

铝合金表面沉积类金刚石薄膜的研究进展

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摘 要: 类金刚石 (Diamond-like Carbon, DLC) 薄膜因其高硬度、良好的化学惰性以及优异的摩擦性能等优势, 有望成为一种理想的铝合金表面防护涂层。对比了物理气相沉积 (Physical vapor deposition, PVD) 技术制备 DLC 改性材料与传统铝合金表面改性技术的优劣, 概述了 DLC 薄膜在提升铝合金表面力学性能、减摩抗磨方面取得的最新成果, 以及在复杂服役工况下面临的抗塑性变形差、易发生结合失效等瓶颈性问题。通过分析铝合金基体上生长高性能 DLC 薄膜的不利因素, 指出界面化学结合强度低、薄膜残余应力大以及软基体/硬质薄膜的结构体系限制是导致上述问题产生的主要原因。在此基础上, 重点综述了国内外研究学者为提高铝合金表面沉积 DLC 薄膜的膜基结合力所采取的有效措施及结果, 包括: 通过基体前处理增强基体力学性能与改善宏观表面缺陷; 采用 PVD 或其他表面处理方法制备一层或多层的中间过渡层, 缓解 DLC 薄膜与铝合金基体结构、性能之间的差异; 调控 DLC 薄膜组分与结构以降低残余应力。最后展望了在铝合金基体表面制备 DLC 防护薄膜的发展趋势。

关键词: 铝合金; 表面改性; 类金刚石薄膜; 物理气相沉积; 耐磨性; 结合力

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Research Progress in Diamond-like Carbon Films Deposited on Aluminum Alloy

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ABSTRACT: Diamond-like carbon (DLC) films are expected to be one of the ideal surface protective coatings for aluminum alloy due to their high hardness, good chemical inertness and excellent friction properties. The physical vapor deposition (PVD) technology used to prepare DLC films was compared with the traditional surface modification techniques of aluminum alloy.

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The latest research achievements for improving the mechanical and tribological properties of aluminum alloy by DLC protecting films were summarized. Meanwhile, the obstacles in the harsh applications such as poor resistance to plastic deformation and low adhesion between the film and substrate were generalized. By analyzing the unfavorable factors of high-performance DLC film deposited on aluminum alloy substrate, it was found that the low interface chemical bonding strength, high residual stress and the structural system limitation of soft matrix/hard film were the main causes of the above problems. On the basis of this, the measures taken by the domestic and foreign researchers to improve the adhesion between DLC film and aluminum alloy and corresponding results were presented, including surface treatment for strengthening mechanical properties and reducing surface defects, preparing single-layer or multi-layer interlayers to reduce the difference of the structure and properties between DLC film and aluminum alloy matrix by PVD or other surface modifying methods, and reducing the residual stress by controlling the composition and structure of DLC film. Finally, the future development trends of DLC protective film on aluminum alloy substrate are proposed.

KEY WORDS: aluminum alloy; surface treatment; diamond-like carbon; physical vapor deposition; wear resistance; adhesion

铝合金具有密度小、比强度高、易加工、装饰效果好等优点,已逐渐成为工业产品轻量化的首选材料,在航空航天、轨道交通、建筑、生物医药等领域均具有广阔的应用前景。但随着科学技术的不断发展,对铝合金表面功能性的要求也在不断提高,受硬度低、耐磨损性能差、抗腐蚀性能不足等局限,其使用面临着严峻挑战^[1-3]。通过表面改性技术对铝合金进行表面强化能够有效解决上述问题,延长其使用寿命,对拓展铝合金的应用具有重要意义^[4-5]。目前,常见的铝合金表面改性技术主要有阳极氧化、电镀、激光熔覆以及 PVD 沉积技术等^[6-9]。其中,相较于其他表面处理技术,PVD 具有低温(能够降低铝合金温度敏感性)、表面光洁度高(能够满足精密部件要求)、均匀性好、薄膜种类丰富等优势,更适用于航空航天、汽车等高技术领域关键核心部件的表面改性与强化,因而受到越来越多的关注。

目前,铝合金表面 PVD 改性薄膜主要包括氮基硬质薄膜(复合或梯度结构)、等离子体浸没离子注入处理形成的强化层(如氮气中的钛或铝等离子体浸没)以及类金刚石薄膜 DLC 等^[10-12]。其中,DLC 是一类含有金刚石结构(sp^3 杂化键)和石墨结构(sp^2 杂化键)的亚稳态非晶薄膜材料,相较于其他硬质薄膜,类金刚石薄膜兼具高硬耐磨、减摩润滑与耐蚀的优异特性^[13],更有潜力成为一种优秀的铝合金表面改性材料。如 Zou 等^[14]利用电弧离子镀技术在 2024 铝合金表面制备了厚度为 3 μm 的 DLC 薄膜,使铝合金表面的硬度和模量分别提升到 30 GPa 和 280 GPa,室温下的干摩擦实验结果显示,与未镀膜时相比,镀膜试样具有低的摩擦系数(低于 0.2)和磨损率。

但是在铝合金表面沉积 DLC 薄膜材料的研究中还存在几个瓶颈问题^[15-19]:一方面是 DLC 薄膜本身存在残余应力大、脆性大、摩擦多环境适应性差的缺点;另一方面是铝元素与碳元素之间难以键合,而且铝合金与 DLC 薄膜存在显著的物理性能(如热膨胀系数)、力学性能(硬度、模量)不匹配,导致铝合

金与 DLC 薄膜之间的膜基结合强度较低。在实际工况中,DLC 改性的铝合金作为装备运动和承载的重要部件,受高承载、摩擦环境复杂等苛刻条件的影响,其失效常由薄膜剥离和破损引起。因此,提高 DLC 薄膜与铝合金基体的结合强度成为首要问题^[20]。纵观国内外相关研究学者针对提升铝合金表面沉积 DLC 薄膜的结合强度与性能的研究进展,本文分别从基体前处理、过渡层以及 DLC 薄膜等三个关键因素展开综述,并展望了铝合金表面沉积 DLC 薄膜的未来发展趋势。

1 基体前处理

众所周知,对硬质合金、钢材及轻合金等常用金属基体进行 PVD 表面改性之前,基体前处理是必不可少的步骤,特别是对于铝合金基体来说,前处理不仅能强化基体,同时能清除表面形成的致密氧化膜(厚度~100 nm),增强膜基结合力^[17]。目前报道的铝合金表面制备 DLC 薄膜前处理方法包括:固溶与时效热处理、表面喷砂、机械抛光、等离子体刻蚀及离子注入等^[21-23]。

