

激光与光电子学进展

飞秒激光制备金属表面微纳结构及其技术应用

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摘要 飞秒激光加工是近年来微纳加工领域中一种重要的加工方法。飞秒激光不仅能够对材料进行表面改性、烧蚀,更具有在特定区域加工高精度三维结构的独特优势,飞秒激光加工在微纳加工领域有着广阔的应用前景。本文主要阐述了飞秒激光与金属相互作用的一般过程,介绍了飞秒激光直写加工、飞秒激光诱导产生表面周期性结构、飞秒激光复合化学方法等表面微纳结构的制备方法。然后,分别从环境工程、航空航天以及生物医学领域阐述了飞秒激光在金属表面制备微纳结构的应用。最后,对当前飞秒激光制备微纳结构的不足和未来研究方向进行总结和展望。

关键词 飞秒激光; 三维结构; 微纳加工; 表面微纳结构

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Fabrication of Micro/Nano Structures on Metal Surfaces by Femtosecond Laser and Its Technical Applications

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Abstract Femtosecond laser has been an important processing technique for micro/nano structures in recent years. It can modify and ablate materials, and is capable of machining high-precision three-dimensional structures in specific areas. Femtosecond laser machining has broad application prospects in micro/nano processing. In this paper, the general interaction process between femtosecond laser and metals is described, and the methods for the preparation of micro/nano structures are introduced, such as femtosecond laser direct writing, femtosecond laser induced surface periodic structure, and femtosecond laser composite chemistry method. Then, the applications of femtosecond laser for the preparation of micro/nano structures on metal surfaces in environmental engineering, aerospace, and biomedicine are discussed. Finally, the shortcomings and future research directions of preparation of micro/nano structures by femtosecond laser are summarized and prospected.

Key words femtosecond laser; three-dimensional structures; micro/nano processing; surface micro/nano structure

1 引 言

飞秒激光峰值功率极高(大于 10^{12} W/cm²)、脉冲宽度在飞秒量级($1\text{ fs}=10^{-15}$ s),与长脉冲激光或者连续激光相比,飞秒激光脉冲宽度远小于被加工材料的电子-晶格弛豫时间($10^{-10}\sim 10^{-12}$ s),在晶格升温之前电子完成对光子能量的吸收,因此在加工过程中电子与晶格处于非平衡态,抑制了热扩散,进而极大地减小热影响区、降低重铸层厚度、减少表面微裂纹,最终实现材料的高精度、高质量加工^[1-5]。当飞秒激光与不同材料相互作用时,根据激光加工方法、加工环境以及加

工参数的不同,可实现表面周期性波纹结构^[6]、高深径比微孔^[7]、微槽^[8]以及不同形貌的表面微纳复合结构的加工。

通过飞秒激光加工构建不同形貌的表面微纳结构,可以改变材料的光学特性,提高材料对不同波长光的吸收率,得到抗反射性能好的表面,同时改变形貌还可以提高光对有机染料的降解速率^[9-11]。在材料表面构建多孔、分层结构可以使入射电磁波在材料中多次反射、吸收衰减,进而提高材料的电磁屏蔽性能^[12]。仿照荷叶表面结构制备微纳乳突结构,能够改变材料的表面浸润性得到超疏水表面,实现材料的表面自清洁、

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油水分离^[13-17]。

综上所述,飞秒激光加工表面微纳复合结构能够改变材料的光学性能、表面浸润性等,在环境工程、航空航天、生物医疗领域具有重要的应用前景,能够为制造领域中的国家重大需求提供技术支撑和保障,具有重大的研究意义。

本文主要从飞秒激光与金属相互作用的一般过程、飞秒激光制备金属表面微纳结构的常用方法以及飞秒激光制备金属表面微纳结构在环境工程、航空航天以及生物医疗领域中的应用阐述了飞秒激光在金属表面制备微纳结构的应用现状。最后对飞秒激光制备金属表面微纳结构的不足和未来发展方向进行总结和展望。

2 飞秒激光制备金属表面微纳结构机理及工艺方法

飞秒激光与物质相互作用是飞秒激光加工的理论基础,研究飞秒激光与物质相互作用的一般过程既可以对实验过程进行理论模拟,又可以对实验结果进行预测和验证。由于飞秒激光是在极端的物理条件下对

材料进行加工,选取合适的飞秒激光加工方法是决定所制备微纳结构质量的关键因素。因此本节对飞秒激光与金属相互作用的一般过程和飞秒激光制备金属表面微纳结构的常用方法进行介绍。

2.1 飞秒激光与金属相互作用的一般过程

飞秒激光与物质相互作用是一个涉及到热力学、传热学、固体物理等多个领域的复杂过程,目前尚无公认、统一的理论模型完整地描述飞秒激光与物质相互作用的全过程。

一般认为飞秒激光与金属相互作用分为三个过程:1)激光与电子相互作用为飞秒激光与金属相互作用的第一阶段,当飞秒激光与金属材料相互作用时,金属表面含有大量的自由电子,飞秒激光作用区域的自由电子吸收光子,自由电子被瞬时加热,这个过程发生在飞秒时间尺度,此时晶格温度未发生变化。2)自由电子将能量传递给声子,在这个过程中电子系统温度逐渐降低,晶格温度逐渐升高,二者最后趋于平衡。3)持续激光照射,当晶格温度高于材料的相变临界值时,材料通过熔化或气化发生相变,通过等离子体膨胀和辐射,完成材料的去除^[18-20],如图 1^[21]所示。

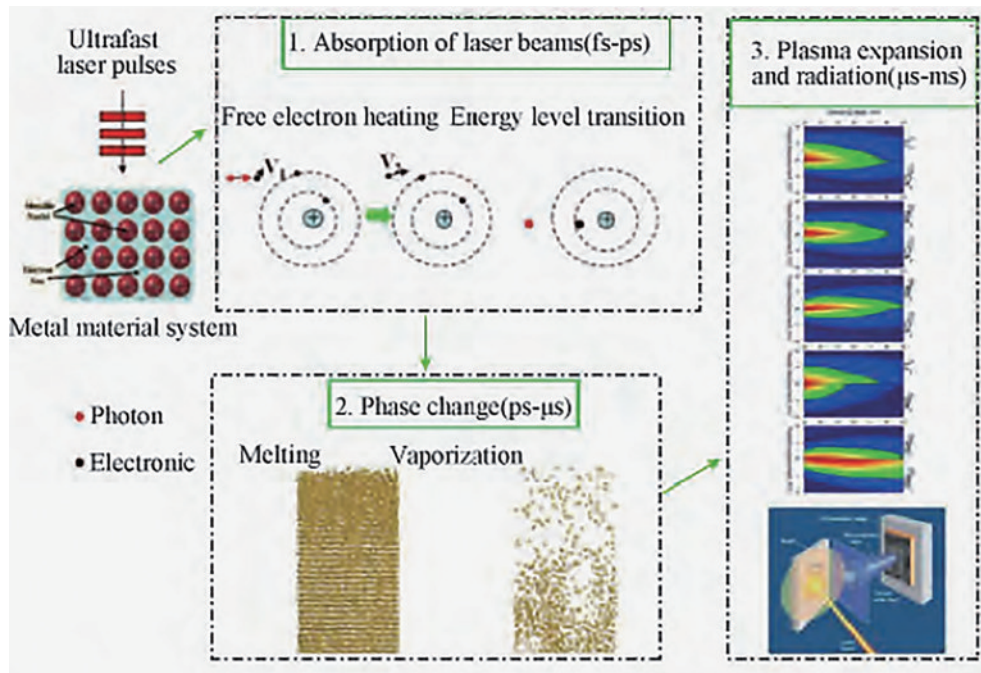


图 1 飞秒激光与金属相互作用的一般过程^[21]

Fig. 1 General process of femtosecond laser interact with metal^[21]

2.2 飞秒激光制备金属表面微纳结构的工艺方法

飞秒激光与金属相互作用不仅可以对材料进行表面改性,也可以对材料进行烧蚀,进而制备不同形貌、不同性能的表面微纳复合结构。飞秒激光直写加工、飞秒激光诱导产生表面周期性结构以及飞秒激光复合化学加工是飞秒激光制备金属表面微纳结构的常用方法。

利用不同加工方法可在不同金属材料表面制备不

同形貌的功能性表面微纳结构,表 1 列举了常见金属材料的飞秒激光表面微纳结构的制备方法。

2.2.1 飞秒激光直写加工

飞秒激光直写加工是一种直接将激光聚焦到待加工材料表面或内部,通过扫描的方式得到二维或三维精密微纳结构的加工方法。该方法无需掩模、灵活可控。通过飞秒激光直写加工不仅可以在材料表面制备不同形貌的微纳复合结构,改变材料表面粗糙度,还能

