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Aachen, November 18-19, 2024

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Development of Pulse-Reverse Electrochemical Machining Methods for Refractory Alloys

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Abstract

Faraday investigated methods to electrochemically machine the refractory alloy, Niobium C103, in neutral electrolytes. This material possesses a high degree of passivity, presenting an obstacle to anodic dissolution. Through the use of pulse-reverse current leading to successive anodic formation and cathodic destruction of the oxide film, the material can be effectively electrochemically machined. We will present a phenomenological model of the ECM process for C103 as well as an optimization algorithm designed by partners St. Louis University (SLU) and Washington University in St. Louis (WashU) to develop pulse-reverse waveforms that maximize machining rate. ECM experiments were used to generate training data for the optimization algorithm and predictions were validated using C103 coupons in a simplified ECM setup. This talk has implications for future efforts to ECM passive and refractory alloys for next-generation applications demanding high-strength and corrosion resistant materials.

1 Introduction

Refractory metals are elements with extraordinary resistance to heat, wear, corrosion, and oxidation. There is no single definition of refractory metals, but the group is generally understood to include metals like Nb, Mo, Ta, W, and Re, as well as their alloys. These metals have found uses in many demanding high-

temperature applications such as turbine engine components, heat shields, rocket nozzles and nose-cones, nuclear control rods, chemical processing equipment, electrical switching contacts, and glass melting electrodes.

Effective electrochemical machining methods for refractory alloys could open up new applications and use-cases. For example, electrochemical machining is the process of choice for many turbine engine components such as blades and vanes due to the repeatability and high-throughput of the process combined with minimal thermal/mechanical surface damage. However, the corrosion and oxidation-resistant nature of these alloys presents challenges to traditional ECM methods.

In this paper, we present an approach to ECM a Nb-Ti-Hf-Zr alloy (C103) through the use of pulse-reverse current in a benign $NaNO_3$ electrolyte. C103 was chosen for its popularity as a feedstock for additive manufacturing and the possibility of its future use in turbine engine components. C103 has a melting point of ~2350°C, as compared to ~1450°C for Ni-based superalloys. And some sources indicate superior creep resistance as compared to Ni-based superalloys [1]. In addition, Nb is the lowest-density refractory metal, potentially enabling lighter engine components.

Results show that high-frequency current pulses consisting of low anodic and high cathodic voltages in a benign electrolyte can successfully machine the C103 alloy, resulting in a smooth surface finish and exceedingly minimal electrolyte waste. We hypothesize that the mechanism of ECM in this electrolyte-material system involves successive anodic formation and cathodic destruction of the oxide film. This method of ECM can likely be extended to other refractory alloys for novel applications of these materials.

2 Experimental Approach

2.1 Technical Approach

Pulse electrochemical machining employs sophisticated electric fields to control oxide film formation and removal. This enables surface finishing and machining of passivating materials (Nb, Ta, Ta, etc...) without the use of HF acid or low water electrolytes. The key benefits for utilizing asymmetric waveforms for ECM include:

- Control of oxide film formation,

- A more homogenous current distribution,
- Increased metal removal rates,
- A smoother surface finish, and
- Water based electrolytes, such as pH neutral salts, dilute sulfuric acid, citric acid, oxalic acid, etc.

Figure 1 shows a generalized pulse/pulse reverse waveform, consisting of an anodic peak current density, i_a, anodic on time, t_a, cathodic peak current density, i_c, cathodic on time, t_c, and an off time, t_0. (*Note: voltage control is often preferred for metal removal; however, it is easier to discuss the theory in terms of current control.*) In contrast to conventional DC processes, pulse electrolytic operation introduces these key parameters that are user defined. Proper selection of these variables is critical for successful process implementation due to the strong influences that the variables have on mass transport, current distribution and metal removal rates. The anodic pulse is tuned (on-time, t_a, and peak voltage, V_a) to enhance mass transport and control current distribution.

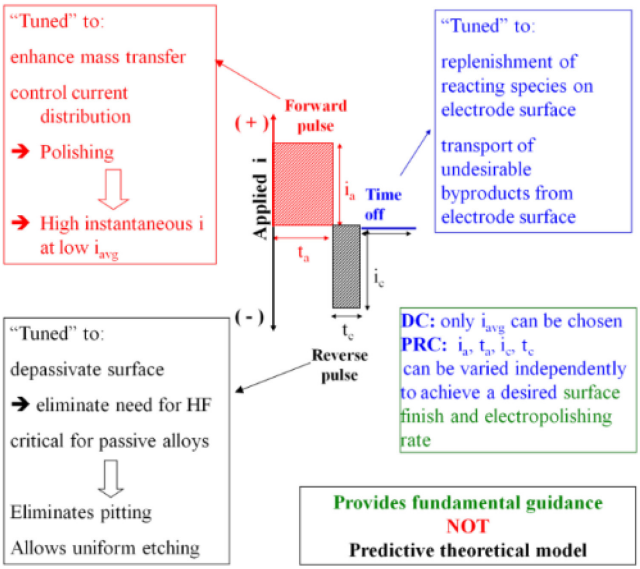

Figure 1: *Generic pulse waveform.*

To depassivate the surface we intersperse cathodic pulses between the anodic pulses, sometimes in conjunction with off-times, t_{off}, [2-4] that are present to facilitate replenishment of reacting species and removal of by-products and heat.

