

氟化钙光学元件等离子体磁控改性
复合超精密加工关键技术研究

摘 要

氟化钙 (CaF_2) 在紫外段具有优良的透光性能, 是发展深紫外光刻机的理想光学元件材料, 但由于材料脆性大、化学惰性高, 机械加工中极易形成微凹坑、微裂纹损伤, 甚至发生解理断裂, 严重影响其固有光学性能。等离子体通过改性作用改善表层材料的理化性能, 可有效降低研磨力, 提高磨具寿命和表面质量。但现有研究中, 等离子体对脆性材料的物理和化学改性机理等关键科学问题尚不明确。受电离非均匀性、等离子体选择性、材料各向异性等因素影响, 等离子体改性均匀性与磨料高精度去除的协同效能还有待提升。

针对上述问题, 首先在分析等离子体化学改性机理及方法的基础上, 研制了可对 CaF_2 表面均匀改性的等离子体磁控均化装置, 进而分析了等离子体磁场作用机理。通过对 CaF_2 光学元件的改性分子动力学模拟和实验, 揭示了等离子体磁控均化改性机理。在此基础上, 搭建了等离子体辅助超精密磨削/研磨试验台, 研究了等离子体磁控改性复合多孔质金刚石超精密磨削机理和延性域磨削工艺、原子层机械化学研磨机理及工艺。以表面粗糙度和面型精度为目标, 对 CaF_2 光学元件的组合加工工艺进行了优化。具体研究内容如下:

(1) 针对 CaF_2 光学元件机械加工易产生裂纹甚至解理等问题, 提出了 $\text{H}_2\text{O}(\text{g})$ 等离子体化学改性方法, 通过理论分析和分子动力学模拟研究了等离子体的化学反应过程和改性层形成过程, 揭示了 $\text{H}_2\text{O}(\text{g})$ 离子体化学改性机理, 明晰了等离子体改性工艺对改性层厚度、改性层原子结构的影响机制, 进而阐明了材料各向异性对等离子体改性厚度及原子结构的影响。通过开展等离子体改性实验, 测试表征了 $\text{H}_2\text{O}(\text{g})$ 等离子体电离可产生强氧化性羟基自由基 OH^* , 从而实现氧化改性效能。通过控制变量法研究了等离子体改性工艺对改性形貌和改性层厚度的影响关系, 结果表明当功率大于 100W 时, 元件将被蚀刻去除; 当功率小于 25W 时, 元件可以被等离子体改性, 否则, 改性和蚀刻将同时进行。对比研究了混合气体 (Ar 、 He 、 O_2 、 H_2 、 H_2O) 之间的化学改性效能, 明确了 $\text{Ar}/\text{O}_2/\text{H}_2\text{O}$ 等离子体的改性优势。

(2) 针对等离子体均匀性难以控制的问题, 提出了环形电磁场均化控制方法, 理论分析了环形电磁场对等离子体的作用机制, 构建了等离子体磁控均化作用数学模型, 从而设计研制了等离子体磁控均化装置。采用 Comsol 和 Lammmps 软件构建了宏微跨尺度模拟模型, 分析了磁场对等离子体的均化作用机理, 明晰了等离子体可均匀分布的磁场控制参数。结果表明: 环型电

磁场最大可产生0.5T的磁场强度，且可通过洛伦兹力诱导等离子体横向扩散运动，通过调控磁场大小而调节等离子体均匀发散面积。磁场作用下，等离子体中的Ar、OH*、O、H离子和电子均向外扩散，其中扩散速率：电子>离子>自由基>分子。在此基础上，采用分子动力学模拟和磁控均化改性实验相结合的方法，研究了Ar/O₂/H₂O等离子体的磁控均化改性机理。阐明了针对氟化钙元件的磁控等离子体改性深度、改性面积可控的工艺参数。结果表明等离子体磁控均化改性面积由 $\phi 2\text{mm}$ 提升至 $\phi 4.5\text{mm}$ ，改性层厚度均可达200nm，且改性层均匀。