表 1 飞秒激光在常见金属材料表面制备不同形貌的微纳结构

Table 1 Femtosecond laser preparation of micro/nano structures with different morphologies on common metal materials

Material	Structure	Central wavelength /nm	Pulse duration /fs	Repetition rate /kHz	Method
Copper	Micron conical structure with nanoparticles	1030	800	400	Femtosecond laser direct writing ^[22]
Stainless steel	Columnar structure arrays	800	50	1	Femtosecond laser direct writing ^[23]
Titanium	Ripples	800	50	1	Femtosecond laser induced surface Periodic structure ^[24]
Tungsten	Ripples	800	50	1	Femtosecond laser induced surface periodic structure ^[25]
Aluminium	Hierarchical micro/nano conical structure arrays	1030	800	200	Femtosecond laser combined chemical oxidation ^[26]

够使加工区域发生氧化,改变材料表面成分等。

崔梦雅等^[27]利用中心波长为 515 nm、脉宽为 800 fs 的飞秒激光对铜离子前驱体溶液进行直写加工,制备出导电性能好的金属铜微结构。研究表明,所制备铜含量及微结构的导电性随光强的增加或扫描速度的降低而逐渐增加。赵强等^[28]利用中心波长为 1030 nm、脉宽为 800 fs 的飞秒激光通过直写的方式辐照银纳米线,制备纳米多孔银材料。研究表明,纳米多孔银材料的力学性能随着飞秒激光功率的增加而增强,晶粒尺寸随飞秒激光辐照功率的增大而减小。对比其他方法制备的纳米多孔金属材料,当纳米多孔银材料的晶粒尺寸为 50 nm 时,飞秒激光辐照制备的柔性纳米多孔银材料的屈服强度最小。

Song 等^[29]利用中心波长为 1030 nm、脉宽为 1000 fs、

重复频率为 75 kHz 的飞秒激光,通过调控激光能量、扫描速度以及扫描间距等参数,在铝表面制备不同形貌的微纳结构,得到黏附性可调的超疏水表面。Li 等^[30]利用中心波长为 1030 nm、脉宽为 290 fs、重复频率为 1 MHz 的飞秒激光,通过调控飞秒激光通量、扫描间距以及偏振等参数在钛合金表面得到超低反射率的微纳复合结构。

Fan 等^[31]利用飞秒激光在铜片表面烧蚀产生微纳花状分级结构,并对其进行了光吸收和光热转化性能测试。研究表明:覆盖微纳分级结构的铜片在紫外-可见-近红外波段的抗反射性能明显优于抛光的铜裸片和商用铜,如图 2 所示。在太阳光照射下对其进行光热转化效率测试,研究表明,覆盖微纳分级结构的铜片其光热转化效率明显优于抛光的铜裸片和商用铜,如图 3 所示。

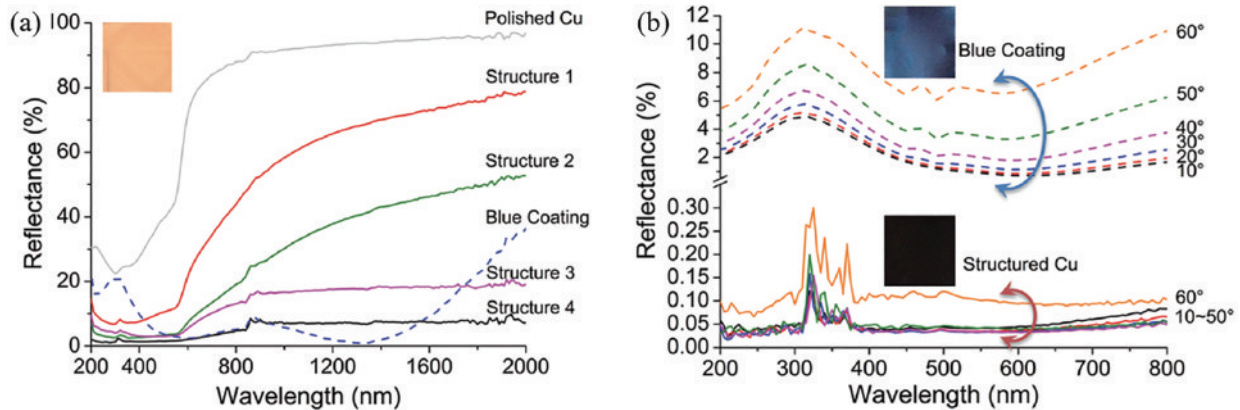


图 2 微纳花状结构的光吸收性能测试^[31]。(a)裸片铜、商用铜以及覆盖微纳分级结构的铜在 200~2000 nm 波段光的反射率;(b)入射角变化时商用铜与覆盖微纳分级结构的铜在 200~800 nm 波段光的反射率测试

Fig. 2 Optical absorption properties test of micro/nano flower structures constructed on copper surface^[31]. (a) Reflectance of bare copper, commercial copper, and copper covered with micro/nano hierarchical structures in the 200–2000 nm wavelength band; (b) reflectance test of commercial copper and copper covered with micro/nano hierarchical structures as the incident angle changes in the 200–800 nm wavelength band

Fan 等^[32]介绍了一种基于超快激光脉冲注入调控金属表面微米、纳米双级结构的新方法。利用中心波长为 1030 nm、重复频率为 200 kHz、脉宽为 800 fs 的飞秒激光,通过对激光脉冲注入数量和注入方式的调控,进而对表面微米结构和纳米结构进行调控。微米结构

与纳米结构共同作用得到抗反射性能好的金属表面。研究表明,该方法对于铜、钛、钨等多种金属均有效,可在其表面分别获得 1.4%、0.29%、2.5% 的表面反射率,工艺流程如图 4 所示。

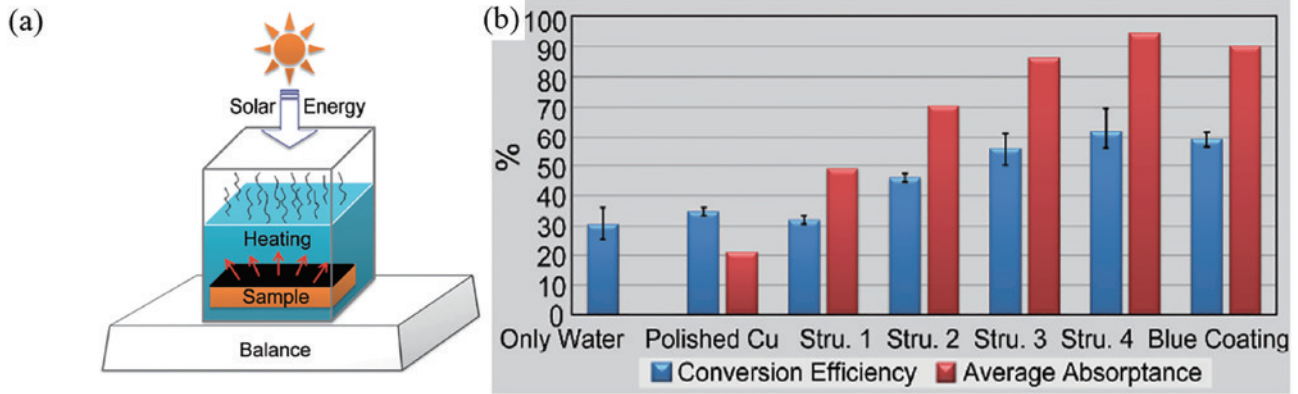


图 3 微纳花状结构的光热转化性能研究^[31]。(a)包含微纳花状结构的铜片光热转化测试示意图;(b)不同样品的光平均吸收率
Fig. 3 Photothermal conversion performance of micro/nano flower structures constructed on copper^[31]. (a) Schematic diagram of photothermal conversion test of copper sheet with micro/nano flower structures; (b) average absorbances of different samples

