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ELECTROCHEMICAL MICROMACHINING FOR NANOFABRICATION, MEMS AND NANOTECHNOLOGY

Bijoy Bhattacharyya

Micro & Nano Technologies Series

Electrochemical Micromachining for Nanofabrication, MEMS and Nanotechnology

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Electrochemical Micromachining for Nanofabrication, MEMS and Nanotechnology

Dedicated

to

my parents,

my teacher, late Prof. Swapan Kumar Sorkhel

and

my beloved wife (Rita), and daughter (Jyotiprana)

About the Author

Dr Bijoy Bhattacharyya is professor and Ex-Head of the Production Engineering Department of Jadavpur University, Kolkata. Prof. Bhattacharyya is the Coordinator of Center of Advanced Study (CAS) with thrust areas: nontraditional machining, micromachining and nanotechnology, and micromanufacturing under the University Grants Commission (UGC), New Delhi. He is also the Chief Coordinator of the Quality Improvement Program (QIP) of Jadavpur University, Kolkata. He completed his B.Tech. in mechanical engineering from Regional Engineering College, Calicut, Kerala in 1983 and ME in production engineering from Jadavpur University, Kolkata in 1985. In 1991, he completed his PhD on electrochemical machining (ECM) system from Jadavpur University. The primary research interest of Prof. Bhattacharyya had always been in the fundamental aspects of manufacturing sciences and he had been working in the area of advanced manufacturing over the last two decades. His areas of interests include nontraditional machining processes, micromachining, advanced manufacturing technology, production management, etc. Prof. Bhattacharyya contributed substantially to the development of new processes, machines and tools, especially in the emerging area of micromachining and nanofabrication. During his PhD, he developed microprocessor-based electrochemical machining (ECM) setup considering cross flow of electrolyte and performed extensive experimentations to investigate the influence of various predominant machining parameters on major machining criteria such as metal removal rate and accuracy in terms of overcut, surface finish, and surface integrity. Also, he developed different mathematical models to establish the relationship between major machining criteria and predominant machining parameters based on different developed mathematical models and carried out in detail analysis of these models to study the influence of various parameters.

His post doctoral research work included, Development of Microprocessor based Electrochemical Machining (ECM) setup and analytical models useful for the optimality search to achieve titanium machining by controlled ECM; development of electrochemical discharge machining setup to enhance machining rate and accuracy during micromachining of advanced nonconducting engineering ceramics; experimental analysis on CNC Nd-YAG laser micromachining as effective solutions to the engineers working in the machining of advanced engineering ceramics; development of pulsed Nd:YAG laser microturning setup for machining of advanced engineering ceramics which will be useful for advanced manufacturing industry; development of electrochemical micromachining (EMM) setup which has a great potential to solve the challenging problems faced by the precession manufacturing industries; development of a novel strategy for sludge removal from narrow inter-electrode gap with the help of microtool vibration for enhancing the electrochemical micromachining performance; minimization of geometrical inaccuracy due to wire lag phenomena in CNC WEDM which has tremendous potential in industrial application for machining precision contours; development of optimization strategy for WEDM of gamma titanium aluminide during single pass and trim cutting operation to provide effective guidelines to the manufacturing engineers; development of unique polarity changing strategy of micro-EDM, which is effective for machining of microhole in Ti-6Al-4V with precision; development of EMM setup for microtool manufacturing for in situ applications during various micromachining operations; development of strategies for generation of microchannel and microfeatures by applying anodic dissolution and development of EMM setup for 3-D fine pattern generation for applications in aerodynamic bearings.

