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Thomas Bergs, Elio Tchoupe Sambou, Timm Petersen,
Tim Herrig, Andreas Klink (Eds.)

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Editors

Thomas Bergs

Elio Tchoupe Sambou

Timm Petersen

Tim Herrig

Andreas Klink

Manufacturing Technology Institute – MTI, RWTH Aachen University

Campus-Boulevard 30

52074 Aachen

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Investigating the by-products generated during ECM and Laser-ECM of NbC-Ni

M. Arshad[a,b], K. Saxena[a,b], D. Reynaerts[a,b#]*

[a]Micro- and Precision Engineering Group, Division Manufacturing Processes and Systems (MaPS), Department of Mechanical Engineering, KU Leuven, Belgium
[b]Member Flanders Make, Belgium

*Corresponding author: muhammadhazak.arshad@kuleuven.be,

#Corresponding author: dominiek.reynaerts@kuleuven.be

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Abstract

Hybrid laser electrochemical machining (LECM) has shown the capability to machine the multiphase and highly passivating NbC-Ni cermet in pH-neutral electrolyte with good surface integrity and removal localisation. In this study, the insoluble by-products were investigated by using metallography and Raman spectroscopy to gain insights into the material removal behaviour of ECM in different electrolytes (pH-neutral and basic) and LECM in pH-neutral electrolyte (aq. $NaNO_3$). The results show that particle breakout was substantially reduced with LECM in aq. $NaNO_3$ to provide better surface integrity than ECM in aq. $NaNO_3$ with NaOH additive, while maintaining an almost neutral pH of 8 for the generated by-products. Additionally, the accelerated generation of nitrate complexes proves the passivation weakening and enhanced transpassive dissolution capability of LECM.

1 Introduction

The continuous advancements in high-end, efficient, extreme environment and specialised applications has pushed for development of advanced materials that posses extreme mechanical properties and corrosion resistance. These material properties coupled with the need for high surface integrity and preservation of properties, has made it challenging for the manufacturing industry.

Electrochemical machining (ECM) presents a compelling use case as it is a thermal and can machine materials independent of hardness. However, it suffers from inhomogeneous material removal when processing advanced materials due to their passivation tendency and disparity in properties of the compositional phases. To facilitate uniform dissolution, either aggressive reagents are needed [1], which are harmful for users and the machine tools, or non-passivating electrolytes [2] are necessary which have low current efficiency. These challenges have further led to the development of hybrid EC-manufacturing techniques to machine these materials with high productivity and surface integrity [3]. Among these techniques, hybrid laser electrochemical machining (LECM) has demonstrated its capability for machining multiphase and highly passivating materials with good surface integrity [4]–[6]. However, LECM is still being developed and the multiphysical process-material interaction is still being researched.

In the same direction, this study investigates the material removal mechanisms of ECM in different electrolytes (pH-neutral and basic) and LECM in pH-neutral electrolyte by analysing the by-products generated during machining of niobium carbide with nickel binder cermet (NbC-Ni), which possesses similar hardness (1960 HV30) as tungsten carbide-cobalt [7]. The machined surfaces were observed to compare the passivation weakening and homogenous multiphase dissolution capability of the different processing conditions. The metallography and Raman spectroscopy analysis of the generated by-products helped in understanding the underlying removal mechanisms and demonstrated that LECM in pH-neutral electrolyte performed better than ECM in basic electrolyte.

2 Experimentation

2.1 Experimental setup

The in-house developed LECM setup [4] was used for the machining experiments. It can simultaneously/sequentially apply microsecond (µs) pulsed voltage and nanosecond (ns) pulsed green laser to perform ECM and LECM. The tooling configuration was modified as shown in Figure 1a to supply the electrolyte from the side using a solenoid metering pump connected to a flow nozzle (exit dia. 0.65 mm) for ease of electrolyte switching and avoiding damage to the machining head by sodium hydroxide (NaOH). Additionally, a solid quartz glass (dia. 0.65 mm) was inserted inside the tubular stainless steel tool (dia. 1.2 mm) to improve the acceptance angle of the laser for propagation through the tool

and stop electrolyte from flowing into the machining head through capillary action. The control (voltage/laser pulses and trajectory) of the machine-tool is achieved through NI® cRIO 9045 and LUMS® software. The setup is also equipped with current and temperature sensors.

