博士学位论文

各向同性电化学刻蚀轮廓包络抛光方法研究

STUDY ON THE ELECTROCHEMICAL POLISHING BASED ON THE ISOTROPIC ETCHING MECHANISM

摘 要

金属由于具有优异的综合性能被广泛应用于航空航天、生物医疗、化工以及消费品领域。随着现代科技的发展，金属材料的应用领域得到了进一步的发展，同时对于金属零件的表面质量要求也越来越高。针对这一需求，金属材料的表面抛光技术得到了大量的研究，其中电化学抛光作为一种无应力抛光技术，可以提供光滑、耐腐蚀的表面，被广泛应用于金属材料的表面抛光。

电化学抛光技术(Electrochemical polishing，ECP)发展至今已有近百年历史，在医疗植入物、半导体装置、3D 打印件等高科技领域有重要的应用。然而关于电化学抛光的理论研究目前仍然没有统一的认识，特别是一些新的工艺和技术的出现，比如离子液体抛光、脉冲电流抛光和磁电抛光，使得建立统一的电化学抛光理论更加困难。本论文以纯钛作为主要研究对象，对其电化学溶解过程中的各向同性刻蚀模式和各向异性刻蚀模式进行了深入的研究，揭示了金属表面电化学刻蚀模式调控的机理，并以此为基础提出了一种具有普适性的电化学各向同性刻蚀轮廓包络抛光技术(Isotropic etching polishing，IEP)，实现了不同金属材料的表面抛光。

论文的主要研究内容如下：

(1) 研究了纯钛表面电化学刻蚀的基本过程，提出了一种基于金属表面各向同性刻蚀轮廓包络原理的 IEP 技术，建立了 IEP 的表面形貌预测模型。通过对纯钛表面各向同性刻蚀孔的形成机理及工艺进行系统研究，实现了纯钛和 TC4 双相钛合金的纳米级表面抛光效果。

(2) 揭示了金属表面各向同性刻蚀与各向异性刻蚀两种模式的产生机理。研究了不同实验参数对纯钛表面刻蚀模式的影响，并掌握了金属材料刻蚀模式调控的基本原理与工艺方法。实现了对于其他常见金属材料如 304 不锈钢，纯镍和 6063 铝合金刻蚀模式的精确调控以及表面抛光。

(3) 从刻蚀行为演变规律的角度对比研究了钨在不同电解液体系中的各向同性刻蚀轮廓包络抛光与粘液层电化学抛光。测量了钨在不同电解液体系中的极化曲线。对比了钨在各向同性和各向异性模式下刻蚀后的表面形貌。钨在两种电解液体系中的抛光过程均存在各向异性到各向同性的刻蚀模式转变，证明了各向同性刻蚀在传统粘液层抛光理论中也具有关键作用。

(4) 研究了多晶金属材料(如：纯钛、纯钨和不锈钢)和非晶 NiP 合金在各向同性刻蚀抛光时的极限表面粗糙度。从 NiP 非晶合金的电化学溶解特性出发，研究了 NiP 非晶合金 IEP 的基本原理，掌握了 NiP 非晶合金的亚纳米级表面加工工艺。在此基础上，验证了 IEP 对 NiP 合金表面微结构阵列的影响。

本论文对金属材料电化学溶解基本过程进行了深入的理论分析与实验研究，提出了一种具有普适性的电化学各向同性刻蚀轮廓包络抛光方法，实现了多种金属材料亚纳米级表面抛光效果。本论文的研究完善了金属材料电化学抛光理论，为金属材料的高效超精密抛光加工提供了切实可行的理论基础与技术支持。

关键词：电化学刻蚀；各向同性；各向异性；金属；抛光

Abstract

Metals are widely used in aerospace, biomedical, chemical, and consumer products due to their excellent comprehensive properties. With the development of modern science and technology, the application field of metal materials has been further developed. At the same time, the requirements for the surface quality of metal parts are getting higher and higher. Therefore, a lot of surface polishing technologies for metal materials have been proposed. Among them, electrochemical polishing, as a stress-free polishing technology, can provide a smooth and corrosion-resistant surface and has found vast engineering applications in many fields.

Electrochemical polishing (ECP) has been developed for nearly a hundred years and has important applications in high-tech fields such as medical implants, semiconductor devices, and 3D-printed parts. However, there is still no unified understanding of the mechanism of electrochemical polishing, especially with the emergence of some new processes and technologies, such as ionic liquid polishing, pulse current polishing, and magnetoelectric polishing, making it more difficult to establish a unified electrochemical polishing theory. In this thesis, the electrochemical dissolution of pure titanium was studied. It was found that isotropic etching and anisotropic etching are two different etching modes of pure titanium. And the control of the etching mode on the surface of pure titanium was realized by adjusting the experimental parameters. Based on this, a generic approach via isotropic electrochemical etching (IEP) has been proposed to realize the surface polishing of different metal materials.

The main research content of the paper is as follows:

(1) The basic process of electrochemical etching of pure titanium was studied. And based on the simulation of the growth process of surface etching pits and the change of surface roughness, a generic

approach via isotropic electrochemical etching has been proposed to realize the surface polishing of different metal materials. Based on the systematic research on the formation and growth mechanism of isotropic etching pits on the surface of titanium and its alloys, the nanoscale surface polishing effect of pure titanium and TC4 two-phase titanium alloy has been realized.

(2) The difference between isotropic and anisotropic etching was explained from the perspective of the metal dissolution process. The basic principle and process of the etching mode regulation of metal materials were clarified by investigating the influence of different experimental parameters on the etching mode of pure titanium. The precise control of the etching mode was realized for metal materials such as stainless steel, pure nickel, and aluminum alloy.

(3) A comparative study of the mechanistic difference between ECP and IEP from the perspective of etching mode was carried out by electropolishing tungsten in two different electrolyte systems. The polarization curves of tungsten in different electrolyte systems were measured to characterize its electrochemical dissolution properties. The surface morphology of tungsten under anisotropic etching and isotropic etching modes were compared. A transition from anisotropic etching to isotropic etching was observed during the polishing of tungsten for both electrolyte systems. It was demonstrated that isotropic etching also plays a key role in ECP.

(4) The ultimate surface roughness of polycrystalline metal materials such as pure titanium, pure tungsten, 304 stainless steel, and NiP amorphous materials that can be achieved by isotropic etching polishing was investigated. Based on the electrochemical dissolution properties of NiP amorphous alloys, the sub-nanometric surface finishing of NiP amorphous alloys was achieved by electrochemical isotropic etching polishing. The effect of isotropic etching polishing on the surface microstructure was verified.

In this thesis, the theoretical analysis and experimental research on the electrochemical dissolution of metal materials were carried out, and a universal polishing method based on electrochemical isotropic etching was proposed, which realizes the sub-nanometer polishing effect of various metal materials. The study of this thesis perfects the theory of electrochemical polishing of metal materials and provides the practical theoretical basis and technical support for the high-efficiency ultra-precision polishing of metal materials.

Keywords: electrochemical etching; isotropic; anisotropic; metal; polishing