

飞秒激光-电化学沉积微结构形性调控关键 技术研究

摘 要

随着微米级金属微结构在航空航天、电子电路、芯片散热等制造领域中的需求日益增长，其高性能制造正面临严峻的技术挑战。因此，开发高效、高精度的微米级金属微结构加工技术已成为微纳制造领域的一项迫切任务。定域电化学沉积技术因具备优异的制造质量、强大的三维成形能力、良好的区域选择性、高材料致密度、形性一体化控制能力以及便于操作等优势，尤其适用于复杂三维金属微结构的制备，已逐步发展成为微金属结构的主流加工方法之一。然而，传统定域电化学沉积过程受多种工艺参数影响，普遍存在沉积质量与制造效率相互制约、沉积结构性能不足等问题。为此，本文提出一种飞秒激光-电化学沉积复合加工新工艺，围绕微结构成形演化机制不明确、加工效率受限、结构性能欠佳及结构沉积路径复杂等关键问题，遵循“激光/电化学耦合机理-结构成形演化机制-性能提升方法-高性能高效率结构一体化制造”的研究路径，系统开展飞秒激光-电化学沉积微结构形性调控技术研究，旨在实现高性能复杂微结构的高效率与高质量制造。主要研究内容如下：

(1) 针对飞秒激光与电化学反应过程的耦合机制问题，基于法拉第定律、巴特勒-伏尔摩方程及双温方程等理论基础，建立涵盖电场、流场、温度场与稀物质传递的多物理场耦合模型，系统研究飞秒激光对电极反应动力学、物质输运及电结晶过程的影响机制。结合飞秒激光加工特性，分析微区电子快速加热对电极反应动力学的加速作用。研究激光在反应微区引发的马兰戈尼效应过程，促进局部电解液微循环。此外，飞秒激光增强了电极反应动力学过程，改变电结晶过程中结晶自由能，促进晶粒的生长，调控电结晶的过程，为高效率、高性能的电化学制造奠定了理论基础。

(2) 面向电化学沉积三维复杂结构件之制造效率低的现状，本研究创新提出跨尺度点-面-体结构成形演化机制，分析点-面、面-体的结构演化过程，进一步丰富传统电化学沉积体元的生长机制。同时，在光/电耦合原理分析的基础上，明确激光在形核、结晶及结构成形过程中的促进作用。基于所提出的演化机制，设计并制造等直径悬垂结构、变直径悬垂结构及三维复杂空间结构阵列，验证点-面-体结构演化机制在复杂结构沉积中的指导意义。此外，重点探讨单脉冲能量和激光重复频率对结构成形阶段的增强作用，随着单脉冲能量的增加，体沉积速率逐渐提高，最高沉积速率可达到 $15.47\mu\text{m}^3/\text{s}$ ，较单一电化学沉积效率提高约 3 倍。

(3) 针对具有高比表面积微米尺度金属管的一步电化学制造难题，提出一种激光与电化学参数协同调控的方法，分析激光能量与环境湿度对管底部成形的协同调控机制。模拟结果显示，液桥边缘的浓度随环境湿度降低而增加，并在激光的作用下促进了空心环的形成。探讨激光能量与电场对金属管成形的协同调控机制，其中环形结构边缘的电场强度显著高于其他区域，随着沉积电位和激光能量的增加，边缘效应更加明显，从而有效制造出理想的金属管结构。此外，采用连续化和体素化方法，实现了外壁光滑和类竹节状金属管的制造。

(4) 为提升微结构的力学性能，研究飞秒激光诱导纳米孪晶的生成机制。复合加工过程高电沉积速率产生的高沉积应力，激活以孪晶界为核心的阻碍位错和自身迁移的应力弛豫机制，从而诱导新孪晶的形核和现有孪晶的细化。通过优化激光能量参数，调控晶粒的形核速率和生长。利用电化学工作站监测复合加工中的电流变化趋势，揭示电流阶梯式变化原因，并建立其与纳米孪晶生成的关系。单因素实验方法验证单脉冲能量对纳米孪晶金属结构形成的影响规律，原位微柱压缩实验表征纳米孪晶金属的力学性能，结果显示，激光诱导的纳米孪晶结构屈服强度达到 1.08GPa，实现了微观结构与宏观性能的一体化调控。

(5) 基于前期对结构成形演化过程及力学性能提升的研究，探讨高性能金属微结构在铜-铜键合中的应用。为满足三维互联电路对微结构的需求，制造三维互联结构和桥连结构，并对键合强度进行测试，结果显示铜-铜键合界面的抗拉强度达到 450MPa，揭示键合强度提高的内在原因。此外，铜线的导电性能检测结果显示，结构电阻率为 $1.92 \times 10^{-6} \text{S/m}$ ，且互联结构的最小直径为 $5 \mu\text{m}$ 。验证了该技术在电路互联领域的潜在应用价值。