由于铝合金的成分与结构特点,普通钢材表面渗氮/碳的强化工艺难以应用,研究学者普遍采用固溶与时效热处理的方法(如 6、7 系合金的 T6 处理(固溶处理+热时效))来改善铝合金基体的整体性能。Łukasz Kaczmarek 等^[24]在 7075 铝合金表面采用 T6I6 两步时效热处理法,即:镀膜前在 813 K 下固溶 6 h,随后在 430 K 下进行第一次时效处理 1 h,镀膜过程中加热到 390 K 进行第二次时效处理 6.5 h。该方法不仅消除了铝合金对温度的软化敏感性,同时强化后的基体为后续沉积梯度 Ti/TiC/a-C:H 薄膜提供足够支撑,沉积薄膜后,基体硬度提升至 19 GPa,纳米划痕结合力超过 30 mN,同时耐磨损性能也明显提高。

Makoto Kano 等^[25]对 A5052 和 A2017 铝合金表面采用尺寸小于 53 μm 的细钨颗粒进行喷丸硬化,并在铝合金表面获得了厚度约为 10 μm 的钨颗粒分散

层, 强化后的表层硬度高出基体硬度 20%~30%。然后通过抛光去除喷丸强化造成的尖锐凸起, 最后采用等离子体增加化学气相沉积 (Plasma-enhanced chemical vapor deposition, PECVD) 在表面沉积厚度为 1 μm 的 DLC 薄膜。结合力测试结果如图 1 所示, 相较于直接抛光的试样, 经喷丸处理并抛光后再沉积 DLC 薄膜的 A5052 和 A2017 铝合金的膜基结合力分别提升了 70% 和 40%。由此可见, 经过钨喷丸强化前处理能够有效改善基体的硬度, 增强铝合金与 DLC 薄膜之间的膜基结合力。

以上前处理方法主要是通过增强基体力学性能与改善宏观表面缺陷来提高膜基结合性能。此外, 采用等离子体前处理对膜基结合强度的影响也非常显著。其中, 氩等离子体处理能够轰击掉铝合金表面的氧化膜, 激活基体表面, 并有效改善基体表面粗糙度。因此, 一般情况下, 铝合金表面进行 PVD 涂层沉积之前, 均会进行氩离子清洗, 并根据后续预沉积薄膜厚度调控清洗时间, 以获得较好的膜基结合^[26]。而氮、钛等高能粒子的注入能够在界面处形成一定深度的较硬的成分渐变层, 进而降低界面不匹配的影响, 而且其制备工艺及结构、性能调控研究成熟, 已应用于

梯度多层 DLC 薄膜的制备前处理步骤中^[27]。夏丽芳和廖家轩等^[28-31]采用 PBII (Plasma-based ion implantation) 技术在 2024 铝合金基体上通过注入 N 离子, 在表层形成硬的 AlN 层以强化基体表面, 随后研究了 Ti-PBII、(Ti,N)-PBII 及 Ti-PBII+(Ti,N)-PBII 三种注入层对顶层 DLC 薄膜力学和摩擦性能的影响, 成功地筛选出硬度超过 40 GPa、摩擦系数接近 0.04 的 AlN/Ti/TiN/DLC 薄膜优化体系。Xu Ming 等^[32-33]系统研究了 Ti 离子注入对铝合金表面薄膜结合性能的影响, 初期的研究中针对 TiN 薄膜体系, 在 40 kV 高压下离子注入 Ti 层, 然后复合磁控溅射沉积 Ti 和 TiN 层, 获得 Ti⁺/Ti/TiN 优化体系, 划痕实验证明, 注入 Ti 层后, 涂层结合力从 1.4 N 提升到 4.1 N。图 2 表征了 Ti 离子注入后基体与薄膜界面处的形貌、元素分布与相组成, 这种结构为薄膜提供了足够的支撑, 后续有限元分析模拟揭示了划痕过程中 Ti 注入层具有缓冲应力作用, 结合性能大幅提升。后期在此基础上采用离子注入复合磁控溅射沉积的方法, 成功制备出超厚 (约 10 μm) 结构和成分渐变的 Ti⁺/Ti/TiN/TiCN/TiC/DLC 薄膜体系, 为铝合金提供了有效的表面防护。

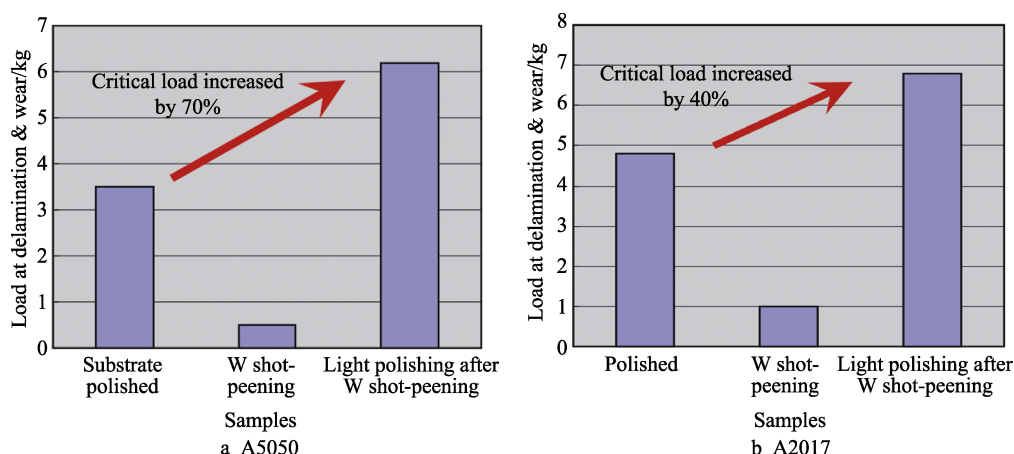
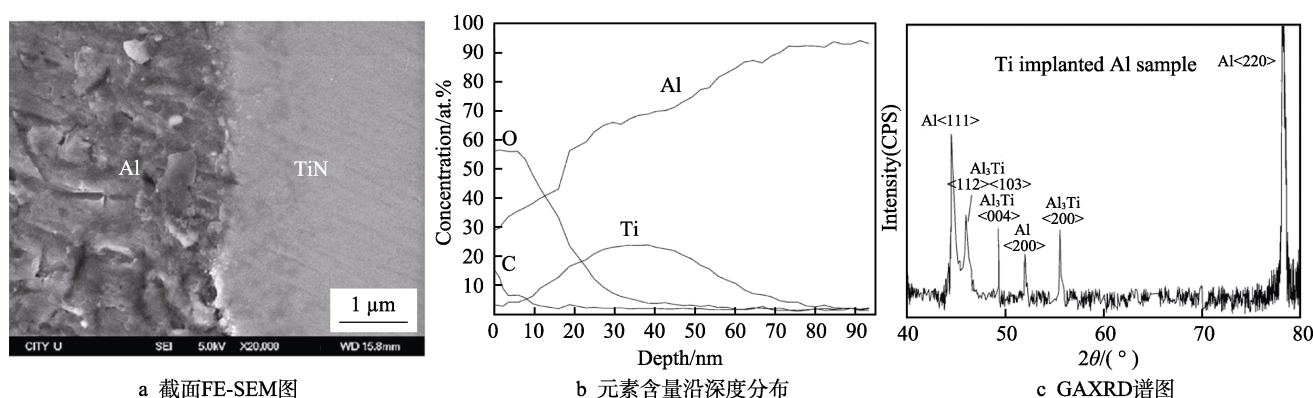


