and pulse duration. Depending on the ratio of \( Q_c \) to \( Q_a \), the machining process can be divided into four regimes, as shown in the experimental results in Fig. 17. At excessive \( Q_a \), corresponding to regime (I), no material removal was achieved owing to the overgrowth of the oxide film.

Fig. 17. Regulation of reaction kinetics of working-electrode oxidation and reduction by controlling the bipolar pulse waveform. (a) Schematic of the bipolar pulse design principle for EJM. Tuning of the positive pulse amplitude and time to achieve controlled oxide film formation. Similarly, adapting the negative pulse to enable electrode depassivation and oxide removal; (b) Four distinct material response regimes based on the charge transfer amount \( Q_a \) and \( Q_c \). The ‘√’ and ‘×’ represent succeeded and failed machining results, respectively. The black dot in regime (II) indicates the machining results that are in the middle of regimes (I) and (III); (c) Variation of material removal rate with \( Q_a \), where \( Q_c \) is fixed. In the ideal machining regime (III), oxidation is the rate-limiting step determining the material removal rate (MRR) of bipolar-EJM.

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which is too thick to be overcome by the cathodic pulse. In contrast, neither oxide growth nor material removal occurs at an excessive $Q_c$, referring to regime (IV). Instead, hydrogen embrittlement was observed.

However, machining can only be realised by maintaining an appropriate ratio of $Q_c$ to $Q_a$. In regime (III), the anodically formed oxide film was completely removed when the $Q_c/Q_a$ is within 6–25. Further, an oxide film could not form in the periphery. However, in regime (II), the prevention of passive film formation is incomplete despite the success of material removal (Fig. 16a). In summary, the kinetics of the electrode reactions in the bipolar process transition from oxidation-dominated to reduction-dominated with an increase in the $Q_c/Q_a$ ratio. The oxidation and reduction reactions were balanced at a suitable ratio range to achieve material removal. The influence of $Q_c$ on the machining efficiency is shown in Fig. 17c, where the anodic pulse was tuned (peak current and on time), whereas the cathode pulse was maintained constant. As observed, with an increase in $Q_c$, the MRR first increased and then decreased. Meanwhile, the machining regime gradually changed from (III) to (II). These results indicate that oxidation is the rate-limiting step in machining regime (III), which determines the MRR.

A detailed characterisation of the Nb machining results is shown in Fig. 18. Fig. 18b shows the measured current and voltage waveforms during the machining process. The SEM images in Fig. 18c and d shows that the centre of the machined cavity exhibits a smooth surface with an imperceptible oxide film. At the cavity edge, we observed some broken oxide residues that were not removed because of the lower cathodic current density in this area (Fig. 18e), resulting in locally increased roughness. An illustration of three different morphological regions of the machined surface resulting from bipolar-EJM ($I_a = 0.1 \text{ A}$, $I_c = -0.6 \text{ A}$, $f = 1000 \text{ Hz}$, duty cycle: 50%, machining time: 3.5 min).

![Characterisation of the machining results in Nb materials by bipolar-EJM.](figure)

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J. Xue et al.
A schematic diagram describing the material removal principle in bipolar-EJM of passivating materials is proposed in Fig. 19, and the key points is summarised as follows:

- The bipolar-EJM requires a relatively high frequency to avoid the overgrowth of oxide removal in every single pulse. The more readily the material oxidises (passivates, influenced by the electrolyte used), the higher the required frequency. A typical range in this study was 500–2000 Hz.

Fig. 19. Schematic of material removal principle in bipolar-EJM of passivating materials. (a) Confined oxide formation by controlled positive pulse. Formation of oxide in surrounding area is completely suppressed. (b) Oxide removal by cathodic reduction in the subsequent negative pulse. To enable the cathodic removal, the dynamic formation of oxide growth should be controlled at a very low level while substantial cathodic charge \( Q_c \) should be provided. This is achieved by accurate waveform design. (c) and (d) shows the repeated oxide formation and reduction process as the machining progresses.

Fig. 20. Characterisation of bipolar-EJM in pit machining with optimized pulse waveform. (a) Evolution of machined pit profile over time, measured by a stylus instrument. Traditional EJM of stainless SUS304 with unipolar pulse is included for comparison. Under the same anodic current, the entrance diameter of the pit by bipolar is consistent with that machined by traditional unipolar-EJM of stainless. Further, the entrance diameter keeps constant with processing time in bipolar-EJM. (b) Optical image of the machined pit at 2 min (\( I_a = 0.1 \) A, \( I_c = -0.6 \) A, \( f = 1000 \) Hz, duty cycle: 50%).
The anodic and cathodic pulses should be balanced by adjusting the current pulse amplitude and time. A larger \( Q_c/Q_a \) is required for the efficient machining of metals that are more readily passivated.