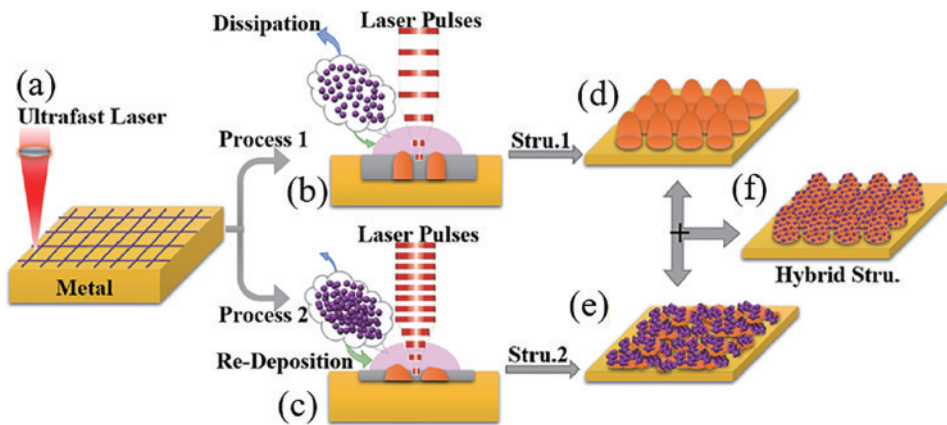


图 4 飞秒激光脉冲注入法在金属表面制备高效抗反射表面工艺流程图^[32]
Fig. 4 Process flow chart of fabricating high-efficiency anti-reflection surfaces on metal surfaces by femtosecond laser pulse implantation^[32]

2.2.2 飞秒激光诱导产生表面周期性结构

当飞秒激光能量处于材料烧蚀阈值附近时,在材料表面会形成表面周期性波纹结构,即 ripple 结构。根据周期长短可将其分为低空间频率周期性结构和高空间频率周期性结构。表面周期性波纹结构形成机理复杂,一般认为当激光照射在材料表面时,入射激光与材料表面等离子激元发生干涉,形成表面周期性波纹结构。入射激光波长、激光能量以及激光偏振方向等都会对 ripple 结构产生影响。

Bonse 等^[33]总结了飞秒激光在 22 种材料表面诱导产生表面周期性波纹结构。Albu 等^[34]利用波长为 775 nm 和 387 nm 的飞秒激光分别在空气环境和液体环境下对钛、铬、钨进行表面加工,得到低空间频率和高空间频率的表面周期性波纹结构。研究表明,在溶液中加工的表面周期性波纹结构其周期远小于空气中所加工结构的周期。

Liu 等^[35]分别利用 s 偏振和 p 偏振飞秒激光通过打点、扫线、扫面的方式在倾斜的不锈钢材料上制备表面周期性结构。研究表明:在 p 偏振条件下产生两种周期不同的表面周期性结构,方向与偏振方向保持垂直;

在 s 偏振条件下,表面周期性结构方向发生旋转且旋转方向随着不锈钢倾斜角度的增加而增加。表明 s 偏振和 p 偏振飞秒激光在不锈钢材料表面激发的表面等离子激元性质不同,只有 s 偏振飞秒激光会影响表面周期性结构的旋转方向。Qiao 等^[36]利用飞秒激光在钨表面制备不同维度的表面周期性结构。与传统方法相比,通过双折射晶体产生的正交脉冲可以制备周期性更好的一维光栅结构,通过调整双折射晶体角度和飞秒激光参数调控表面结构由一维光栅状结构向二维表面结构转化。

Vorobyev 等^[37]利用波长为 800 nm、脉宽为 65 fs、重复频率为 1 kHz 的飞秒激光通过 BBO 晶体倍频得到波长为 400 nm 的飞秒激光。分别用波长为 400 nm 和 800 nm 的飞秒激光对钨材料进行表面加工,尽管在这两种波长下没有表面等离子激元,但由于强脉冲激光加热以及表面结构在纳米尺度上的变化,钨的介电常数发生显著变化,进而产生表面等离子激元和周期小于波长的波纹状表面周期性结构,扫描电镜 (SEM) 图如图 5、图 6 所示。

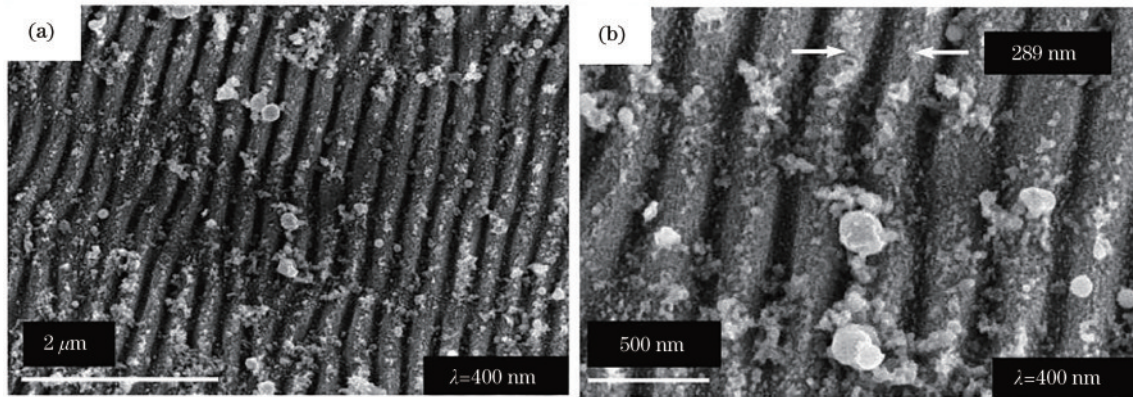


图 5 飞秒激光在波长为 400 nm 时,偏振方向平行于扫描方向时在钨表面制备表面周期性波纹结构^[37]。(a)激光诱导产生表面周期性结构的 SEM 形貌图;(b) (a)图中心位置的放大图

Fig. 5 When the femtosecond laser wavelength was 400 nm, and the polarization direction was parallel to the scanning direction, the surface periodic structure was prepared on the tungsten surface^[37]. (a) SEM image of the periodic structure induced by laser; (b) enlarged view of the center position of Fig. (a)

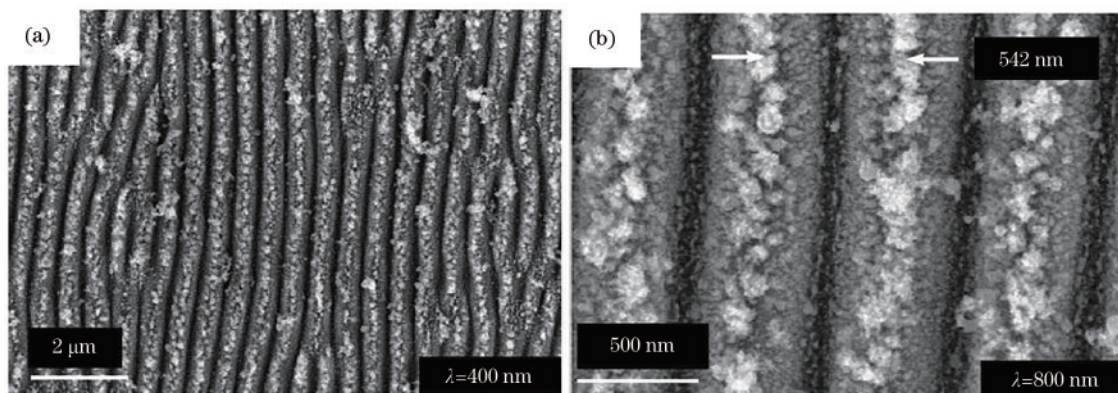


图 6 飞秒激光在波长为 800 nm 时,偏振方向平行于扫描方向时在钨表面制备表面周期性波纹结构^[37]。(a)激光诱导产生表面周期性结构的 SEM 形貌图;(b) (a)图中心位置的放大图

Fig. 6 When the femtosecond laser wavelength was 800 nm, and the polarization direction was parallel to the scanning direction, the surface periodic structure was prepared on the tungsten surface^[37]. (a) SEM image of the periodic structure induced by laser; (b) enlarged view of the center position of Fig. (a)

2.2.3 飞秒激光复合化学方法

飞秒激光具有极高的峰值功率和超短的脉冲宽度,当飞秒激光与物质相互作用时,激光与电子的相互作用是整个加工过程的重要阶段。通过飞秒激光预处理,在材料表面制备不同形貌的微米结构阵列,不仅可以调控材料的表面形貌,更能够改变材料的物理、化学性能。对飞秒激光预处理后的材料利用化学氧化等化学方法进行二次生长,能够在微米结构阵列表面进一步制备纳米结构,得到多级微纳复合结构。