The cathodic pulse allows for the use of water and eliminates the need for HF, fluoride salts or other chemicals to remove the surface oxide. While the exact mechanism of depassivation is unknown, we speculate that the cathodic pulses remove the oxide either by direct electrochemical reduction, indirect chemical reduction, or mechanical destruction and restore the virgin metal surface prior to the next anodic pulse. The amplitude of the cathodic pulses required for depassivation is material specific, and appears to be based on the strength of the passive film.

In the experiments presented here, the pulse-reverse waveforms applied between the C103 test coupons and cathode tool. The coupon and tool were kept at a constant gap and machining rates were measured by the maximum depth of the machined divot (determined with an optical profilometer) divided by the machining time. First, a stationary tool was used to establish a preliminary machining rate. Then, the tool was advanced toward the surface to investigate a long-term machining rate that more closely replicates industrial processes.

1.1 Materials and Setup

Test coupons consisted of round C103 pucks with a diameter of 2.375” and thickness of either 0.125” or 0.250”. A schematic of the setup used for performing ECM experiments on C103 coupons is shown in Figure 2 with images of the setup given in Figure 3. In this setup, a 1-cm diameter titanium tube coated with a mixed-metal oxide was used as the cathode tool. This tool was held perpendicular over the C103 coupon with a 250 µm gap and could be driven toward the surface using a linear actuator. A flow housing with an O-ring seal around the cathode tool and against the flat C103 surface was used to contain the electrolyte. Electrolyte was continuously flowed through the MMO tool and across the C103 coupon surface with an outlet in the top of the flow housing.

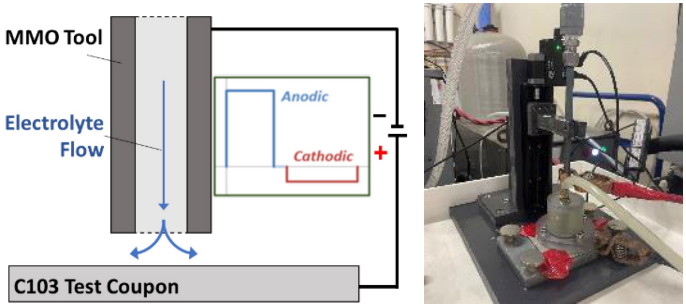

Figure 2: Cross-section schematic of vertical ECM test setup with a flat coupon and cylindrical cathode tool (left) and image of the total ECM test setup during experiments (right).

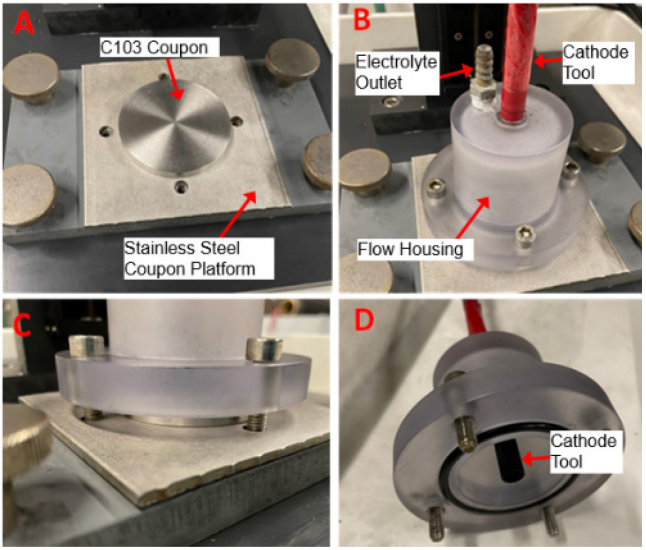

Figure 3: A) Coupon platform for the vertical ECM rig. B) Flow-chamber. C) Close-up of flow-chamber sealed to a C103 coupon. D) Cylindrical MMO tool in flow-chamber.

3 Results & Discussion

3.1 C103 ECM Results

Initial results of applying a pulse-reverse current to the C103 material provided valuable information in terms of the waveform features necessary to effectively dissolve the alloy to achieve machining. For example, a purely anodic current does not result in any appreciable machining and simply passivated the surface

with a thick oxide layer, as shown in Figure 4. In addition, a large or long anodic pulse is often unnecessary and can increase stray machining. A large enough cathodic pulse is required to achieve high machining rates. However, if the cathodic pulse is too long, machining will cease.