(3) 针对氟化钙元件的高效低损伤加工难题，提出了氟化钙元件等离子体磁控改性复合多孔质金刚石超精密磨削技术。采用热化学腐蚀法制备了具有纳米孔径的多孔质金刚石磨粒(W10、W5、W2)，开展了单颗金刚石磨粒(W10)划擦对比实验，阐明了多孔质金刚石磨粒低损伤划擦效能。进而采用Lammps分子动力学模拟的方法，构建了等离子体复合多孔质金刚石磨粒磨削模型，研究了单晶CaF₂(111)、(110)、(100)面的材料去除机理。在此基础上，通过等离子体复合单颗粒划擦实验分析了单晶CaF₂不同晶面等离子体改性层/未改性层的划擦机理，阐明了多孔质金刚石的“纳米多刃”延性域磨削机理。在此基础上，采用超声振动辅助浇注法在近真空环境中制备了多孔质金刚石磨具(W2)，进而通过开展Ar/O₂/H₂O(g)等离子体辅助超精密研磨实验，分析了多孔质金刚石磨具磨削工艺参数对CaF₂表面粗糙度的影响机制。模拟结果表明：等离子体辅助单颗磨粒划擦CaF₂的切削力、切削热显著降低，应力降至4.41Gpa。实验结果表明：各晶面的磨削裂纹主要以(11 $\bar{1}$)和(1 $\bar{1}$ 1)解理断裂为主，其中(100)<110>是主要的滑移面，不易发生断裂。在磁控等离子体改性条件下，磨削效率提升至8.3 $\mu\text{m/h}$ ，磨削表面粗糙度可达11.7nm，研究成果为氟化钙元件高效低损伤加工提供了技术支撑。

(4) 针对氟化钙元件磨损残留的亚表面损伤问题，提出了原子层机械化学近零损伤研磨技术。设计了机械化学磨具的组成成分及含量，分析了磨具在研磨过程中的化学反应路径，进而采用超声振动辅助浇注法在近真空环境中研制了含软磨料方解石和氧化剂高锰酸钾的机械化学磨具，并对机械化学磨具的综合性能进行了测试。通过分子动力学模拟和机械化学研磨实验相结合的方法研究了机械化学原子尺度研磨机理，阐明了氟化钙元件原子层更迭去除效能，并达成线性且稳定的原子层级去除工艺。研究表明：机械化学磨具往复研磨20次可以去除一层原子，机械化学研磨材料去除率可达235nm/h，研磨表面粗糙度可达0.89nm，为氟化钙元件的原子尺度去除提供了工艺借鉴。

(5) 针对单一工艺加工氟化钙元件的面形误差问题, 搭建了组合加工工艺设备, 优化了组合氟化钙元件的组合加工工艺, 研究了组合工艺对加工表面粗糙度的影响机制。基于准确获取的面形误差与解算的中高频误差, 采用等离子体修整技术制备了磨粒出刃高度一致的平面磨具, 优化了研磨轨迹以确保研磨轨迹的均匀性。通过控制平面磨具在误差高点长驻留、低点短驻留, 以差异化的材料去除率实现面形误差的确定性修正。对口径为 $\phi 100\text{mm}$ 的氟化钙平面镜进行了组合工艺迭代加工实验, 组合加工工艺为等离子体磁控改性-多孔质金刚石磨削-机械化学研磨三个阶段。组合加工工艺材料去除量 $9.5\mu\text{m}$, 面型精度PV值收敛至 30.58nm ($\phi 100\text{mm}$), RMS收敛至 3.59nm ($\phi 100\text{mm}$), 表面粗糙度Sa收敛至 0.56nm 。该组合工艺实现了单晶 CaF_2 光学元件的高效率近零损伤制造。

关键词: 氟化钙光学元件; 等离子体改性; 多孔质金刚石磨削; 机械化学研磨; 组合工艺优化

Abstract

Calcium fluoride (CaF_2) exhibits excellent optical transparency in the ultraviolet range, making it an ideal optical component material for deep ultraviolet lithography. However, due to its high brittleness and chemical inertness, mechanical processing easily causes micro-pits, micro-cracks, and even cleavage fractures, severely compromising its inherent optical properties. Plasma modification can improve the physicochemical properties of surface materials, effectively reducing grinding forces and enhancing tool life and surface quality. Yet, existing research lacks clarity on key scientific issues such as the physical and chemical modification mechanisms of plasma on brittle materials. Influenced by factors like ionization non-uniformity, plasma selectivity, and material anisotropy, the synergy between plasma modification uniformity and high-precision abrasive removal remains to be optimized.