卢金龙等^[38]利用中心波长为 1030 nm、脉冲宽度为 800 fs 的飞秒激光烧蚀钛片,在其表面制备方形微米结构阵列,然后利用水热法在加工后的钛片基底制备三维二氧化钛纳米花,分别对未用激光处理和不同激光参数预处理所得结构进行光催化性能测试,可知利用飞秒激光预处理的钛基微纳复合结构其光催化降解性能明显优于未用激光预处理的钛片。

Liu 等^[39]利用中心波长为 800 nm、脉宽为 50 fs、重

复频率为 1 kHz 的飞秒激光在铜表面制备凸起/凹槽微纳结构,对加工后的结构进行化学氧化,并对其干燥处理,得到由氢氧化铜、氧化铜纳米线构成的海胆状微纳复合结构。通过飞秒激光预处理在铜表面得到微米沟槽结构,经过化学氧化等处理后在铜表面得到以氢氧化铜纳米线为主、少量氧化铜纳米花状团簇为辅的微纳复合结构,如图 7 所示。在紫外-远红外波段对加工结构进行宽波段反射测试,得出飞秒激光复合化学氧化方法所制备氢氧化铜、氧化铜海胆状微纳结构在宽波段具有较好的抗反射性能。

综上所述,利用飞秒激光直写、飞秒激光诱导产生表面周期性结构以及飞秒激光复合化学方法可以在不同金属材料表面制备不同形貌的功能性微纳复合结构,是飞秒激光制备表面微纳复合结构的常用方法。然而随着科技的不断进步,对微纳结构的加工效率、加工精度等提出了更高的要求。基于空间光调制的空间光整形技术以及激光干涉加工技术等^[40-42]方法逐渐成

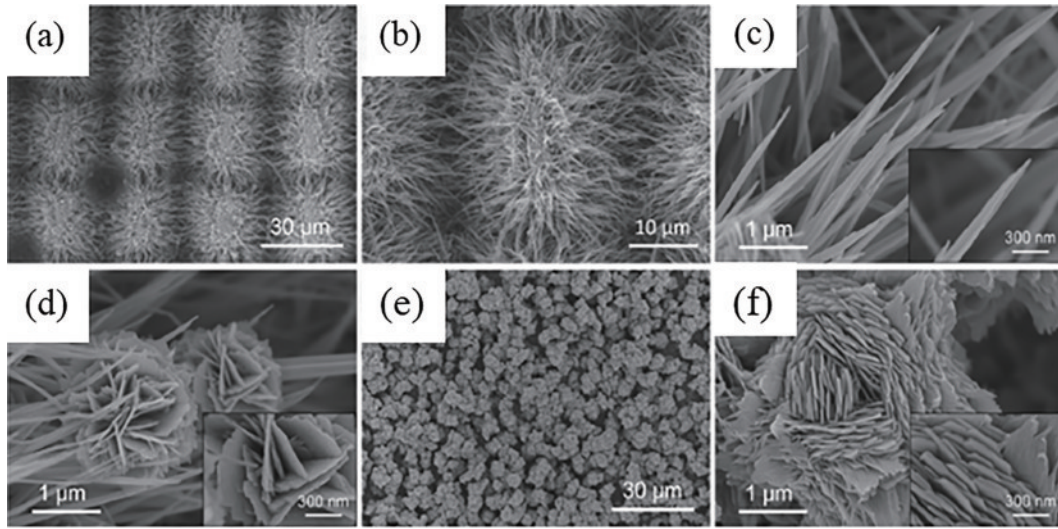


图7 飞秒激光复合化学氧化在铜表面制备氢氧化铜、氧化铜海胆状微纳结构阵列^[39]。(a)(b)海胆状结构 SEM 形貌图;(c)(d)纳米线和纳米花 SEM 形貌图;(e)(f)单独化学氧化制备纳米花状结构 SEM 形貌图

Fig. 7 Preparation of copper hydroxide and copper oxide urchin like micro/nano structures with wide band antireflection properties on copper surface by femtosecond laser composite chemical oxidation^[39]. (a) (b) SEM images of the urchin-like arrays; (c) (d) SEM images of nanowires and nanoflowers; (e) (f) SEM images of the nanoflowers fabricated by chemical oxidation alone

为实现飞秒激光高效率、高质量加工的重要方法。

3 飞秒激光制备金属表面微纳结构的技术应用

在材料表面制备功能性微纳结构可以调控材料表面的光学性能、表面润湿性等,在污水处理、光催化降解以及功能器件表面防覆冰等方面具有广泛应用。随着科技的不断发展,对功能性表面微纳结构的制备也提出了更高的要求。作为微纳加工的前沿技术,飞秒激光具有加工成本低、操作灵活等独特优势,逐渐成为制备高精度、高质量功能性表面微纳结构的重要方法。本节主要从环境工程、航空航天以及生物医学等领域阐述飞秒激光在金属表面制备微纳结构的技术应用。

3.1 飞秒激光制备金属表面微纳结构在环境工程中的应用

随着工业化进程的加深,工业废水、近海石油污染、有机染料污染等问题日益严重,油水分离、光降解染料等作为环境领域的研究热点,越来越引起研究者的关注。随着仿生学的蓬勃发展,仿照荷叶^[43]等表面结构构建功能性微纳复合结构逐渐成为解决油水分离等环境污染问题的重要途径之一,如图8所示。飞秒激光作为一种前沿精密加工技术,能够在材料表面得到不同形貌的微纳复合结构,一方面可以调控材料对不同溶液的润湿性,实现油水混合物的高效率分离,另一方面能够改变材料对不同波长的光吸收率,诱导材料产生晶格缺陷,降低材料的能带宽度,实现可见光条件下有机染料的高效率分解。表2列举了飞秒激光在环境工程领域中常用金属材料表面制备微纳结构及其功能应用。

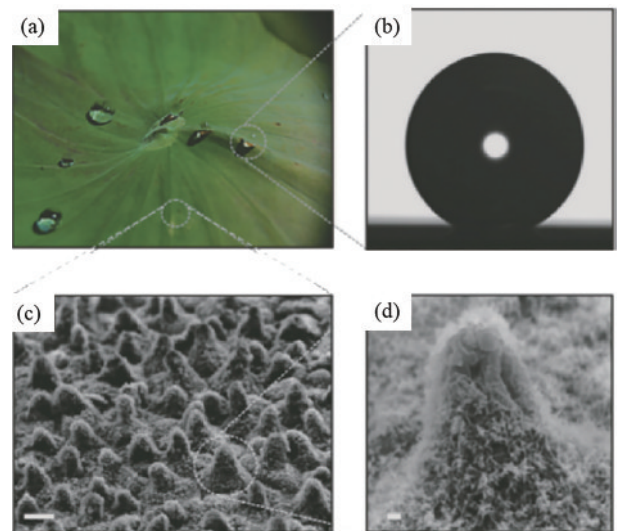


图8 荷叶表面结构及浸润性^[43]。(a)荷叶外观图;(b)荷叶表面浸润性;(c)(d)荷叶表面 SEM 形貌图

Fig. 8 Surface structure and wettability of lotus leaf^[43]. (a) Appearance of lotus leaf; (b) infiltration of lotus leaf surface; (c) (d) SEM images of lotus leaf

Yin 等^[48]利用飞秒激光诱导产生周期性波纹结构制备超亲水、水下超疏油的不锈钢网格。研究表明,该结构对不同的油水混合物的分离效率均大于 99%。分别对筛网进行磨损和腐蚀后,其浸润性能和分离效率没有明显变化,表明该方法制备的不锈钢油水分离筛网具有良好的稳定性。Li 等^[49]在铝箔表面利用飞秒激光一步法制备出不同尺度的微孔阵列,得到超亲水、水下超疏油结构。研究表明,该结构不仅可以对重/轻油和水的混合物进行高效率分离,还可对溶液中不同尺度的二氧化硅颗粒进行分离。

表 2 飞秒激光制备金属表面微纳结构在环境工程中的应用

Table 2 Application of femtosecond laser fabrication of metal surface micro/nano structures in environmental engineering

Material	Structure	Function application
Copper	Groove and ripple composite structures	Efficient oil-water separation and surface self-cleaning ^[44]
Aluminium	Micropores with micro/nano structures	Underwater superoleophobic surface with low adhesion for oil-water separation ^[45]
Stainless steel	Ripples and periodic cone-shaped spikes	Superhydrophobic surfaces ^[46]
Titanium	Hierarchical micro/nano conical structure arrays	Improve the efficiency of photocatalytic degradation of organic dyes ^[47]