图 1 A5052 和 A2017 铝合金基体上沉积 DLC 薄膜的临界载荷^[25]
Fig.1 Critical load of DLC films deposited on A5052 (a) and A2017 (b) aluminum alloys^[25]



a 截面FE-SEM图

b 元素含量沿深度分布

c GAXRD谱图

图 2 Ti 注入铝合金的截面 FE-SEM 图、GAXRD 谱图及不同元素含量沿深度分布图^[32-33]
Fig.2 (a) FE-SEM image of cross-section of Ti-implanted aluminum; (b) Depth profiles of Al, Ti, O and C in Ti-implanted aluminum; (c) GAXRD spectrum of Ti-implanted aluminum^[32-33]

2 过渡层

为缓解 DLC 薄膜与铝合金基体结构、性能之间的差异,通过一层或多层中间过渡层设计,能够在膜基界面处形成原子混合的过渡层或伪扩散层,有利于改善膜基结合力,提高 DLC 薄膜的减摩耐磨性能及使用寿命^[34-36]。理论模拟结合实验证明,当过渡层的热膨胀系数介于薄膜和基体之间时,可以缓冲沉积 DLC 伴随的生长应力及冷却过程中的热应力;而硬度和弹性模量等介于薄膜和基体之间的过渡层,可以提供足够的承载力,协调变形,减弱基体的影响^[37-41]。在铝合金表面沉积 DLC 薄膜,目前常见的有单一过渡层(Al、Si、Ti、Cr 及 TiC、TiN、Si-DLC、WC 等硬质薄膜或涂层)和梯度过渡层(如 Ti/Ti_xC_y、Ti/Si-DLC、NiP/CrC 等多层薄膜或涂层)两种类型,而不同的过渡层可采用 PVD、化学气相沉积(Chemical vapor deposition, CVD)、电镀、热喷涂等方法获得。

2.1 PVD 沉积制备的过渡层

根据铝合金基体以及 DLC 薄膜材料的特点与性能,采用 PVD 技术制备的过渡层和 DLC 薄膜,具有方法简单、不易污染、薄膜质量高等特点。众多研究表明,过渡金属及其化合物(Si、Ti、Cr、TiN、TiC、CrC)以及元素掺杂 DLC(Si-DLC、Ti-DLC),可作为单一过渡层或参与构筑复合过渡层。此外,作为基体元素,Al 及其化合物(AlN 等)可以首先沉积在基体表面,增强薄膜的结合力。从表 1 中对不同过渡层添加后薄膜的结合力与性能的统计结果来看,因制备方法与过渡层种类的不同,对膜基结合力的影响作用也明显不同。从单一过渡层的研究结果来看,过渡层的添加能够在一定程度上提高铝合金基体表面 DLC 薄膜的膜基结合力。如苏永要等^[42-43]通过非平衡磁控溅射(UBMS)制备了 Si 过渡层,与后续射频辅助等离子体浸没离子注入(RF-PIII&D)的 C,在过渡层与 DLC 薄膜界面处形成了 C/Si 杂化混合过渡层,降低了镀层内应力的同时,一定程度上提高了承载能力。纳米划痕结果显示,结合力从 6 mN 大幅提

升至 23 mN,后续研究中采用非平衡磁控溅射制备硬度更高、承载更好的 TiN 中间层,电子回旋共振等离子体增强化学气相沉积(ECR-PECVD)沉积 DLC 薄膜,结合力提升至 23 mN。Hidenobu Maruno 等^[44]通过划痕实验比较了 Al/DLC、Al/Ti/DLC、Al/Si-DLC/DLC 三种体系的膜基结合强度,相较于直接沉积 DLC 薄膜,Ti 和 Si-DLC 过渡层的添加分别使膜基结合力提升至 14.3 N 和 13.7 N,这是因为过渡层能够有效减小膜基的热膨胀系数失配,增强界面原子的亲和性;同时,过渡层的弹性模量接近于基体,能够协调基体塑性变形,因此两种过渡层均能够提高膜基结合临界载荷。

但由于单一过渡层一般呈柱状晶体生长,膜厚增大会伴随晶粒粗大、脆性增大的缺陷,不利于薄膜体系整体厚度的增加,且结合性能提升有限。近年来,研究者开始通过控制沉积参数和沉积薄膜的成分配比,形成梯度过渡层,使成分、组织、力学性能从基材到表面薄膜呈现无界面连续变化,从而增强膜层间界面结合强度,降低内应力及缓冲塑性变形的影响^[45-50]。如 Masashi Nakamura 等^[45]设计了 Al_xN_y 硬度随成分变化的梯度过渡层,逐步缓冲了铝合金与 DLC 薄膜之间的硬度差异,相较于直接在铝合金上沉积 DLC,摩擦寿命提高了 80 倍。时惠英等^[46]采用非平衡磁控溅射技术分别沉积了 Cr/Cr-C/GLC 和 Al/Al-Cr-C/GLC 涂层,如表 1 中划痕实验结果显示,这两种梯度 DLC 涂层结构均能够提高膜基结合力,Al 过渡层的作用尤其显著,其膜基结合力可达到 35 N。这是因为 Cr 和 Al 晶体结构不同,bcc 结构的 Cr($a=0.288$ nm)与 fcc 结构的 Al($a=0.405$ nm)晶格常数相差较大,导致形成的膜基界面结构差异很大。如图 3 所示,Cr 过渡层垂直于基体表面呈柱状晶生长,与铝合金基体形成清晰的锯齿状界面,而 Al 打底层与铝合金基体间无明显界面,呈外延生长特征。因此,Cr 过渡层的界面结合强度较 Al 过渡层弱。此外,Cr 的热膨胀系数远小于 Al,对热应力的缓冲效果也相对较弱。摩擦实验结果如表 1 所示,两种复合过渡层均具有较低的摩擦系数,差别不大。