He was awarded with Career Award at 1995 from the University Grants Commission (UGC), New Delhi for outstanding young teachers from engineering fields during 1994–1995; Certificate of Merit at 2003 from The Institution of Engineers (India), Kolkata for three research papers; Certificate of Achievement at 2004 and Certificate of Achievement at 2008 from Indian Society for Technical Education, New Delhi for supervising the best M.Tech. thesis in mechanical engineering; Institution Award and Gold Medal at 2009 from The Institution of Engineers (India), Kolkata for his research paper and Certificate of Achievement at 2009 from Indian Society for Technical Education, New Delhi for guiding the best M.Tech. thesis in mechanical engineering. He successfully completed several projects funded by various organizations like UGC, DST, AICTE, BARC and completed various other consultancy projects. He organized different national and international conferences and various workshops. He authored a chapter in "Introduction to Micro Machining, 2010, ISBN-978-81-7319-915-8" and edited several proceedings. He published about 103 research papers in reputed national and international journals like International Journal of Material Processing Technology, International Journal of Machine Tools and Manufacture, Institution of Mechanical Engineers (IMechE), American Society of Mechanical Engineers (ASME), International Journal of Precision Engineering, etc., with an h-index of 24 and about 256 research papers in proceedings of national and international conferences which had been a standing testimony to his valuable contributions to micromachining. He reviewed several research papers for international and national journals and attended several national and international conferences, where he acted as Chairman of various technical sessions. He guided several PhD and ME thesis and filed several patents in his credit. He is also the member and fellow of academic bodies and other national and international professional bodies and advisory committees.

Foreword

Even before 1834 when the British scientist Michael Faraday defined the laws of electrolysis that bear his name, applications for electrochemical phenomena had started to emerge. The invention of the voltaic pile around the year 1800 was the basis on which Brugnatelli, an Italian, performed electrodeposition in 1805. Following these findings, Faraday's researches spurred a major part of the industrial revolution of the nineteenth century in Europe. The process of electroforming was discovered by Jacobi of the Russian Academy of Science in 1838. In 1840 patents were filed in the UK to protect electroplating processes that were used in industry. In Germany the first electroplating production plant was established during 1876. The reverse process to electro-deposition of anodic dissolution was also being put to use with development of etching, polishing, and smoothing of metal parts.

This technological progress continued into the twentieth century. The year 1929 saw Gusseff filing the first patent on what we now term "electrochemical machining (ECM)," a method of shaping very hard alloy metals. Yet it was almost another 30 years before the widespread use of this new technology began notably in North America, Europe, and Asia. The aircraft engine manufacturers were the prime users faced with the challenge of the need to use alloy metals that were difficult to machine by traditional methods; other industries—automotive, and die and mold manufacturers—were also quick to see its use. The process fell into some disfavor in the latter part of the twentieth century: owing to the need for very high currents, the difficulties in cathode tool design, choice of electrolyte for new materials, and control of its hydrodynamic flow, and other disadvantages. Perhaps a saving feature for ECM toward the end of the twentieth century was the achievement of its use in micromachining and particularly that for domestic electric razors; the need for ECM in medical industry with a growing need for human joint replacement and the micromachining for microelectronics also have been contributory factors, that have simulated a fresh look at the process, taking us in the twenty-first century.

It is appropriate that with India's place as a major player in manufacturing, this should be the country from which this new book comes. ECM has been extensively researched over the years in India and a series of books and research papers has made its researchers well respected over all five continents. With this book Professor Bhattacharya has sought to place ECM firmly on the micro and nanomachining stage. He covers the basics, drawing attention to the need for a much better understanding of the fundamental electrochemistry. He describes the various types of micro- and nano-ECM that are available now and could be available in near future. He discusses micro tools, power supplies, and other significant facets of these fresh aspects of ECM. The book takes into the role of ECM for Micro electromechanical systems (MEMS), Electrochemical Microsystem (EMST) and Electrochemical Nanotechnology (ENT), he deals with accuracy and the relevance of Atomic force microscopy (AFM) and Scanning electrochemical microscopy (SECM), and other measurement techniques used in nanotechnology, and aspects of micro fabrication. The book serves a most useful purpose putting ECM back at the forefront as an electrochemically based process that provides solutions to twenty-first century technology challenges, more than 200 years after the first applications were first found.