Ye 等^[50]通过调控飞秒激光能量和脉冲数量在钛箔表面加工微孔,得到大面积、均一性好的微孔阵列。经过飞秒激光加工,钛箔表面发生氧化出现二氧化钛,表面成分的改变和微纳结构共同作用得到超亲水、水下超疏油的微孔阵列。该方法制备的微孔阵列不仅能够实现油和水的分离,而且具有较好的耐酸、碱腐蚀性,如图 9 所示。

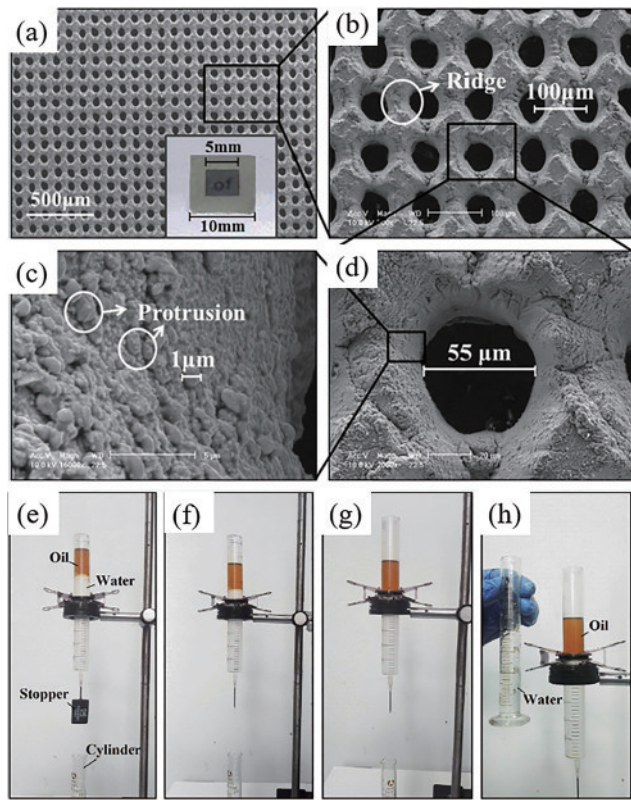


图 9 飞秒激光在钛箔表面制备超亲水、水下超疏油微孔结构^[50]。(a)~(d)微孔结构 SEM 形貌图;(e)~(h)包含微孔结构的钛箔油水分离实验

Fig. 9 Preparation of superhydrophilic and underwater superoleophobic microporous structures on titanium foil surface by femtosecond laser^[50]. (a)–(d) SEM images of microporous; (e)–(h) oil-water separation experiment of titanium foil contains microporous structures

Sun 等^[51]利用飞秒激光空间光整形技术在铜表面制备大面积微孔结构,得到超亲油、疏水结构,如图 10 所示。通过对微孔结构阵列进行表面浸润性测试,可

知该结构能够实现油和水的分离,如图 11 所示。

Khan 等^[52]利用线偏振飞秒激光在水溶液中辐照铜和金红石二氧化钛粉末颗粒,分别在太阳光和可见光条件下对甲基蓝染料进行催化降解,二者均具有较高的降解效率。Huang 等^[53]通过控制飞秒激光参数在钛表面制备形貌可调的微纳结构,之后在双氧水溶液中对其化学氧化并热处理,在钛表面制备纳米花状锐钛矿二氧化钛微纳复合结构,如图 12 所示。分别对比了单独使用飞秒激光加工、飞秒激光复合化学氧化并热处理、单独使用化学氧化、飞秒激光复合化学氧化未热处理的钛片在波长为 200~1000 nm 波段光的反射率。单独使用化学氧化制备微纳结构,其反射率远低于飞秒激光预处理后钛片的反射率。紫外光照射下对复合方法制备的锐钛矿二氧化钛微纳复合结构进行甲基橙染料降解,表明飞秒激光复合化学氧化方法制备的二氧化钛微纳结构能够提高光吸收率、加快染料降解,如图 13 所示。

Liang 等^[54]利用飞秒激光在钛表面构建微米锥状结构,在氟化铵溶液中对其进行电化学阳极氧化,最后在 450 °C 恒温环境下热处理 1 h,得到钛氧化物纳米管覆盖的锥形微纳复合结构。通过飞秒激光预处理材料出现晶格缺陷,后续进行电化学阳极氧化,得到微米锥和纳米管的复合结构,降低了能带宽度、提高了光吸收率。将其作为光电极,产生 0.52 mA/cm² 的光电流,其性能是未经飞秒激光预处理电极的 8 倍,极大地提高了电极光电流。不仅如此,该电极在可见光照射下对甲基蓝染料具有较好的催化降解作用,如图 14 所示。

3.2 飞秒激光制备金属表面微纳结构在航空航天中的应用

飞秒激光具有加工精度高、热效应低等独特优势,在航空航天领域具有广泛的应用,比如飞秒激光加工引擎喷嘴微孔^[55]、航空发动机涡轮叶片气膜孔阵列^[56]、零件表面散热微槽^[57]等,如图 15 所示。此外利用飞秒激光还可以在材料表面制备不同形貌的微纳复合结构构建超疏水表面,在航空飞行器表面抗结冰、减阻等方面有着广泛的应用。表 3 列举了飞秒激光在航空航天领域中常用金属材料表面制备微纳结构及其功能应用。

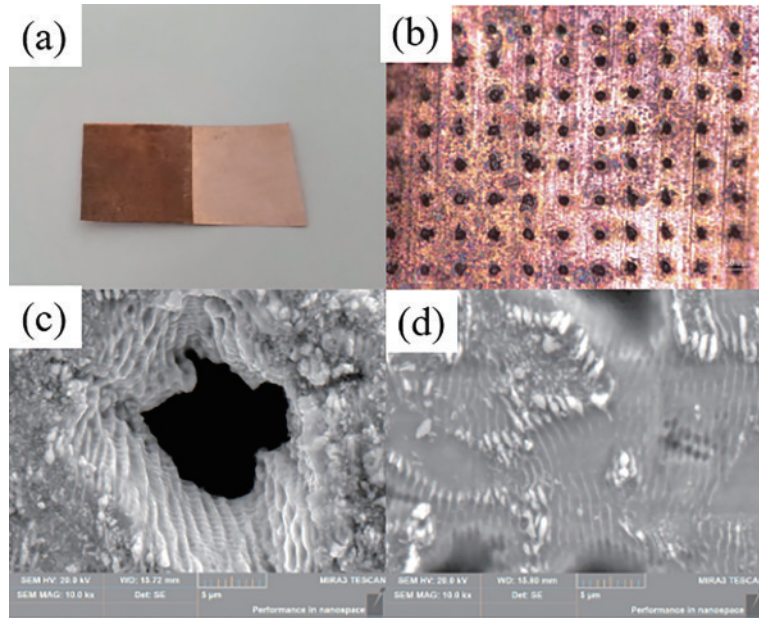


图 10 飞秒激光空间光整形在铜箔表面制备微孔阵列^[51]。(a)铜片光学图片,其中左侧包含微孔结构,右侧为铜裸片;(b)微孔显微镜图片;(c) (d)铜片表面微孔 SEM 形貌图

Fig. 10 Preparation of microporous arrays on the surface of copper foil by femtosecond laser spatial light shaping^[51]. (a) Optical image of copper sheet with microporous, the left one contains microporous and the right one was pristine copper sheet; (b) microscope picture of microporous; (c)(d) SEM images of microporous on copper sheet

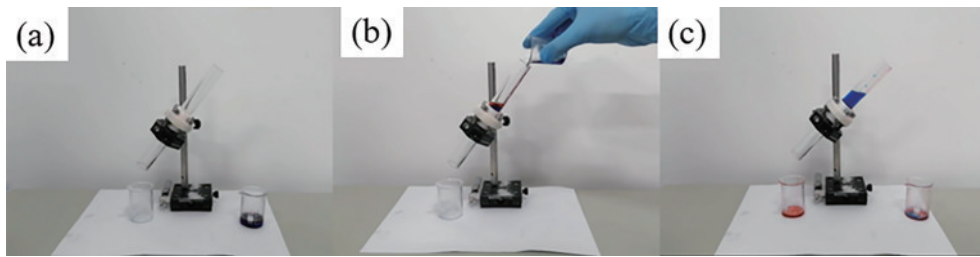


图 11 飞秒激光空间光整形制备微孔结构油水分离实验^[51]。(a)油水混合物以及分离装置;(b) (c)油水分离过程图

Fig. 11 Experiment of oil-water separation with microporous structure prepared by femtosecond laser spatial light shaping^[51]. (a) Oil-water mixture and separation device; (b)(c) oil-water separation process diagram