表 1 添加 PVD 过渡层对铝合金表面制备 DLC 的结合强度和摩擦性能的影响^[42-50]

Tab.1 Effect of PVD transition layer on adhesion strength and friction coefficient of DLC prepared on aluminum alloy^[42-50]

Sample	Preparation process	Film	Critical load/N	Friction coefficient(dry conditions)	References
7A04	UBMS + RF-PIII&D	Si/DLC	0.023(nanoscratch)	~0.6(Load 0.49 N)	[42]
7A04	UBMS + ECR-PECVD	TiN/DLC	0.023(nanoscratch)		[43]
A2024	Sputtering +PECVD	Ti/DLC	14.3	0.15(Load 5 N)	[44]
A2024	PECVD	Si-DLC/DLC	13.7	0.18(Load 5 N)	[44]
LY12	UBMP	Cr/Cr-C/GLC	17.6	0.06~0.07(Load 2 N) 0.06~0.07(Load 8 N)	[45]
LY12	UBMP	Al/Al-Cr-C/GLC	35	0.06~0.07(Load 2 N) 0.07~0.08(Load 8 N)	[45]
Al alloys	Arc ion plating	Ti/TiN/Si/(TiC/a-C:H)	>20	0.16(Load 5 N)	[47]
A2024	PECVD	[Si-DLC/DLC] _N	15.2	~0.15(Load 5 N)	[50]

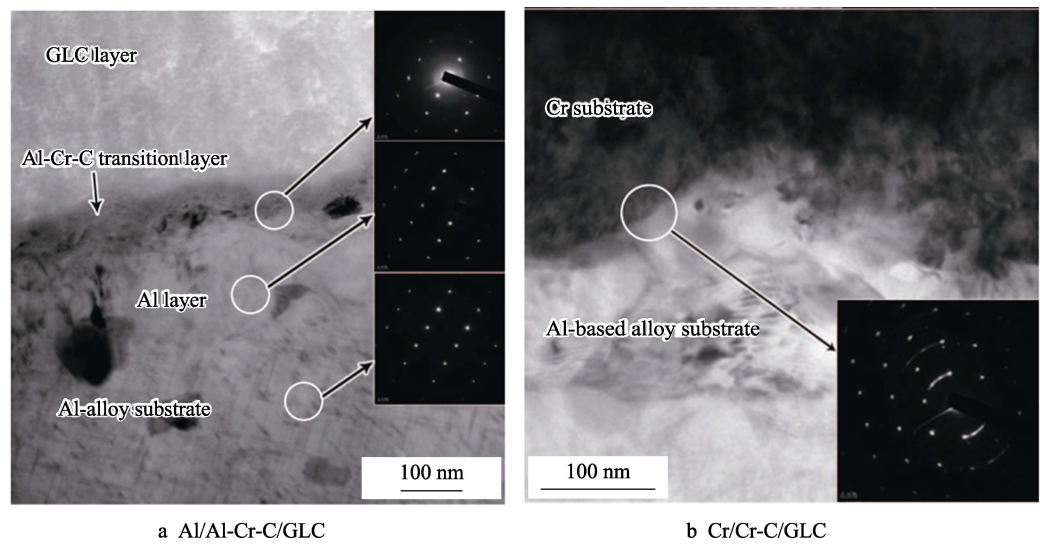


图 3 复合镀层截面的 TEM 像及铝合金基体与过渡层界面处的 SAEDP^[46]

Fig.3 Cross-section TEM image of composite coating and SAEDP of interface between sublayer and Al-based alloy^[46]

通过具有异质结构的多种梯度复合过渡层综合调控，提高结合力的同时可以实现表层功能性的改善。如王立平等^[47]利用电弧离子镀（Arc ion plating）与磁控溅射在铝合金表面制备 Ti/TiN/Si/(TiC/a-C:H) 多层薄膜，如图 4—5 所示，通过中间层的硬度梯度结构设计，实现了软基体到硬膜的过渡，为碳膜提供

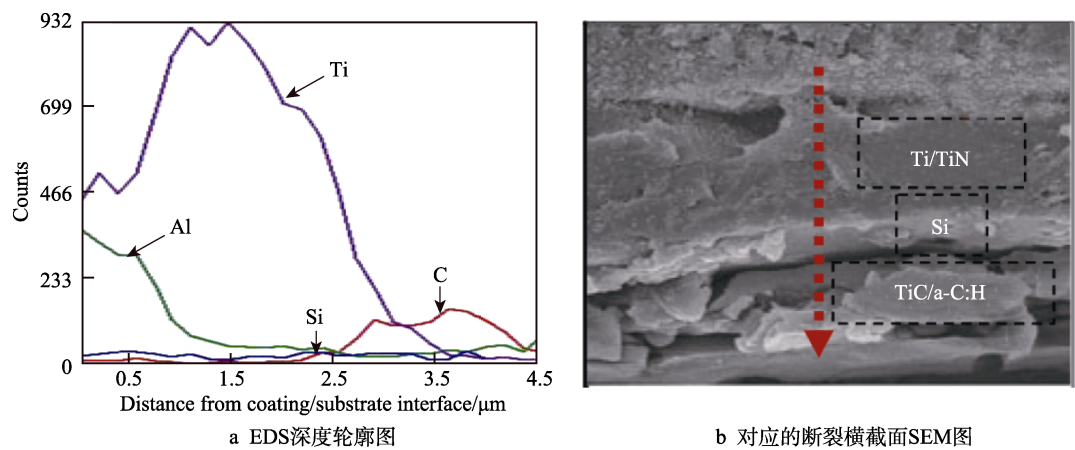


图 4 Ti/TiN/Si/(TiC/a-C:H)薄膜 EDS 深度轮廓图及对应的断裂横截面 SEM 图^[47]