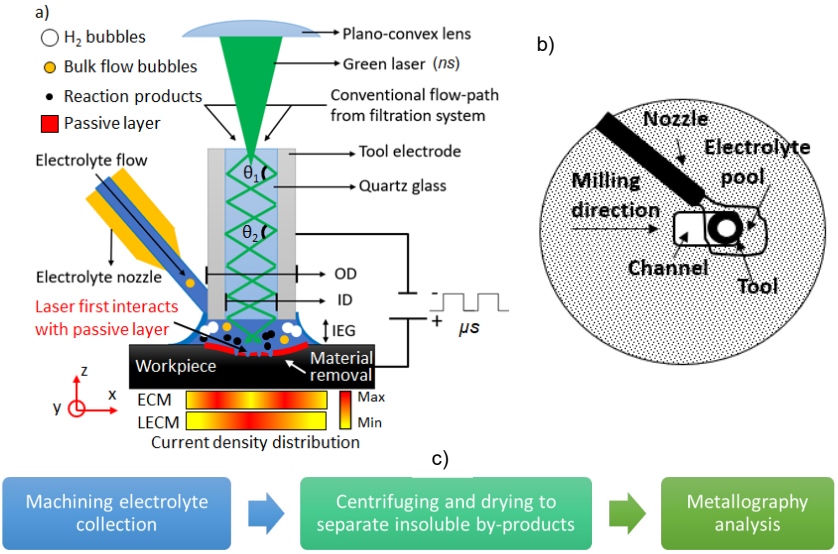


Figure 1: a) LECM process scheme with side electrolyte flow, b) machining methodology and c) procedure for by-products evaluation.

2.2 Materials and methods

EC milling experiments (Figure 1b) were conducted on sintered 76NbC-12Ni-8WC-4Mo_2C (wt.%) disc samples using parameters listed in Table 1 to study the generated by-products and machined surface morphology. Three channels (8 mm length) were machined for each processing condition: (i) ECM in 20% $NaNO_3$, (ii) ECM in 20%$NaNO_3$, 2.5%NaOH and (iii) LECM in 20% $NaNO_3$. The samples were prepared using wire-EDM and the surface was grinded using a diamond resin grinding wheel to achieve a surface roughness (Sa) of ~1.17 µm, as measured on Sensofar S Neox® (objective of 10x, 1 x 1 mm acquisition area, cutoff wavelength of 25 µm as per ISO 16610-61). After the experiments, the machined surface was observed using Philips XL30 FEG SEM microscope after ultrasonic cleaning in deionised water for 20 mins.

Figure 1c illustrates the steps for the by-products study. The electrolyte was collected after the experiments in beakers and centrifuged at 4200 RPM for 2 mins using the Heraeus SEPATECH® megafuge 1.0 to separate the insoluble by-products. Subsequently, the liquid was drained and the solid palettes were dried in an oven for 24 hours at 30 °C. The palettes were pressed between glass slides to level and prepare powder samples for further metallography analysis using the SEM microscope and a custom setup [8] for Raman spectroscopy using 40x objective, 5 mW laser power, 514 nm wavelength and 1 µm spot size.

Table 1: Experimental process parameters.

Parameter	***Value***	***Parameter***	***Value***
Voltage	*30 V*	*Laser pulse energy*	*45 µJ*
IEG	*80 µm*	*Laser pulse width*	*50 ns*
Voltage pulse width	*10 µs*	*Laser pulse frequency*	*150 kHz*
Voltage duty cycle	*50 %*	*Electrolyte flow rate*	*0.75 ml/s*
Feed rate (V_f)	*80 µm/s*	*Electrolytes: (i) 20% $NaNO_3$ (ii) 20% $NaNO_3$, 2.5% NaOH*	

3 Results and discussion

The surface morphology of the machined samples was observed to compare the passivation weakening and homogenous dissolution capability of ECM in aq. $NaNO_3$+NaOH with LECM in neutral aq. $NaNO_3$ electrolyte. The analysis of the by-products was done to help in understanding the removal behaviour and particle breakout tendency as well as toxicity of the generated waste, which is important for industrial and safety considerations.