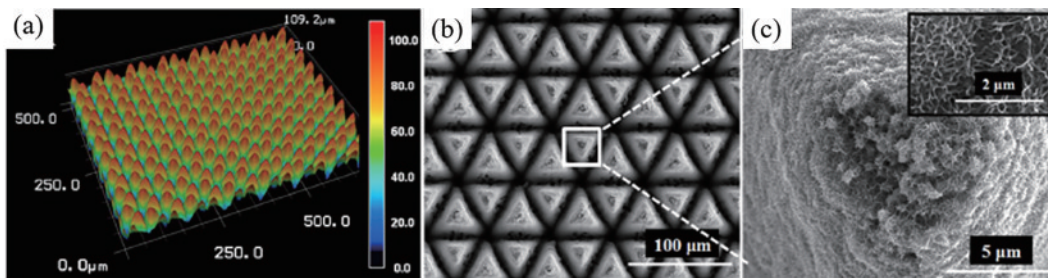


图 12 飞秒激光复合化学氧化制备锥形结构阵列形貌图^[53]。(a)微纳复合结构三维形貌图;(b) (c)微纳复合结构的 SEM 形貌图
Fig. 12 Morphology of the titanium sheet processed by the combination of femtosecond laser combined chemical oxidation^[53]. (a) Three-dimensional image of the micro/nano structures; (b) (c) SEM images of the micro/nano structures

吴先福等^[61]利用飞秒激光在航空用铝靶材表面分别制备柱形结构和沟槽形结构分别制备出超疏水和超亲水表面,表面浸润性的改善对航空飞行器外壳防冰技术的发展有着重要的应用意义。薛磊等^[62]利用飞秒激光在铜表面构建微纳复合结构,改变材料浸润性。通过表面结冰性能测试可知,覆盖表面微纳结构的铜

片在低温环境下能够延缓水滴结冰。

崔静等^[63]针对航空发动机进气口前缘唇口积冰问题,采用飞秒激光在钛合金材料上加工出不同深度的覆盖微纳颗粒的拱形沟壑结构,改变了材料的表面浸润性。研究表明,飞秒激光加工后延迟了材料表面液滴冻结时间,如图 16 所示。

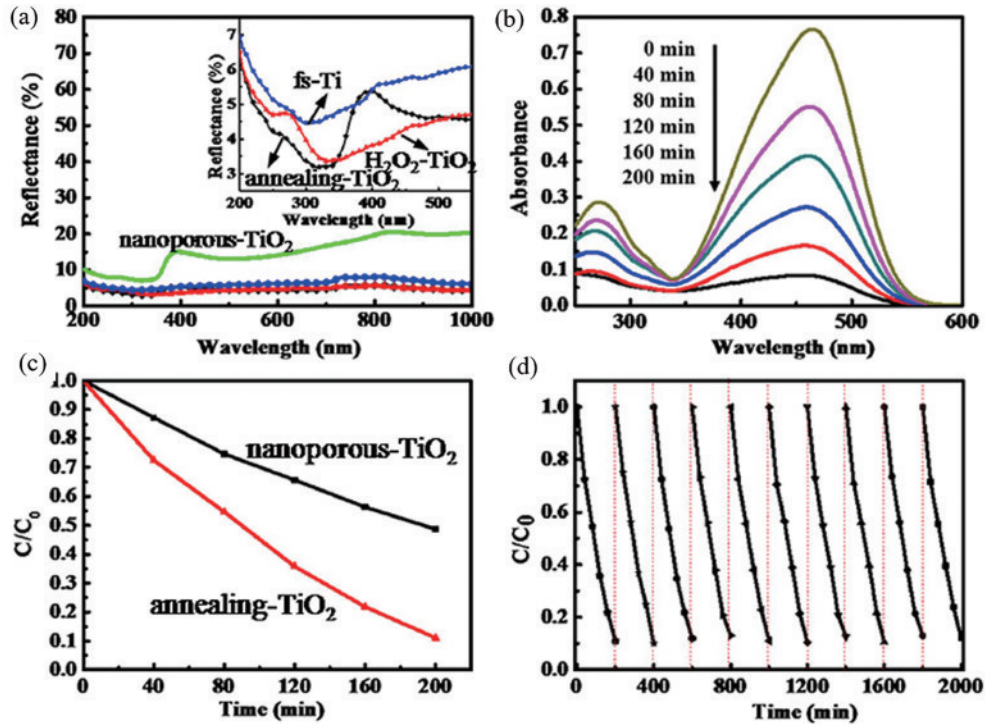


图 13 飞秒激光复合化学氧化制备二氧化钛微纳结构光催化性能的研究^[53]。(a)不同形貌二氧化钛覆盖的钛片的光反射性能测试；(b)二氧化钛降解后有机染料的光谱吸收测试；(c)复合方法与单独化学氧化制备二氧化钛光降解速率测试；(d)二氧化钛光降解的循环性能测试

Fig. 13 Preparation of TiO₂ micro/nano structures by femtosecond laser combined chemical oxidation and research its photocatalytic performances^[53]. (a) Test of light reflection performances of titanium sheet covered with various TiO₂ micro/nano structures; (b) spectral absorption test of organic dyes after TiO₂ degradation; (c) photodegradation rate test of TiO₂ prepared by composite method and chemical oxidation alone; (d) cyclic performance test of photodegradation of TiO₂

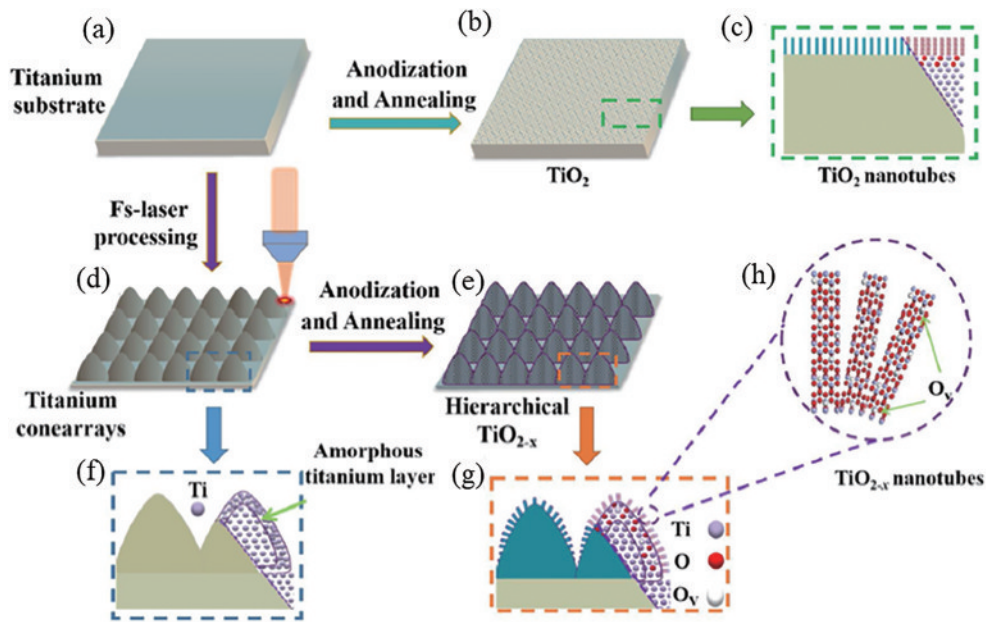


图 14 飞秒激光复合电化学阳极氧化制备二氧化钛纳米管^[54]。(a)原始钛片；(b) (c)单独阳极氧化制备二氧化钛纳米管；(d)飞秒激光加工制备微米结构阵列；(e)微纳多级二氧化钛纳米管；(f)飞秒激光加工后钛片表面的非晶层；(g)(h)微纳多级结构示意图

Fig. 14 Preparation of TiO₂ nanotubes by femtosecond laser processing combined chemical oxidation^[54]. (a) Original titanium sheet; (b) (c) preparation of TiO₂ nanotubes by anodization alone; (d) microstructure arrays fabricated by femtosecond laser; (e) hierarchical TiO₂ nanotubes; (f) amorphous layer on the surface of titanium sheet after femtosecond laser processing; (g) (h) schematic diagram of hierarchical structures