Prof. J.A. McGeough
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Preface

Micromachining and nanotechnology play an increasing decisive role in the miniaturization of components ranging from electronics, biomedical to chemical microreactors and sensors. Introduction to micromachining and nanofabrication is presented as the key technology in microelectromechanical systems (MEMS). Electrochemical micromachining (EMM) appears to be a very promising micromachining technology due to its advantages that include higher machining rate, better precision and control, rapid machining time, reliable, flexible, environmentally acceptable, and it also permits machining of chemically resistive materials which are widely used in biomedical, electronic, and MEMS applications. There is urgent need to emphasize the technological applications of electrochemical reactions, rather than fundamental knowledge of electrochemistry. However, in microscopic domain electrochemical dissolution process needs special developments in the field of microgalvanics, microengineering, electrochemical material science, microelectronics, electroanalysis, and biology, etc. These wide applications form interdisciplinary bridges between science and technology. Machining is one of the primary domains of manufacturing engineers; however, successful utilization of anodic dissolution for micromachining, nanofabrication as well as in nanotechnology, emphasizes the need of knowledge, based on various interdisciplinary areas which make the development of EMM more critical and complicated.

I started my research work in electrochemical machining (ECM) during my postgraduate thesis work which focused on the development of microprocessor controlled ECM setup. Thereafter, during PhD research, in depth investigation into the influence of various parameters for achieving controlled ECM had been carried out. I was always fascinated by knowing the special capabilities of ECM and initiated postdoctoral research to utilize anodic dissolution for micromachining purposes. During my last 30 years of service in the field of academic and research, I was involved in studying and carrying out research in the numerous fields of applications of ECM in microengineering. I was excited about the anodic dissolution/deposition which can be effectively applied in micro as well as nanofabrications and finally, this motivated me to take up this endeavor of developing this book project with Elsevier to combine all the facets of EMM together not only highlighting micromachining but also MEMS, nanofabrication as well as nanotechnology applications.

Few books are available in this area mainly focusing on ECM which hardly cope up with today's needs of micromachining and nanofabrication. This may be the first attempt to stay abreast of all the developments of EMM which is rapidly expanding its scope of utility in various fields starting from micromachining, nanofabrication to nanotechnology. Chapter 1 presents an introductory overview of the concerned topics of discussion, such as micromachining, nanofabrication, EMM, MEMS, etc. Possibility of utilizing electrochemical technology for microsystems and nanofabrication has also been reported. The role of STM and AFM to fabricate nanofeatures as well as nanostructure have been introduced which will open up new horizon for nanotechnology applications. Chapter 2 provides a detailed view about the progress of ECM from macro to microdomain. Several electrochemical and other influencing factors including present status of EMM is reported which appears to be superior considering machining speed, accuracy, and economy.

Chapter 3 deals with in depth discussion on basic mechanism of material removal for EMM. Moreover, equivalent electrical circuit, material removal rate (MRR) model, formulation of MRR based on equivalent electrical circuit model as well as comparison of basic model and electrical circuit model of

MRR for EMM have been established and validated with the support of experimental results. Chapter 4 gives detail classification of EMM technique. New techniques of EMM such as layer-by-layer, sinking and milling method have been reported for the first time. Experimental results of these new techniques of EMM have also been presented to evaluate their performance.

Development of EMM setup is still at the research level. Chapter 5 describes developments of EMM setup. Important features of this chapter cover current status of EMM setup developed by various researchers working in this area around the globe. Various strategies of inter-electrode gap (IEG) control, developed and successfully implemented by various researchers have also been elaborated.

Microtool is an integral part of any micromachining and nanofabrication operations. In recent years, there is significant breakthrough in fabrication of microtools. Chapter 6 presents different types of EMM tools which have been identified and discussed for the first time. Design and developments of microtools have also been reported. Different features of microtool such as, shape, size, and surface quality fabricated by EMM have also been highlighted in this chapter.