关键词：定域电化学沉积；飞秒激光；金属微结构；结构成形；力学性能

ABSTRACT

With the increasing demand for micron-scale metal microstructures in manufacturing fields such as aerospace, electronic circuits, and chip heat dissipation, the high-performance fabrication of metal microstructures is facing severe technical challenges. Therefore, developing efficient and high-quality machining technologies for micron-sized metal microstructures has become one of the most urgent tasks in the field of micro/nano manufacturing. Localized electrochemical deposition (LECD) technology has gradually emerged as one of the primary machining methods for micro metal structures due to its exceptional manufacturing quality, strong capability for three-dimensional shaping, high localization, dense material formation, simultaneous control of form and properties, and ease of manipulation, making it particularly suitable for complex three-dimensional metal microstructures. However, the traditional LECD process is influenced by multiple factors, resulting in a trade-off between deposition quality and manufacturing efficiency, as well as insufficient performance of the deposited structures. To address these issues, this paper proposes a novel hybrid process combining femtosecond laser with electrochemical deposition. Focusing on challenges such as the unclear forming evolution mechanisms of microstructures, limited improvement in machining efficiency, suboptimal structural performance, and complex structural deposition paths, this study follows the research approach of “laser/electrochemical coupling mechanism-structural formation evolution mechanism-performance enhancement methods-integrated manufacturing of high-performance and high-efficiency structures” to investigate the form and property control technology of microstructures fabricated by femtosecond laser-assisted electrochemical deposition. The aim is to achieve high-efficiency and high-quality manufacturing of high-performance complex microstructures. The main research work includes:

(1) To address the coupling mechanism between electrochemical reactions and femtosecond laser interactions, a multi-physics model integrating the electric, flow, and temperature fields, along with dilute mass transport, is established based on fundamental principles including Faraday’s law, the Butler-Volmer equation, and the two-temperature model. The model aims to investigate the laser’s effects on electrode reaction kinetics, mass transport, and electrocrystallization processes. Utilizing femtosecond laser processing, the acceleration effect due to rapid, localized electron heating on electrode reaction kinetics is analyzed. The Marangoni effect, induced by the laser within the micro-reaction zone, is also examined for its role in enhancing local electrolyte micro-circulation. Furthermore, the laser enhances electrode reaction kinetics, modifies the free energy of crystallization, promotes grain growth, and regulates the electrocrystallization process. This work provides a theoretical foundation for high-efficiency and high-performance electrochemical manufacturing.

(2) A novel point-surface-volume evolution mechanism is proposed to address the low manufacturing efficiency of producing three-dimensional complex components via electrochemical deposition. This study analyzes the structural evolution from point to surface

and subsequently to volume, thereby enriching the understanding of the growth mechanisms in traditional electrochemical deposition voxels. Simultaneously, based on an analysis of laser-electrochemical coupling principles, the promotional effect of the laser on nucleation, crystallization, and structural formation is elucidated. By applying the proposed evolution mechanism, uniform-diameter overhang structures, variable-diameter overhang structures, and arrays of complex three-dimensional spatial structures were designed and fabricated, demonstrating the utility of the point-surface-volume mechanism for depositing complex structures. Furthermore, the enhancement effects of single-pulse energy and laser repetition rate on the structural formation stage were investigated. As the single-pulse energy increased, the volumetric deposition rate rose, reaching a maximum of $15.47 \mu\text{m}^3/\text{s}$ -approximately three times that achieved by conventional electrochemical deposition alone.

(3) To address the challenges associated with one-step electrochemical manufacturing of micron-scale metal tubes characterized by a high specific surface area, a method for the synergistic regulation of laser and electrochemical parameters is proposed based on previous research, which reveals the control mechanisms at various deposition stages. The synergistic control mechanisms of laser energy and environmental humidity on the formation at the tube bottom are analyzed in this study. Simulation results indicate that the concentration at the liquid bridge edge increases as environmental humidity decreases, thereby promoting the formation of hollow rings under the influence of laser energy. Additionally, the synergistic control mechanisms of laser energy and electric field on the formation of metal tubes are investigated. Electric field simulation results indicate that the electric field strength at the edge of the annular structure is significantly higher than that in other regions; as the deposition potential and laser energy increase, the edge effect becomes more pronounced, effectively facilitating the fabrication of optimal metal tube structures. Furthermore, a continuous and voxel-based approach is employed to produce smooth, bamboo-like metal tubes. To address the issue of poor surface quality on the inner walls of the tubes, a method utilizing bubble optimization is proposed, and its effectiveness is validated.

(4) To enhance the mechanical properties of the fabricated structures, the mechanism of femtosecond laser-induced nanotwin formation is studied. The high stress generated by the elevated electrodeposition rate during the hybrid process activates a stress relaxation mechanism centered on twin boundaries, which hinders dislocation motion or self-migration, thereby inducing the nucleation of new twins and the refinement of existing ones. By optimizing laser energy parameters, the nucleation rate and grain growth were effectively regulated. The variation in current during the hybrid process was recorded using an electrochemical workstation, revealing the cause of the step-like current fluctuations and establishing a correlation with nanotwin generation. Single-factor experiments were performed to investigate the influence of single-pulse energy on the formation of nanotwinned metallic structures and to analyze its relationship with nanotwin thickness. Finally, in situ micropillar compression tests were carried out to characterize the mechanical properties of the nanotwinned metal. The laser-induced nanotwinned structure achieved a yield strength of 1.08 GPa, outperforming structures produced by pure electrodeposition, thus enabling integrated control of microstructure and

macroscopic properties.

(5) Based on previous research regarding the evolution of structural formation and the enhancement of mechanical properties, the application of microstructures in the bonding strength of copper is investigated. To meet the requirements for microstructures in three-dimensional interconnect circuits, three-dimensional interconnect structures and bridge structures have been fabricated, and the bonding strength has been tested, yielding a tensile strength of 450 MPa at the copper-copper bonding interface. The reasons for the exceptional bonding strength have been revealed, indicating the potential application value of this technology in bonding applications. Furthermore, the electrical conductivity test results for copper wires indicate a resistivity of 1.92×10^{-6} S/m, with a minimum diameter of the interconnect structure measuring 5 μm .

Keywords: Localized electrochemical deposition; Femtosecond laser; Metallic microstructures; Structural formation; Mechanical properties