3.1 Observation of machined surface and generated by-products

The machined surfaces in Figure 2(a-c) showed a distinct surface pattern characterised by less dissolution regions (ridge) and preferential dissolution regions (crevice). This occurred because the passive layer was not uniform across the surface due to the multiphase cermet composition, resulting in more dissolution in regions with weaker passive resistance barrier (more Ni phase) and less dissolution in regions with more passivation (more NbC phase) [5]. The following observations can be made for the different processing conditions:

(i) The low passivation weakening capability of ECM in pH-neutral $NaNO_3$ (Figure 2a) led to inhomogeneous dissolution, which is apparent by the high preferential crevice dissolution and high passivation at ridge sites marked by amorphous Nb_2O_5 formation.

(ii) The surface with ECM in $NaNO_3$+NaOH (Figure 2b) exhibited less passivation since NaOH could chemically dissolve the oxides, which also facilitated partial ridge dissolution.

(iii) LECM in pH-neutral $NaNO_3$ could weaken passivation and improved homogenous material dissolution similar to ECM with $NaNO_3$+NaOH (Figure 2c). This was facilitated by the local workpiece surface heating induced increase in current density and transpassive dissolution, which enhances removal of less reactive phases and passive layer spalling due to accelerated material removal through gaps in the passive layer [5].

The collected electrolyte and separated by-products are shown in Figure 2(d-f) which were further analysed. The colour of the collected electrolyte for all processing conditions was white/off-white due to formation of passivated products, metal hydroxides and metal-salt complexes. The similar colour of ECM and LECM by-products indicates that material removal occurs primarily though

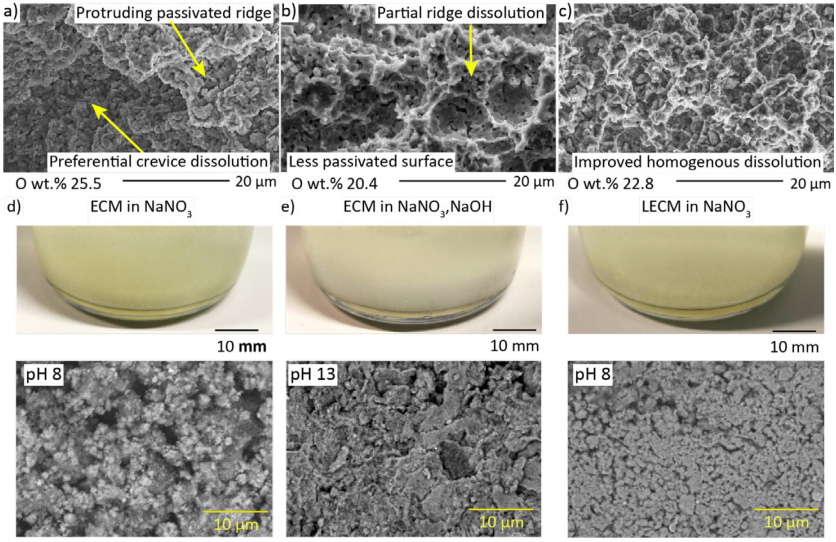


Figure 2: SEM micrographs of machined surfaces at 1000x with a) ECM in NaNO3, b) ECM in NaNO3+NaOH and c) LECM in NaNO3. Collected electrolyte and SEM micrographs at 15000x of powder samples with d) ECM in NaNO3, e) ECM in NaNO3+NaOH and f) LECM in NaNO3.

anodic dissolution and laser only serves to enhance ECM process performance. Additionally, the pH of collected electrolyte with ECM and LECM in $NaNO_3$ shifted slightly from neutral to 8 due to metal hydroxide formation whereas, the pH became highly basic (13) with ECM in $NaNO_3$+NaOH. Although NaOH addition improves passivation weakening during ECM, the highly corrosive electrolytic waste requires additional steps for safe handling and disposal to protect the machine-tool, user and environment.

3.2 Analysis of generated by-products

It was not possible to distinguish different by-products visually from the SEM micrographs (Figure 2(d-f)) due to similar product size therefore, area energy dispersive X-ray spectroscopy (EDS) and Raman spectroscopy were used. The results in Figure 3 provide quantified comparison of by-products to study their nature and the particle breakout tendency, which is common in ECM of cermets due to preferential binder removal.

ECM in $NaNO_3$ had higher C and Nb wt.% of 2.91 and 45.12, respectively (Figure 3a) than LECM which indicates presence of metal carbide breakout particles. It also had a higher O wt.% of 24.10 than LECM which shows that most of the products remained passivated due to low passivation weakening capability of ECM in $NaNO_3$, which limited material dissolution and generation of other metal complexes. This was also validated by the lowest peak level of metal nitrate complexes [9] in the Raman spectrum (Figure 3b).