To address the aforementioned issues, a plasma magnetron homogenization device capable of uniform surface modification of CaF_2 was first developed based on the analysis of plasma chemical modification mechanisms and methods. Subsequently, the mechanism of plasma magnetic field interaction was analyzed. Through molecular dynamics simulations and experiments on the modification of CaF_2 optical components, the plasma magnetron homogenization modification mechanism was elucidated. Building on this foundation, a plasma-assisted ultra-precision grinding/polishing test bench was constructed to investigate the ultra-precision grinding mechanism of composite porous quality diamond with plasma magnetron modification and the ductile domain grinding process, as well as the atomic layer mechanistic chemical polishing mechanism and process. With surface roughness and form accuracy as objectives, the combined processing technology for CaF_2 optical components was optimized. The specific research content is as follows:

(1) A H_2O (g) plasma chemical modification method was proposed to address the issues of cracking and even cleavage in the mechanical processing of CaF_2 optical components. Through theoretical analysis and molecular dynamics simulation, the chemical reaction process of plasma and the formation process of the modified layer were studied, revealing the mechanism of H_2O (g) plasma chemical modification and clarifying the influence mechanism of plasma

modification process on the thickness and atomic structure of the modified layer. Furthermore, the influence of material anisotropy on the thickness and atomic structure of plasma modification was elucidated. By conducting plasma modification experiments, it was tested and characterized that H_2O (g) plasma ionization can generate strong oxidative hydroxyl radicals OH^* , thereby achieving oxidative modification efficiency. The influence of plasma modification process on the modified morphology and modified layer thickness was studied by controlling variables. The results showed that when the power was greater than 100W, the component would be etched and removed; When the power is less than 25W, the component can be modified by plasma; otherwise, modification and etching will occur simultaneously. The chemical modification efficiency between mixed gases (Ar, He, O_2 , H_2 , H_2O) was compared and studied, and the modification advantages of Ar/ O_2 / H_2O plasma were clarified.

(2) To address the challenge of controlling plasma uniformity, a ring-shaped electromagnetic field homogenization control method was proposed. The mechanism of the ring-shaped electromagnetic field's effect on plasma was analyzed theoretically, and a mathematical model for plasma magnetically controlled homogenization was constructed. This led to the design and development of a plasma magnetically controlled homogenization device. A macro-micro cross-scale simulation model was constructed using COMSOL and LAMMPS software to analyze the homogenization mechanism of magnetic fields on plasma, clarifying the magnetic field control parameters enabling uniform plasma distribution. Results indicate that the ring-shaped electromagnetic field can generate a maximum magnetic field strength of 0.5 T. It induces lateral diffusion motion of plasma through the Lorentz force, and the uniform divergence area of plasma can be adjusted by regulating the magnetic field strength. Under magnetic influence, Ar, OH^* , O, H ions, and electrons in the plasma diffuse outward, with diffusion rates following: electrons > ions > radicals > molecules. Building on this, molecular dynamics simulations combined with magnetically controlled homogenization experiments investigated the mechanism of magnetically controlled homogenization modification for Ar/ O_2 / H_2O plasma. Process parameters enabling controllable modification depth and area for fluoride calcium components via magnetically controlled plasma modification were elucidated. Results demonstrated that the magnetically controlled plasma modification area increased from $\phi 2$ mm to $\phi 4.5$

mm, with a uniform modification layer thickness consistently reaching 200 nm.