Chapter 7 elaborates various important influencing factors of EMM. Influence of IEG, temperature, concentration, electrolyte flow, and tool feed rate has also been described with the help of large number of practical results. Chapter 8 concentrates on various strategies to improve machining accuracy of EMM. Hybrid EMM techniques which are the newer developments to improve the effectiveness of EMM have also been included. Selections of optimal combination of EMM parameters validated by test results have also been incorporated to enhance the machining efficiency and accuracy. Chapter 9 includes numerous practical and industrial applications of EMM. Various factors which restrict the wider usability of this process have been discussed. This Chapter also focuses on how to minimize these adverse factors by applying various remedial measures.

Microdevices fabrication for MEMS and other microengineering applications have been reported in Chapter 10. It presents a clear view on fabrication of microfeature of aluminum, copper, stainless steel, nickel, and titanium, etc., for MEMS. Some of the interesting topics included in this chapter are fabrication of high aspect ratio features for MEMS as well as micromachining of semiconductor by EMM. Here, EMM has successfully demonstrated its capability as an alternative technique for machining of microdevices with three-dimensional features of higher resolutions on metals as well as semiconductors.

In the area of electrochemical micro and nanofabrication, electrochemical microsystem technology (EMST) is an emerging and fast developing field with many challenging opportunities. Chapter 11 focuses on different features of EMST. Applications of EMST in microsystem technology and other miscellaneous applications of EMST have been reported. EMST has the possibility to establish a link between the conventional macroscopic electrochemistry and the electrochemical nanoscience.

Chapter 12 focuses on recent advancements in EMM for micro and nanofabrication. It contains various emerging variants of EMM. Various interesting factors of surface structuring of aluminum, stainless steel, and titanium, etc., by EMM have been presented considering not only simple flat surfaces but also complex curved surfaces. EMM can also be successfully utilized for fabrication of three-dimensional nanostructures which has also been reported.

Chapter 13 reports on how EMM can be utilized to generate nanofeatures on metals and semiconductors for nanotechnology applications. It focuses on electrochemical nanotechnology (ENT). Nanofeatures on metals and semiconductors utilizing different techniques, e.g., electrochemical printing, electrochemical etching, etc., have been illustrated. Electrochemical nanofabrication including surface nanostructuring utilizing some of the most sophisticated instruments, such as SPM, STM, and SECM has been highlighted to achieve resolutions at atomic level. Electrochemical nanofabrication by AFM tip has also been explored to demonstrate that EMM has set up its foot prints in the nanotechnology applications.

This book presents information from hundreds of sources, such as numerous articles, technical papers, and reports which have been published over the recent years as well as our own research outcomes in these areas of EMM. To assure that the reader is exposed to wider coverage of EMM, the book includes EMST and ENT for updating further applicability of anodic dissolution or deposition which promises significant advances not only in micromachining but also for nanofabrication as well as nanotechnology applications. It is impossible to include details of all the technologies; however, an inclusive list of references is given at the end of each chapter to provide further linkages. This book offers a comprehensive treatment of EMM techniques, processes, and future directions representing a valuable reference to engineers and R&D researchers involved in micromachining, micromanufacturing, or nanofabrication as well as academics and postgraduate level students with mechanical engineering, manufacturing engineering, machining processes, or nanotechnology as specialization.

At the end, critical suggestions from the readers are sought forward to improve the quality of the book in future.

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Symbols

m = Mass of a substance altered at an electrode
Q = Total electric charge passed
F = Faraday constant
M = Molar mass of a substance
z = Valency
I = Current
t = Time
n = Number of moles
n_e = Number of electrons
A = Area; Atomic weight (Chapter 1); Aspect ratio (Chapter 13)
i' = Current density
i = Partial current; number of machining parameters (Chapter 8)
E = Electrode potential
E_{eq} = Equilibrium electrode potential
E_i = Electrode potential at current i
E_0 = Electrode potential at zero current
ΔE = Electrode polarization
$E^{0'}$ = Formal potential which is the adjusted form of standard potential
v = Reaction rate
v_{rxn} = Net rate of the electrode reaction
H = Heat generated
R = Electrical resistance
V = Voltage
C = Concentration
δ_0 = Nernst diffusion layer thickness
v_{mt} = Rate of mass transfer
m_0 = Mass transfer coefficient of species O
C_0^* = Bulk concentration of species O
D_0 = Diffusion coefficient at $x = 0$
C_O = Concentration of species O
C_R = Concentration of species R
C_R^* = Bulk concentration of species R
m_R = Mass transfer coefficient of species R
T = Temperature in Kelvin
R' = Universal gas constant
R_{ct} = Charge transfer resistance
η = Over potential
η_{ac} = Activation overpotential
j_i = Partial current density
j = Total current density
$\dot{m}$ = Actual observed mass removal