Fig.4 EDS depth profile of the Ti/TiN/Si/(TiC/a-C:H) coatings (a) and corresponding SEM micrographs of the fracture cross-sections (b)^[47]

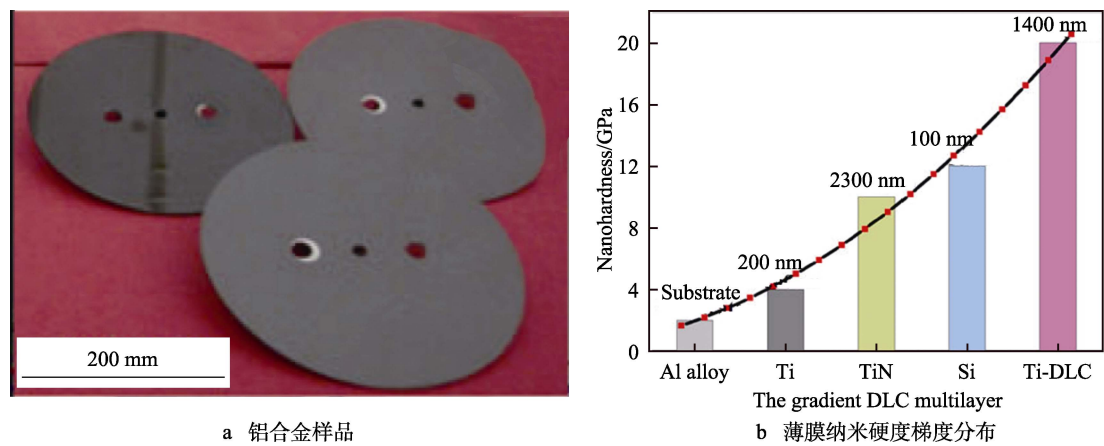


图 5 镀膜后的铝合金样品及薄膜纳米硬度梯度分布图^[47]

Fig.5 Aluminum alloy samples coated by DLC-based multilayer (a) and gradient distribution of nano-hardness of coatings (b)^[47]

了足够承载力；成分渐变的多层膜界面设计，消除了薄膜间的宏观界面，抑制了裂纹的萌生和扩展，划痕结合力超过 20 N，实现了强膜基界面结合；表层断裂韧性强的 TiC/a-C:H 碳基纳米复合薄膜，则可以发挥其低摩擦（干摩擦条件下的摩擦系数为 0.16）、高耐磨（约 $2.5 \times 10^{-6} \text{ mm}^3/(\text{N} \cdot \text{m})$ ，低于基底 2 个数量级）的优异性能。

此外，在金属基体表面沉积软硬交替的多层薄膜也是一种增强膜基结合的设计思路^[48-50]。如 Hidenobu Maruno 等^[50]设计制备了厚度为 2 μm 的具有不同调制比的多层 Si-DLC/DLC 体系。结合力及摩擦实验结果显示，调制比为 3:1、调制周期为 4 时，薄膜具有最高的临界载荷(15.2 N)和最低的磨损体积($1.7 \times 10^{-3} \text{ mm}^3$)。

2.2 其他技术制备的过渡层

除上述 PVD 技术制备的单一或梯度过渡层外，

为了尽量减弱软质铝合金基体对表层硬质 DLC 薄膜的影响，研究人员也采用其他制备技术沉积超厚的过渡层，为顶层 DLC 薄膜提供足够的支撑，从而获得更好的结合性能^[51-55]。表 2 为复合工艺过渡层对结合力与性能影响的统计结果，其中 Staia 等^[53]采用化学镀的方法在铝合金基体上制备了厚度为 50 μm 的 NiP 支撑层，然后再沉积厚度为 2 μm 的 DLC 减摩抗磨层，划痕实验显示结合力提升到 46.5 N，磨损率低于基体 3 个数量级，低于 NiP 层 2 个数量级，说明 NiP 过渡层对于提高结合力和改善摩擦性能具有显著作用。Picas^[54]和 Takayuki Utsumi^[55]分别通过超音速火焰喷涂（HOVF）和等离子喷涂（Plasma-spray）在铝合金表面预先制备厚且硬的 $\text{Cr}_3\text{C}_2\text{-NiCr}$ 、WC 中间层，也达到了类似效果，尤其 WC 过渡层的添加可以获得大于 60 N 的膜基结合力。

表 2 添加梯度复合过渡层对铝合金表面制备 DLC 的结合强度和摩擦性能的影响^[53-55]

Tab.2 Effect of gradient composite transition layer on adhesion strength and friction coefficient of DLC prepared on aluminum alloy^[53-55]

Sample	Preparation process	Film	Critical load/N	Friction coefficient	References
LY12	Electroless deposition+Sputtering+PECVD	NiP/CrC/DLC	35	0.12 (Load 2 N) 0.1 (Load 5 N)	[53]
AW-7022	HOVF+Sputtering+PECVD	$\text{Cr}_3\text{C}_2\text{-NiCr/DLC}$	25	0.1 (Load 5 N)	[54]
A5052	Plasma spray+PECVD	WC/DLC	>60		[55]

3 DLC 薄膜调控

研究者发现对于铝合金与 DLC 薄膜这种硬膜-软基体结构，其机械失效受薄膜自身内聚力失效和膜基界面结合力失效共同影响^[56-58]。由于 DLC 薄膜通常是高能沉积，内部具有高的残余应力，且随膜厚的增加而增大，过高的残余应力容易导致薄膜从基体界面处剥落，因此为了提高薄膜的膜基结合力，降低残余应力至关重要。

在制备 DLC 薄膜时，常通过调控功率密度、偏压、溅射气压和沉积温度等工艺参数，实现高能量、低沉积速率条件下沉积碳膜，引起薄膜结构弛豫，降低应力^[24,59-60]。Łukasz Kaczmarek 等^[24]在 7075 铝合金上沉积 Ti/TiC/a-C:H 时，通过调节偏压在 150~600 V 变化，实现了薄膜硬度在 10~19 GPa 区间内变化，纳米划痕实验显示，当偏压处于 600 V 时，结合力达到最高，为 33 mN，见图 6。

此外，研究者也采用掺杂一定含量的单一元素（如 Si、Ti 等），形成的掺杂 DLC 薄膜能有效降低薄膜内应力，增强薄膜的韧性和结合力^[49,61-62]。胡亚威等^[61]在 LY12 铝合金基体上研究了 TiC/a-C:H 薄膜体系中金属 Ti 含量对其成分、结构、力学及摩擦学性能的影响，发现当钛含量为 39%~46%时，硬度和弹性模量明显提高，同时掺杂金属元素 Ti 形成的特