(3) To address the challenge of efficient, low-damage processing for calcium fluoride components, a plasma magnetron-modified composite porous diamond ultra-precision grinding technology was proposed. Porous diamond abrasive particles with nanopores (W10, W5, W2) were prepared using a thermochemical etching method. Scratch comparison experiments were conducted on single diamond particles (W10), demonstrating the low-damage scratching efficiency of porous diamond abrasive particles. Subsequently, a plasma-composite porous diamond abrasive grinding model was constructed using LAMMPS molecular dynamics simulations to investigate material removal mechanisms on single-crystal CaF_2 (111), (110), and (100) surfaces. Building on this, plasma-composite single-particle scratch experiments analyzed the scratch mechanisms of plasma-modified versus unmodified layers on different crystal planes of single-crystal CaF_2 , elucidating the ductile-zone grinding mechanism of porous diamond via its “nano-multi-blade” effect. Subsequently, porous diamond abrasive tools (W2) were fabricated in a near-vacuum environment using ultrasonic vibration-assisted casting. $\text{Ar}/\text{O}_2/\text{H}_2\text{O}(\text{g})$ plasma-assisted ultra-precision grinding experiments were conducted to analyze the influence mechanism of grinding process parameters on CaF_2 surface roughness. Simulation results indicate that plasma-assisted single-abrasive-grain scratching significantly reduces cutting force and heat generation on CaF_2 , with stress decreasing to 4.41 GPa. Experimental findings reveal that grinding cracks on various crystal planes primarily occur via (111) and (111) cleavage fractures, while the (100)<110> plane serves as the dominant slip plane and is less prone to fracture. Under magnetron plasma modification conditions, grinding efficiency increased to 8.3 $\mu\text{m}/\text{h}$, with surface roughness reaching 11.7 nm. These findings provide technical support for efficient, low-damage processing of calcium fluoride components.

(4) To address subsurface damage caused by wear residues in calcium fluoride components, an atomic-layer mechanical-chemical near-zero-damage polishing technique was proposed. The composition and content of the mechanochemical grinding tool were designed, and the chemical reaction pathways during the grinding process were analyzed. Subsequently, a mechanochemical grinding tool containing the soft abrasive calcite and the oxidant potassium permanganate was developed using an ultrasonic

vibration-assisted casting method in a near-vacuum environment. The comprehensive performance of the mechanochemical grinding tool was tested. Combining molecular dynamics simulations with mechanical chemical polishing experiments, the atomic-scale polishing mechanism was investigated. This revealed the atomic-layer removal efficiency of calcium fluoride components, achieving a linear and stable atomic-layer removal process. The results indicate that 20 cycles of reciprocating grinding with the mechanochemical tool can remove one atomic layer. The mechanochemical grinding material achieves a removal rate of 235 nm/h and a surface roughness as low as 0.89 nm, providing a process reference for atomic-scale removal of calcium fluoride components.

(5) To address surface profile errors in single-process machining of calcium fluoride components, a combined machining process system was established. The combined machining process for calcium fluoride components was optimized, and the influence mechanism of the combined process on machined surface roughness was investigated. Based on accurately acquired surface profile errors and calculated mid-to-high frequency errors, a planar grinding tool with uniformly protruding abrasive grains was fabricated using plasma dressing technology. The grinding trajectory was optimized to ensure uniformity. By controlling prolonged dwell at high error points and brief dwell at low error points, deterministic correction of surface profile errors was achieved through differential material removal rates. Iterative combined processing experiments were conducted on a $\phi 100$ mm calcium fluoride flat mirror using a three-stage process: plasma magnetron modification, porous diamond grinding, and mechanical-chemical polishing. The combined process achieved a material removal rate of 9.5 μm , with surface profile accuracy converging to a PV value of 30.58 nm ($\phi 100$ mm), RMS convergence to 3.59 nm ($\phi 100$ mm), and surface roughness S_a convergence to 0.56 nm. This integrated process enables highly efficient, near-zero-damage manufacturing of single-crystal CaF_2 optical components.

Key Words: CaF_2 optical components, plasma modification, porous diamond grinding, mechanochemical lapping, combined process optimization