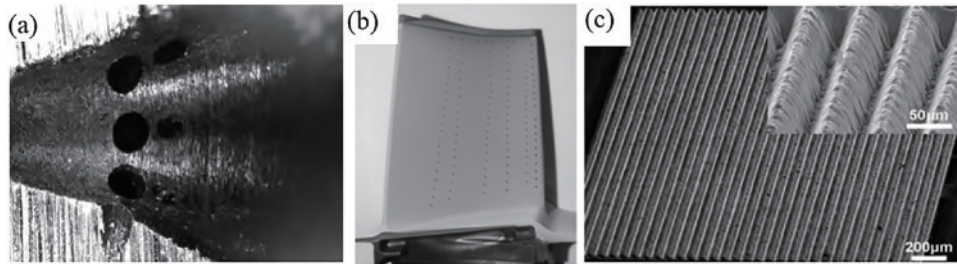


图 15 飞秒激光加工金属材料在航空航天中的应用。(a)飞秒激光制备引擎喷嘴微孔^[55]; (b)飞秒激光制备涡轮叶片气膜孔阵列^[56]; (c)飞秒激光金属表面制备散热槽^[57]

Fig. 15 Application of femtosecond laser processing metal materials in aerospace. (a) Micro-holes of engine fuel injector fabricated by femtosecond laser^[55]; (b) air film holes array of turbine blade fabricated by femtosecond laser^[56]; (c) heat sink fabricated on metal surface by femtosecond laser^[57]

表 3 飞秒激光制备金属表面微纳结构在航空航天中的应用

Table 3 Application of femtosecond laser fabrication of metal surface micro/nano structures in aerospace

Material	Structure	Function application
Copper	Three-dimensional micro/nano conical structure arrays	Delayed icing of material surfaces ^[26]
Aluminum alloy	Micro/nano square structure arrays	Surface self-cleaning and anti-icing ^[58]
Stainless steel	Three-dimensional columnar structures with ripples	Regulate the freezing time of droplets to achieve surface anti-icing ^[59]
Titanium alloy	Three-dimensional groove and stripe composite structure arrays	Regulate droplet freezing time and inhibit surface frosting ^[60]

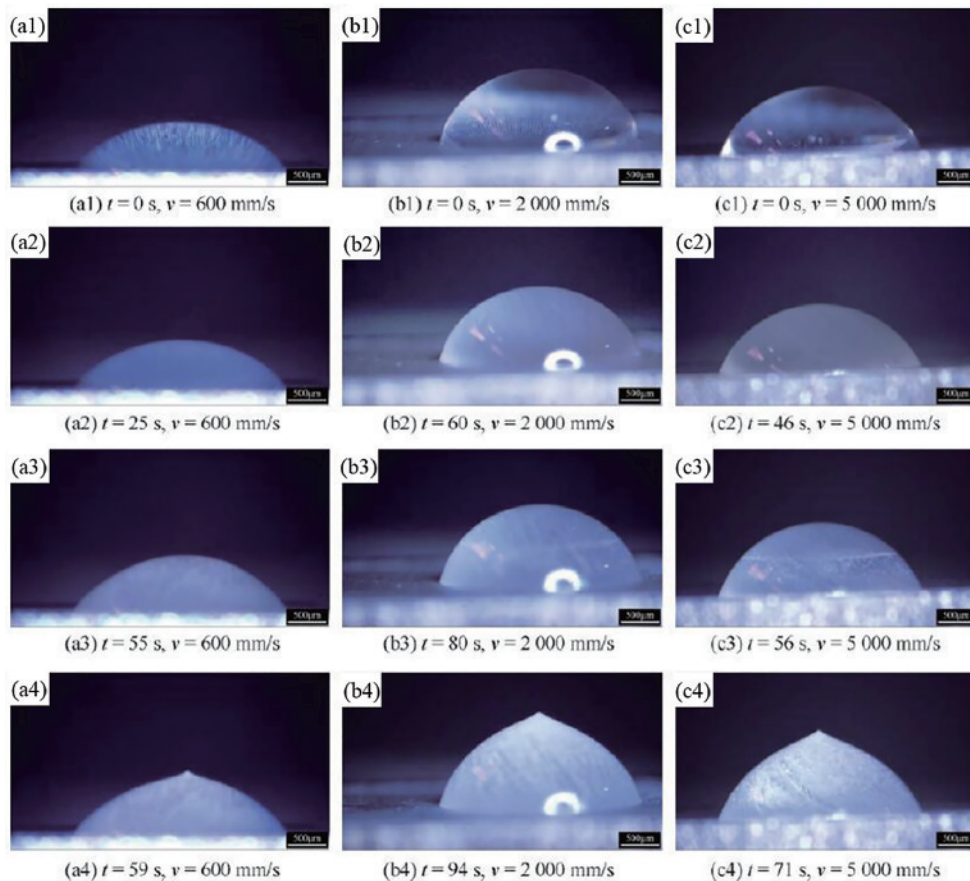


图 16 飞秒激光在钛合金表面制备微纳结构及其抗结冰性能测试^[63]。(a1)~(a4)扫描速度为 600 mm/s 时液滴的结冰过程; (b1)~(b4)扫描速度为 2000 mm/s 时液滴的结冰过程; (c1)~(c4)扫描速度为 5000 mm/s 时液滴的结冰过程

Fig. 16 Preparation of micro/nano structures on titanium alloy by femtosecond laser processing and test its anti-icing performance^[63]. (a1)-(a4) Freezing process of droplets when the scanning speed was 600 mm/s; (b1)-(b4) freezing process of droplets when the scanning speed was 2000 mm/s; (c1)-(c4) freezing process of droplets when the scanning speed was 5000 mm/s

龙江游等^[64]利用飞秒激光在铜表面制备不同形貌的微纳结构,使材料表面浸润性由亲水向超疏水转变。在低温环境下,飞秒激光制备的超疏水表面疏水性会降低,黏附性增加。研究表明,超疏水表面在-5℃和

-10℃下均可延缓水滴结冰。黏附性较小的超疏水表面比高黏附的超疏水表面具有更为优异的抗结冰性能,如图 17 所示。

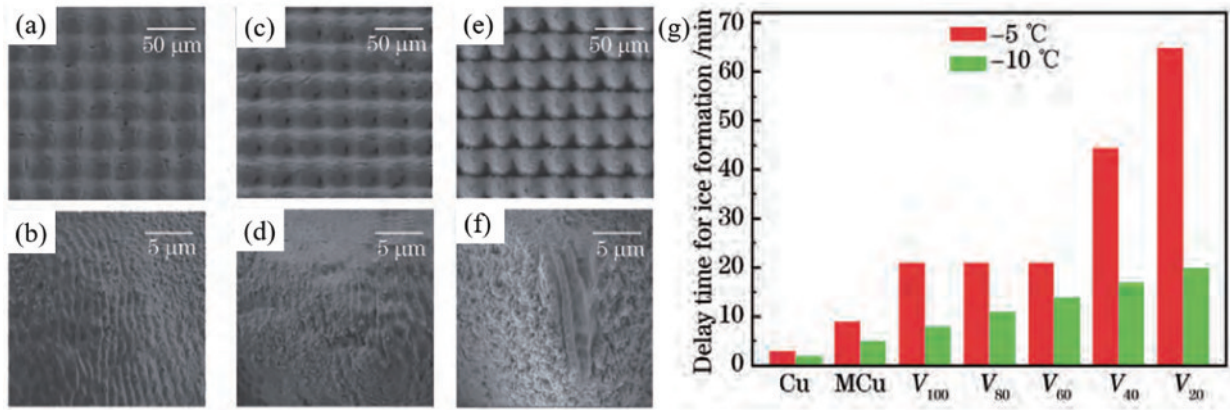


图 17 飞秒激光在铜表面构建不同形貌的微纳结构并测试其抗结冰性能^[64]。(a) (b)激光扫描速度为 20 mm/s 时铜表面形貌 SEM 图;(c) (d)激光扫描速度为 60 mm/s 时铜表面形貌 SEM 图;(e) (f)激光扫描速度为 100 mm/s 时铜表面形貌 SEM 图;(g)低温下铜片的结冰延时测试

Fig. 17 Femtosecond laser fabricates micro/nano structures with different morphologies on copper surface and tests its anti-icing^[64]. (a) (b) SEM images of copper surface morphologies when the laser scanning speed was 20 mm/s; (c) (d) SEM images of copper surface morphologies when the laser scanning speed was 60 mm/s; (e) (f) SEM images of copper surface morphologies when the laser scanning speed was 100 mm/s; (g) freezing delay test of copper sheets at low temperatures