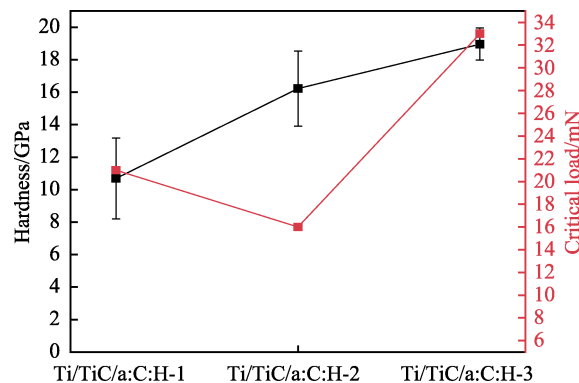


图 6 不同偏压下在 7075 合金上沉积的梯度薄膜的硬度和临界载荷^[24]

Fig.6 Critical load and hardness of gradient Ti/TiC/a-C:H-1, Ti/TiC/a-C:H-2, Ti/TiC/a-C:H-3 coatings deposited on 7075 alloy for different bias voltage (150 V, 300 V and 600 V)^[24]

殊纳米弥散 TiC 相颗粒不仅具有高硬度，而且有效增强薄膜的承载力及韧性，从而提高薄膜的摩擦性能。采用适当的退火工艺处理也是一种有效降低 DLC 薄膜内应力的方法^[63]，但并不适用于软化温度低的铝合金基体。

4 总结与展望

随着航空航天、舰船制造、高铁运输等行业的高

速发展,对铝合金表面性能的要求越来越高,只有通过表面改性技术,赋予铝合金更加优异的表面性能,才能满足苛刻工况下的使用要求。DLC 薄膜凭借低温制备、高硬度、优异的减摩抗磨等性能特点有望成为铝合金表面一种理想的防护薄膜材料。但强界面结合仍然是铝合金表面沉积 DLC 薄膜的瓶颈问题。目前通过喷丸前处理可以改善该问题,但会增加表面粗糙度,不适于高精密部件的铝合金表面处理。采用热喷涂、化学镀等技术制备的过渡层,对提高膜基结合力的效果最显著,但由于引入了多种制备手段,导致处理步骤复杂,不利于工业应用的推广。调控 DLC 薄膜本征内应力可在一定范围内改善膜基结合力,但效果并不明显,仍需要结合过渡层的使用,才能进一步增强界面结合。因此,围绕强界面结合的铝合金表面沉积 DLC 薄膜的制备与应用研究,还存在诸多难点有待深入完善:一是如何通过简单、便捷的制备手段获得强的膜基界面结合,仍属于关键瓶颈问题,同时如何评价铝合金/DLC 薄膜这种软基体/硬膜的结合以及失效机制,目前还没有形成有效的测试方法;二是针对苛刻环境下的服役工况,如何实现铝合金/DLC 薄膜的多功能化结构设计,以及该薄膜体系的长期使用可靠性,也是未来研究中需要重点关注的地方。

参考文献:

- [1] 郑晖,赵曦雅. 汽车轻量化及铝合金在现代汽车生产中的应用[J]. 锻压技术, 2016(2): 1-6.
ZHENG Hui, ZHAO Xi-ya. Lightweight automobile and application of aluminum alloys in modern automobile production[J]. Forging and stamping technology, 2016(2): 1-6.
- [2] 李宾,周恒竹,苏学伟,等. 铝合金建筑材料的发展现状及应用[J]. 科技视界, 2018(14): 56.
LI Bin, ZHOU Huan-zhu, SU Xue-wei, et al. The development status and application of aluminum alloy building materials[J]. Science & technology vision, 2018(14): 56.
- [3] DURSUN G, SOUTIS C. Recent developments in advanced aircraft aluminum alloys[J]. Materials and design, 2014, 56(4): 862-871.
- [4] 路炜. 提高发动机铝合金件耐磨性的表面处理工艺[J]. 电镀与精饰, 2007, 29(3): 25-27.
LU Wei. Surface treatment technology for increasing wear resistance of aluminum alloy engine parts[J]. Plating and finishing, 2007, 29(3): 25-27.
- [5] 张高会,黄国青,徐鹏,等. 铝及铝合金表面处理研究进展[J]. 中国计量学院学报, 2010, 21(2): 92-96.
ZHANG Gao-hui, HUANG Guo-qing, XU Peng, et al. Research progress in surface treatment of aluminum alloys[J]. Journal of China University of Metrology, 2010, 21(2): 92-96.
- [6] 陈海燕,朱有兰,李风,等. 铝硅合金表面电沉积铬工艺的优化[J]. 腐蚀与防护, 2007, 28(8): 417-419.
CHEN Hai-yan, ZHU You-lan, LI Feng, et al. Optimization of chromium plating process of Al-Si alloy[J]. Corrosion and protection, 2007, 28(8): 417-419.
- [7] 孙衍乐,宣天鹏,徐少楠,等. 铝合金的阳极氧化及其研发进展[J]. 电镀与精饰, 2010, 32(4): 18-21.
SUN Yan-le, XUAN Tian-peng, XU Shao-nan, et al. Research advances on anodic oxidation of aluminum alloy[J]. Plating and finishing, 2010, 32(4): 18-21.
- [8] 张鹏飞,李玉新,吴利芸. 铝合金表面激光熔覆技术[J]. 兵器装备工程学报, 2017, 38(10): 157-161.
ZHANG Peng-fei, LI Yu-xin, WU Li-yun. Status and development of laser cladding on aluminum alloys[J]. Journal of ordnance equipment engineering, 2017, 38(10): 157-161.
- [9] LUGSCHEIDER E, KRAMERK G, BARIMANI C, et al. PVD coatings on aluminum substrates[J]. Surface and coatings technology, 1995, 74-75(part-P1): 497-502.
- [10] 章凡勇,闫牧夫,何继宁. 5083 铝合金表面镀钛/渗氮复合层组织结构与摩擦学性能[J]. 材料热处理学报, 2017, 38(3): 172-176.
ZHANG Fan-yong, YAN Mu-fu, HE Ji-ning. Microstructure and wear properties of duplex coatings fabricated by plasma nitriding of Ti-coated 5083 aluminum alloy[J]. Transactions of materials and heat treatment, 2017, 38(3): 172-176.
- [11] LIU Y M, LI L H, XU M, et al. Effects of nitrogen ion implantation and implantation energy on surface properties and adhesion strength of TiN films deposited on aluminum by magnetron sputtering[J]. Materials science and engineering: A, 2006, 415(1/2): 140-144.
- [12] SASAKI Y, NOSE K, KAMIKO M, et al. High adhesion of diamond-like carbon thin film to an aluminum alloy achieved by substrate sputtering and redeposition method[J]. Surface and coatings technology, 2011, 206(1): 143-148.
- [13] 薛群基,王立平. 类金刚石碳基薄膜材料[M]. 北京: 科学出版社, 2012.
XUE Qun-ji, WANG Li-ping. Diamond-like carbon-based film material[M]. Beijing: Science Press, 2012.
- [14] ZOU Y S, ZHOU K, WU Y F, et al. Structure, mechanical and tribological properties of diamond-like carbon films on aluminum alloy by arc ion plating[J]. Vacuum, 2012, 86(8): 1141-1146.
- [15] ROBERTSON J. Diamond-like amorphous carbon[J]. Materials science & engineering reports, 2002, 37(4): 129-281.
- [16] LI L H, TIAN X B, CHU P K, et al. Growth and nucleation of diamond-like carbon (DLC) film on aluminum[J]. Nuclear instruments and methods in physics research section B: Beam interactions with materials and atoms, 2003, 206: 691-695.
- [17] 郅睨. 铝合金类金刚石多层薄膜表面改性及其机械性能研究[D]. 成都: 西南交通大学, 2011.
XIAN Gui. Study on synthesis and mechanical properties of diamond-like carbon multilayer films on aluminum