The improvement in passivation weakening through chemical dissolution to generate other by-products with ECM in $NaNO_3$+NaOH can be observed by the largest Raman spectrum nitrate peak (Figure 3b). Additionally, the highest O wt.% of 45.88 (Figure 3a) shows formation of sodium niobate (Nb_2O_5 in NaOH [10]). However, it did not suppress preferential Ni removal and particle breakout indicated by the slightly higher C wt.% (3.34) than ECM in $NaNO_3$. NaOH addition chemically dissolves the surface passive layer but the EC-dissolution still proceeds according to the electrochemical properties of the cermet phases, resulting in preferential Ni dissolution. Interestingly, no W could be detected possibly due to chemical dissolution of tungsten oxide into water soluble sodium tungstate.

The improvement in passivation weakening and homogenous multiphase dissolution with LECM in $NaNO_3$ is reflected in the lowest C wt.% of 1.06 (Figure 3a), which represents decrease in particle breakout. Homogenous dissolution is facilitated by the increase in current density with LECM, which focuses on the

sharp protruding ridges to weaken passivation and increase transpassive dissolution at ridges, while suppressing preferential Ni dissolution in the deeper crevices [5]. The higher nitrate content (Figure 3b) than ECM in $NaNO_3$ also demonstrates the increased transpassive dissolution with LECM.

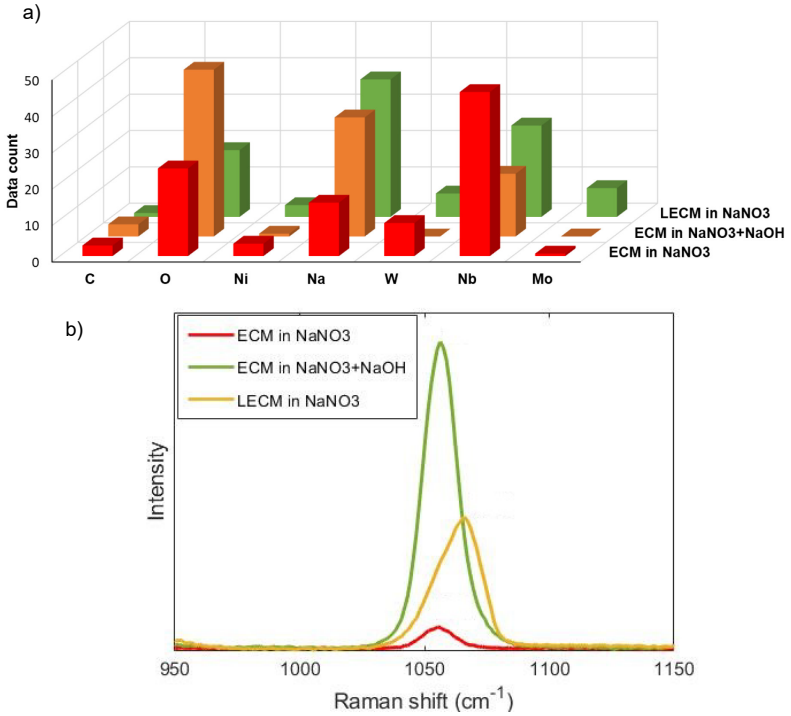


Figure 3: a) Area EDS (10 x 10 µm scan area) and b) Raman spectra indicating nitrate content of by-products powder samples.

4 Conclusion

This study investigated the generated by-products while processing the NbC-Ni cermet with ECM and LECM in $NaNO_3$ as well as ECM in $NaNO_3$+NaOH to gain insights into the material removal behaviour. The multiphase and passivating nature of the cermet makes ECM in pH-neutral electrolyte difficult, resulting in particle breakout and inhomogeneous material dissolution. The addition of NaOH improves passivation weakening through chemical dissolution, but the

generated electrolytic waste is highly corrosive (pH of 13) which makes its handling and disposal challenging. LECM in $NaNO_3$ improves homogenous multiphase dissolution and accelerates transpassive dissolution better than ECM in $NaNO_3$+NaOH by decreasing particle breakout and passivation, while maintaining a nearly neutral pH (8) of the by-products, which makes it suitable and more sustainable for processing multiphase and passivating materials.

Acknowledgement

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