η' = Power conversion efficiency
U_{oc} = Open-circuit potential
J_{sc} = Short-circuit current density
FF = Fill factor
E^0 = Irradiance
τ = Charging time constant
R_{C_d} = Resistance of double layer
ω = Radial frequency
C_d = Double-layer capacitance
R_W = Warburg Impedance
σ = Warburg coefficient
R_{ct} = Charge transfer resistance
i_0 = Exchange current density
T_b = Boiling temperature
T_0 = Temperature at the inlet
U_0 = Velocity at the inlet
e_a = Electrochemical equivalent of anode
c_e = Specific heat of electrolyte
h_0 = Equilibrium gap width at gap inlet
ρ_a = Anode metal density
ρ_0 = Density at gap inlet
f' = Feed rate of the tool
ρ_s = Specific resistance or resistivity of electrolyte
h = Inter-electrode gap
Q_v = Volume of material removed
K = Electrochemical constant for a particular material
η_c = Efficiency of dissolution or current efficiency
Q_{act} = Actual weight loss or actual material removed
Q_{th} = Theoretical weight loss or theoretical material removed
J = Anodic limiting current density
D = Effective diffusion coefficient
C_{sat} = Surface concentration
J_{mt} = Current density due to migration and diffusion
D' = Diffusivity
$\partial V/\partial X$ = Potential gradient
$\partial C/\partial X$ = Concentration gradient
q = Charge stored in the capacitor
C', C (Chapter 3) = Capacitance
R_i = Inter-electrode gap resistance
R_e = Electrolyte resistance
i_c = Charging current
R_{short} = Resistance across small flow path between the front end of the tool and workpiece surface i.e., IEG
R_{long} = Resistance across long flow path between longitudinal surface of the tool and workpiece along the side of tool
R_P = Polarization resistance
η'_a = Over potential at anode

η'_c = Over potential at cathode
j_{mt} = Current density due to mass transfer
j_{et} = Current density due to electron transfer
C_{eq} = Equivalent capacitance
V_0 = On-time voltage
α = Charge transfer coefficient
M' = Molecular mass
$Q_{V_{on-time}}$ = Volume of material removed per pulse
t_{on} = Pulse on time
t^* = Time required for charging of double layer
V^* = Flat shape waveform voltage
f = Pulse frequency in Hz
m' = Mass of material dissolved
C_{dl} = Specific double layer capacitance
ϵ = Relative permittivity of solution
ϵ_0 = Permittivity of vacuum in farad/meter
x_2 = Stern layer thickness in meter
D_O = Diffusion coefficient of the oxidant
D_R = Diffusion coefficient of the reductant
C'_O = Bulk concentration of oxidant
C'_R = Bulk concentration of reductant
R_{eq} = Equivalent resistance
R_{equ} = Total equivalent circuit resistance
T_{abs} = Absolute temperature
h' = Thickness of metal substrate
θ = Taper angle of the micro nozzle
r = Ratio of undercut
b = Thickness of metal film
G_T = Machining gap at top surface
G_B = Machining gap at bottom surface
Y_u = Response of the electrochemical micromachining (EMM) process
u = Number of experiments
x = Coded value (Chapter 8)
k = Total number of factors
β = Second-order regression coefficient
Df = Composite desirability function
W = Atomic weight (Chapter 9)

Contents