- alloy[D]. Chengdu: Southwest Jiaotong University, 2011.
- [18] 万善宏, 张广安, 王立平, 等. 铝合金表面复合沉积功能梯度 DLC 薄膜的耐磨性能[C]//第九届全国摩擦学大会论文集. 兰州: 中国机械工程学会摩擦学分会, 2009: 84.
- WAN Shan-hong, ZHANG Guang-an, WANG Li-ping, et al. Wear resistance of functionally graded DLC films deposited on aluminum alloy surface[C]//Proceedings of the ninth national tribology conference. Lanzhou: Tribology Branch of Chinese Mechanical Engineering Society 2009: 84.
- [19] WANG P, WANG X, XU T, et al. Comparing internal stress in diamond-like carbon films with different structure[J]. Thin solid films, 2007, 515(17): 6899-6903.
- [20] 张而耕, 张体波. 类金刚石在汽车零部件上的应用[J]. 南京理工大学学报, 2014, 38(1): 129-133.
- ZAHNG Er-geng, ZHANG Ti-bo. Application of diamond-like carbon in automobile parts[J]. Journal of Nanjing University of Science and Technology, 2014, 38(1): 129-133.
- [21] ZIA A W, ZHOU Z, SHUM P W, et al. The effect of two-step heat treatment on hardness, fracture toughness, and wear of different biased diamond-like carbon coatings[J]. Surface and coatings technology, 2017, 320: 118-125.
- [22] TAKAHASHI K, OSEDO H, SUZUKI T, et al. Fatigue strength improvement of an aluminum alloy with a crack-like surface defect using shot peening and cavitation peening[J]. Engineering fracture mechanics, 2018, 193: 151-161.
- [23] JIANG J, AMELL R D, TONG J. Some special tribological features of DLC coatings deposited on soft substrates[J]. Wear, 1997, 211(2): 254-264.
- [24] KACZMAREK L, ADAMCZYK-CIESLAK B, MIZERA J, et al. Influence of chemical composition of Ti/TiC/a-C:H coatings deposited on 7075 aluminum alloy on their selected mechanical properties[J]. Surface and coatings technology, 2015, 261: 304-310.
- [25] KANO M. Coating technology for vehicle applications[M]. Switzerland: Springer, Cham, 2015.
- [26] WASY A, BALAKRISHNAN G, LEE S H, et al. Argon plasma treatment on metal substrates and effects on diamond-like carbon (DLC) coating properties[J]. Crystal research and technology, 2014, 49(1): 55-62.
- [27] WADA T, NAKANISHI J, MIKI Y, et al. Surface modification of aluminum alloy using plasma based ion implantation and deposition[J]. Advanced materials research, 2012, 488-489: 960-966.
- [28] XIA L F, YAN Z H, LIAO J X. Effects of intermediate layers on the tribological behavior of DLC coated 2024 aluminum alloy[J]. Wear, 2004, 257(5/6): 599-605.
- [29] ZHNAG Z L, LIAO J X, XIA L F, et al. Structure and tribological properties of modified layer on 2024 aluminum alloy by plasma-based ion implantation with nitrogen/ titanium/carbon[J]. Transactions of nonferrous metals society of China, 2003, 13(6): 1371-1375.
- [30] LIAO J X, XIA L F, SUN M R, et al. Tribological behavior of gradient modified layer on 2024 aluminum alloy modified by plasma-based ion implantation[J]. Wear, 2004, 256(7): 840-845.
- [31] LIAO J X, TIAN Z, LI E Q, et al. Thick gradient layers prepared by plasma-based ion implantation on 2024 aluminum alloy[J]. Journal of physics D: Applied physics, 2007, 40(16): 4916-4921.
- [32] XU M, LIU Y M, LI L H, et al. Experimental and numerical evaluations of adhesion strength and stress in TiN films deposited on Ti-implanted aluminum[J]. Journal of vacuum science & technology A: Vacuum surfaces and films, 2006, 24(2): 212-217.
- [33] XU M, CAI X, LIU Y M, et al. Tribological properties of graded diamond-like carbon films on Ti ion-implanted aluminum substrate[J]. Diamond and related materials, 2008, 17(11): 1844-1849.
- [34] HOU Q R, GAO J. Enhanced adhesion of diamond-like carbon films with a composition-graded intermediate layer[J]. Applied physics A (materials science processing), 1999, 68(3): 343-347.
- [35] CAI H S, QI F G, OUYANG X P, et al. Effect of Ti transition layer thickness on the structure, mechanical and adhesion properties of Ti-DLC coatings on aluminum alloys[J]. Materials, 2018, 11: 1742.
- [36] LI X W, LI L, ZHANG D, et al. Ab initio study of interfacial structure transformation of amorphous carbon catalyzed by Ti, Cr, and W transition layers[J]. ACS applied material and interfaces, 2017, 47(9): 41115-41119.
- [37] WEI C, CHEN C H. The effect of thermal and plastic mismatch on stress distribution in diamond like carbon film under different interlayer/substrate system[J]. Diamond and related materials, 2008, 17(7): 1534-1540.
- [38] WEI C, YANG J F, TAI F C. The stress reduction effect by interlayer deposition or film thickness for diamond like carbon on rough surface[J]. Diamond and related materials, 2010, 19(5/6): 518-524.
- [39] WEI C, WANG Y S, TAI F C. The role of metal interlayer on thermal stress, film structure, wettability and hydrogen content for diamond like carbon films on different substrate[J]. Diamond and related materials, 2009, 18(2): 407-412.
- [40] BURNETT P J, RICKERBY D S. The relationship between hardness and scratch adhesion[J]. Thin solid films, 1987, 154(1/2): 403-416.
- [41] SRINIVASAN N, BHASKAR L K, KUMAR R, et al. Residual stress gradient and relaxation upon fatigue deformation of diamond-like carbon coated aluminum alloy in air and methanol environments[J]. Materials and design, 2018, 160(5): 303-312.
- [42] 苏永要, 王锦标. 7A04 铝合金表面 DLC 薄膜制备及性能研究[J]. 真空科学与技术学报, 2015, 35(5): 608-613.
- SU Yong-yao, WANG Jin-biao. Synthesis of diamond-like carbon coatings on 7A04 Al-alloy surfaces modified with