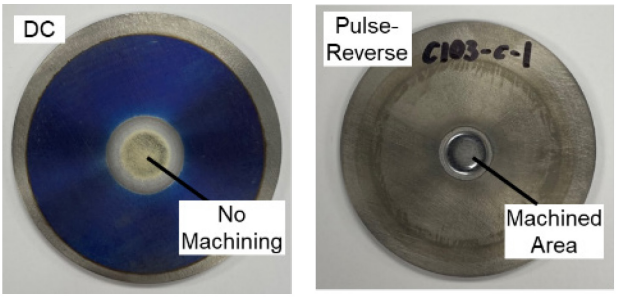

Figure 4: *Comparison of the results of a DC (left) and a pulse-reverse (right) ECM process on C103 coupons.*

An empirical approach to optimizing the waveforms for enhanced machining rates was first used after initial trials proved the ability to use pulse-reverse to ECM C103. Figure 5 shows a comparison of the machined surface of C103 coupons from two different pulse-reverse waveforms with a deep machined feature and highly-polished surface finish.

The overall machining rate for the ECM of C103 is much slower than for other materials such as nickel alloys. The empirical approach to optimizing

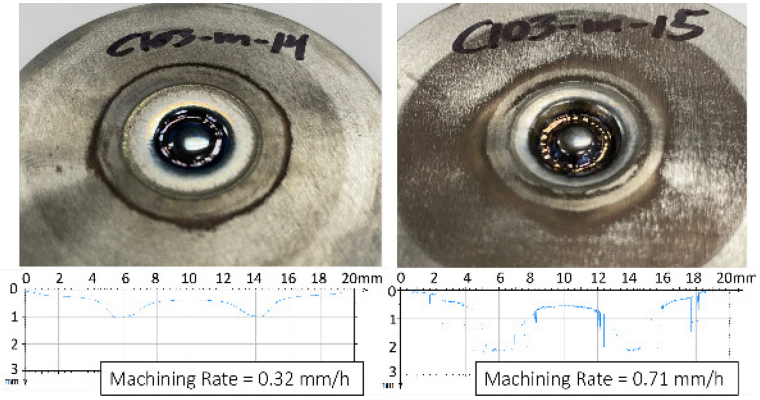

Figure 5: *Comparison between coupons machined with two different pulse-reverse waveforms and associated line profiles of the machined surfaces.*

waveforms indicated the existence of a large potential search-space which

could be amenable to a data-driven approach. As part of the data-driven appraoch to optimizing pulse-reverse Data from empirical trials using pulse-reverse waveforms were used to build an electrochemical model of the ECM process and predict waveforms with greater machining rates. This is described in the next section.

3.2 Electrochemical Model

The practice of electrochemical interface modeling via the analysis of electrical circuit analogs is common in the field of electrochemistry due to its ability to accurately predict material behaviors such as metal oxidation rates (often called “material dissolution”, in the case of electrochemical machining) and the kinetics of side reactions.

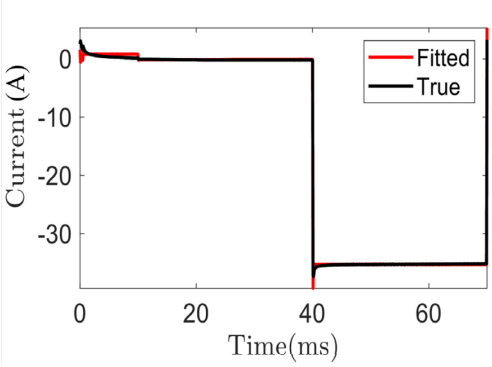

Figure 6: *Comparison between experimental and simulated waveforms.*

A model of the C103 electrochemical interface was built in collaboration with partners at SLU by considering an equivalent circuit representing metal dissolution, double-layer capacitance, and water-splitting reactions. More detailed explanations of the theory of equivalent circuit modeling are given by Barsoukov and MacDonald. [5] Examples of the use of this theory for predicting metal dissolution under alternating voltages is given in Ghanbari [6] and Moran [7]. Equations were derived to describe the relationships between voltage, current, and material dissolution kinetics. Data gathered from experiments was then used to determine the values of independent variables and predictions of the current response to a pulsed voltage signal was compared to the empirical data, showing good agreement between model predictions and the real current response (see Figure 5).

From the fitted data and electrochemical model of metal dissolution during ECM, our partners at WashU developed a pulse-reverse waveform optimization scheme to predict waveforms with the highest potential to increase machining rates in this system. These predictions were verified with experiments. Optimized waveforms could achieve machining rates greater than three times the rate achieved with a naïve waveform search.

The highest rate of machining for C103 achieved in this study was about 0.71 mm per hour. This is likely too slow for practical commercial implementation of this material (ECM of Ni can be machined at 1 mm per *minute*) in high-volume production scenarios. We anticipate that future developments in pulse-reverse ECM will be able to enhance the machining rate of C103 by an order of magnitude, enabling practical ECM. Efforts are ongoing to extend this optimization method to improve surface finish and entrainment (reduce stray machining) as well and to apply this methodology to other materials.

4 Conclusions

A method to ECM C103 alloys was developed by utilizing pulse-reverse current in a benign electrolyte. A phenomenological model of the electrochemical process was developed and applied to waveform selection to improve the machining rate of the process and explicate the underlying mechanisms. Results show that pulse-reverse current can successfully machine a C103 alloy, resulting in a smooth surface finish and exceedingly minimal electrolyte waste. This method of ECM is likely applicable for other refractory or passive alloys, potentially leading to novel uses of these materials.

Acknowledgements

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