3.3 飞秒激光制备金属表面微纳结构在生物医学中的应用

在医学研究领域,医用金属植入材料与血液接触,易产生凝血和血栓,损害人体器官^[65],因此提高植入材料的抗凝血、抗血栓极为重要。随着激光技术的不断进步,飞秒激光以其独特的优势,可以对医用金属植入物进行表面改性制备微纳结构,构建生物相容性好、溶血性能好的生物传感器,在生物医学领域具有重大意义。此外飞秒激光还可作为超精密外科手术刀,用于角膜屈光手术,如图 18^[66]所示。表 4 列举了生物医学领域中常用金属材料飞秒激光制备表面微纳结构及其功能应用。

何婉盈等^[70]分别用飞秒激光和皮秒激光在钛表面加工出微凹槽和微凸起结构,对比了两种激光技术在钛表面加工的微凸起和微凹槽结构在表面形貌、亲疏水性和生物相容性等方面的差异,分别对其进行细胞黏附性测试。结果表明,飞秒激光加工的微凸起或微

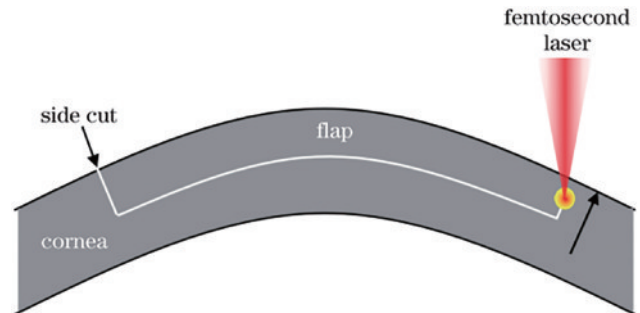


图 18 飞秒激光制作角膜瓣用于屈光手术原理^[66]
Fig 18 Principle of making corneal flap with femtosecond laser^[66]

凹槽有利于细胞的黏附,而皮秒激光加工的微凸起或微凹槽有利于促进细胞的铺展和迁移。姚燕生等^[71]利用飞秒激光扫描医用钴基块体非晶合金,使其由亲水向超疏水转变,激光加工后材料的电化学腐蚀开路电位提高,与未加工样品相比耐腐蚀性更强,提升了植入体在人体内的适用性,如图 19 所示。

表 4 飞秒激光制备金属表面微纳结构在生物医学中的应用

Table 4 Application of femtosecond laser fabrication of metal surface micro/nano structures in biomedicine

Material	Surface structure	Functional application
Magnesium alloy	Ripples, micropores with ripples, and irregular grooves with particles	As a medical implant, it can promote cell proliferation and differentiation ^[67]
Stainless steel	Ripple and conical structures	Good blood compatibility ^[65]
Titanium alloy	Nanoparticles, ripple, and microgroove	Glucose detection ^[68]
Titanium	Nanoripples	Antibacterial ^[69]

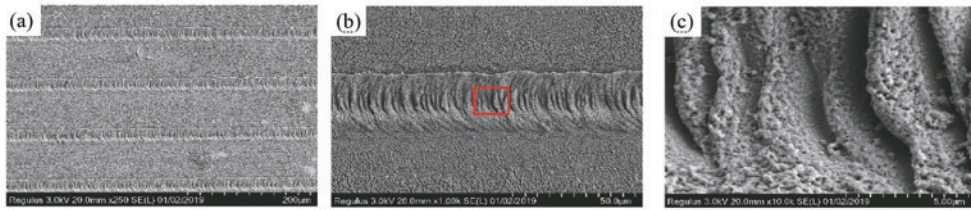


图 19 飞秒激光加工锆基材料制备表面微纳结构^[71]。(a)激光扫描后材料表面形貌 SEM 图;(b)(c)材料表面形貌的放大图
Fig. 19 Preparation of micro/nano structures of zirconium-based materials by femtosecond laser processing^[71]. (a) SEM image of the materials processed by femtosecond laser; (b) (c) magnification images of material surface

Ma 等^[72]利用时域整形飞秒激光在镍钛合金表面制备多孔微纳复合结构。利用迈克耳孙双脉冲光路通过调整两个子脉冲之间的时间间隔,调控瞬态电子吸收率。当子脉冲时间间隔为 5 ps 时,能够在镍钛合金表面制备大面积、均一性好的多功能三维微纳复合结

构,最后对其进行氟化处理得到血液相容性、零细胞毒性以及生物相容性好的三维微纳结构,该结构可广泛应用于具有抗血栓和抗菌感染功能的生物医学器件,如图 20 所示。

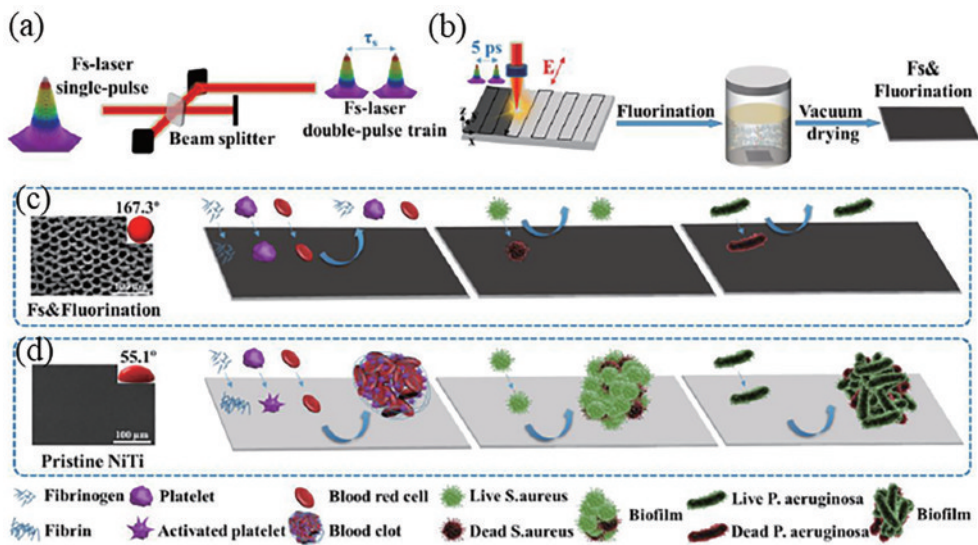


图 20 时域整形飞秒激光在镍钛合金表面制备抗凝血、抑菌微纳结构^[72]。(a)单脉冲激光整形形成双脉冲;(b)多孔结构的制备;(c)多孔结构的抗凝血、抑菌性能测试;(d)镍钛合金裸片的抗凝血、抑菌性能测试
Fig. 20 Preparation of anticoagulant and antibacterial micro/nano structures on nitinol alloy by temporally shaped femtosecond laser^[72].

(a) Single-pulse laser shaping into double-pulse; (b) preparation of porous structures; (c) anticoagulant and antibacterial performance test of porous structure; (d) anticoagulant and antibacterial performance test of nitinol alloy bare sheet

4 结束语

随着激光技术的不断发展,飞秒激光微纳加工作为一种高端精密的加工方法,逐渐成为微纳加工领域中的研究热点之一,越来越引起国内外学者的关注。当前飞秒激光加工仍存在诸多问题:理论方面,飞秒激光加工过程复杂,没有统一的理论模型做指导;工艺方面,飞秒激光可实现复杂结构的高精密加工,但相比传统方法其加工效率较低,限制了飞秒激光微纳加工在工业中的应用。然而,随着新工艺方法的不断涌现和激光器性能的不断提升,飞秒激光微纳加工技术未来在以下领域具有极大的发展潜力。

1) 飞秒激光微纳加工的理论研究。飞秒激光加工过程复杂,缺乏统一的理论模型为指导。因此完善并

深入探究飞秒激光加工的多尺度理论模型是飞秒激光加工的理论基础,不仅能够对飞秒激光微纳加工结果进行准确预测,更能够为飞秒激光微纳加工未来发展方向提供理论指导。

2) 表面微纳结构的高质量、高效率加工。优化飞秒激光空间光整形技术并探索新的飞秒激光微纳加工工艺方法,实现大面积、高质量功能性微纳结构的制备。高质量功能性微纳结构可广泛地应用在防污自清洁、隐形材料以及太阳能电池等领域。

3) 高精密三维微纳结构/器件的加工。形貌可控的高精密三维微纳结构/器件是航空航天、生物医疗等国家重大需求中的核心关键部件,利用飞秒激光制备高分辨复杂三维微纳结构是未来飞秒激光加工的重点研究方向之一。

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