### 5.4. Characteristics of pit and groove machining with bipolar-EJM

The evolution of the pit profile over time in bipolar-EJM is characterized using optimized pulse waveform, as shown in Fig. 20. As can be seen, the machining was confined at the jet centre, about two times the internal diameter of nozzle used. This is very close to the state-of-the-art unipolar EJM of stainless, see the black line in Fig. 20a, in which the pit size is commonly about 2–3 times the nozzle internal diameter. Further, the confined machining diameter keeps constant with increasing the processing time, showing no widening. Meanwhile, the machining shows a typical Gaussian profile, indicating a dominating effect of current density distribution. A typical optical image of the machined pit at \( t = 2 \) min is shown in Fig. 20b.

Further, a groove was successfully machined with bipolar pulse by reciprocally translating the jet over the workpiece, as shown in Fig. 21. No oxide film can form in the surrounding area owing to the proposed bipolar effect. A small amount of residual oxide exists on the scan path due to secondary oxidation caused by jet trail, which can be removed by the next scan.

### 6. Conclusion

For the first time, this study reveals a generic principle for waveform design of bipolar-EJM to effectively machine a susceptible-to-passivation material. The waveform design approach employs dedicated electric fields to regulate the anodic oxide formation and cathodic reduction, thereby achieving material removal. A theoretical model describing the process mechanism was established and the effectiveness of this new method was verified by applying it to different materials. The key findings are summarised as follows.

1) A cathodic pulse enables the breakdown of the anodically formed oxide film, thereby depassivating the electrode and restoring the original metal surface. Two breakdown mechanisms are clarified: (I) Electrochemical reduction of the oxide film by cathodic reactions, manifested as the occurrence of nano-pitting, local oxide dissolution, and the reduction of the film impedance. (II) Mechanical breakdown by hydrogen incorporation into the oxide and oxide/metal interface manifested as cracking, flaking-off, and exfoliation of the oxide film. Mechanical breakdown occurs much slower than electrochemical reduction.

2) Cathodic reduction occurs at the oxide surface owing to increased conductivity at weak spots of the oxide film (e.g. grain boundaries) or electron tunnelling. An increase in the cathodic pulse enhances the oxide breakdown, manifested explicitly as an increase in the crack density and exfoliation area of the oxide film. However, excessive cathodic charge transfer promotes the permeation of hydrogen into the substrate material, resulting in hydrogen-induced substrate damage; for example, hydrogen embrittlement of Nb.

3) The thickness of the passive oxide film had a significant influence on the cathodic electron-transfer reactions. The thicker the oxide film, the more significant the hindering effect. This is evidenced by the reduced damage degree of both the oxide and substrate materials with increasing oxide film thickness.

4) In a continuous pulse bipolar-EJM, the machining process significantly depends on the pulse waveform. For example, the bipolar-EJM of Nb exhibits distinctive machining results with varying pulse frequencies, amplitudes, and duty cycles. Notably, machining is not achievable with a pulse frequency that is neither too high nor too low.

5) The material removal process of bipolar-EJM includes the alternative formation and reduction of the oxide film. The bipolar pulse waveform determines the reaction kinetics of anodic oxide formation and cathodic oxide reduction, enabling the control of oxide film formation and elimination to achieve effective machining.

6) The pulse frequency influences machining by influencing the kinetics of the electrode reactions. Excessive pulse frequency results in neither oxide film formation nor material removal. However, hydrogen embrittlement of the substrate material occurs, indicating excessive hydrogen deposition which passivates the electrode surface by adsorbing to the electrode surface, blocking the anodic oxidation process.

7) The waveform shape, quantitatively described by \( Q_c/Q_a \), in this study, significantly influences machining. The cathodic pulse (amplitude and time) required for oxide removal depended on the thickness (i.e. strength) of the transiently formed passive film in the previous anodic pulse. Four different machining regimes in the bipolar-EJM of Nb were distinguished based on \( Q_c/Q_a \). With excessive \( Q_c/Q_a \), material removal could not be achieved owing to the overgrowth of the oxide film, which is too thick to be overcome by the cathodic pulse. In contrast, neither oxide growth nor material removal occurs at excessive \( Q_c/Q_a \). Instead, hydrogen embrittlement was observed. Bipolar-EJM can only succeed by balancing the charge quantity \( Q_c \) and \( Q_a \) considering the degree of passivation of the working electrode.

8) The effectiveness of bipolar-EJM was verified on different metals (e.g. Nb, Ti, and W) and on different electrolytes (\( \text{NaNO}_3 \) and \( \text{H}_2\text{SO}_4 \)).
Therefore, the proposed method can be considered a universal approach for bipolar electrochemical machining.

This study demonstrates that the interactions of anodic oxides with cathodic reduction can be manipulated through parameterised control of the bipolar pulse waveform. This provides a novel pathway for the effective machining of susceptible-to-passivation materials using eco-friendly electrochemical machining approaches.

Credit author statement

Jinbao Xue: Conceptualization, Data curation, Investigation, Validation, Writing - original draft. Bangyan Dong: Data curation, Formal analysis, Visualization. Yonghua Zhao: Formal analysis, Funding acquisition, Methodology, Project administration, Supervision, Resources, Writing - reviewing & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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