- Si-layer[J]. Chinese of journal of vacuum science and technology, 2015, 35(5): 608-613.
- [43] SUY Y, GUI X, XIE D, et al. The effect of a TiN interlayer on the tribological properties of diamond-like carbon films deposited on 7A04 aluminum alloy[J]. IEEE transactions on plasma science, 2011, 39(11): 3144-3148.
- [44] MARUNO H, NISHIMOTO A. Adhesion and durability of multi-interlayered diamond-like carbon films deposited on aluminum alloy[J]. Surface and coatings technology, 2018, 354: 134-144.
- [45] NAKAMURA M, KUBOTA S, SUZUKI H, et al. Wear and friction characteristics of AlN/diamond-like carbon hybrid coatings on aluminum alloy[J]. Journal of materials engineering and performance, 2015, 24(10): 3789-3797.
- [46] 时惠英, 龙艳妮, 蒋百灵, 等. 打底层对铝合金表面 GLC 镀层组织和摩擦学特性的影响[J]. 金属学报, 2012, 48(8): 983-988.
- SHI Hui-ying, LONG Yan-ni, JIANG Bai-ling, et al. Effect of sublayer of the structures and tribological properties of GLC coating on Al-based alloy[J]. Acta metallurgica sinica, 2012, 48(8): 983-988.
- [47] WANG L P, WANG S H, WANG S C, et al. Gradient DLC-based nanocomposite coatings as a solution to improve tribological performance of aluminum alloy[J]. Tribology letters, 2010, 38(2): 155-160.
- [48] LIN Y, ZIA A W, ZHOU Z, et al. Development of diamond-like carbon (DLC) coatings with alternate soft and hard multilayer architecture for enhancing wear performance at high contact stress[J]. Surface and coatings technology, 2017, 320: 7-12.
- [49] WANG J J, PU J B, ZHANG G, et al. Interface architecture for super-thick carbon-based films toward low internal stress and ultrahigh load-bearing capacity[J]. ACS applied material and interfaces, 2013, 5(11): 5015-5024.
- [50] MARUNO H, NISHIMOTO A. Effect of number of multilayer repetitions and thickness ratio on coating properties of Si-DLC/DLC multilayer coatings on aluminum alloys[J]. Journal of the Japan Institute of Metals and Materials, 2019, 83: 82-86.
- [51] NIE X, WILSON A, LEYLAND A, et al. Deposition of duplex Al_2O_3 /DLC coatings on Al alloys for tribological applications using a combined micro-arc oxidation and plasma-immersion ion implantation technique[J]. Surface and coatings technology, 2000, 131(1/3): 506-513.
- [52] YANG W, KE P L, FANG Y, et al. Microstructure and properties of duplex (Ti:N)-DLC/MAO coating on magnesium alloy[J]. Applied surface science, 2013, 270: 519-525.
- [53] STAIA M H, PUCHI CABRERA E S, IOST A, et al. Tribological response of AA 2024-T3 aluminum alloy coated with a DLC duplex coating[J]. Tribology international, 2015, 85: 74-87.
- [54] PICAS J A, MENARGUES S, MARTIN E, et al. Characterization of duplex coating system (HVOF+PVD) on light alloy substrates[J]. Surface and coatings technology, 2016, 318: 326-331.
- [55] UTSUMI T, OKA Y, FUJIWARA E, et al. Effect of a hard supra-thick interlayer on adhesion of DLC film prepared with PBIID process[J]. Nuclear instruments & methods in physics research, section B: Beam interactions with materials and atoms, 2007, 257(1/2): 706-709.
- [56] FAVACHE A, SACRE C H, COULOMBIER M, et al. Fracture mechanics based analysis of the scratch resistance of thin brittle coatings on a soft interlayer[J]. Wear, 2015, 330-331: 461-468.
- [57] SANDER T, TREMMEL S, WARTZACK S. A modified scratch test for the mechanical characterization of scratch resistance and adhesion of thin hard coatings on soft substrates[J]. Surface and coatings technology, 2011, 206(7): 1873-1878.
- [58] NOSE K, SASAKI Y, KAMIKO M, et al. Nanoindentation fracture behaviors of diamond-like carbon film on aluminum alloy with different interface toughness[J]. Japanese journal of applied physics, 2012, 51(9): 090127.
- [59] DAI W, ZHENG H, WU G S, et al. Effect of bias voltage on growth property of Cr-DLC film prepared by linear ion beam deposition technique[J]. Vacuum, 2010, 85(2): 231-235.
- [60] GUI X, SU Y Y, LI S Y, et al. Tribological properties of hydrogenated amorphous carbon (a-C:H) films on aluminum alloy substrate under different substrate bias voltages[C]// Materials science forum. London: Trans Tech Publications, 2011, 687: 784-790.
- [61] 胡亚威. TiC/a-C:H 薄膜的制备及性能研究[D]. 上海: 上海交通大学, 2007.
- HU Ya-wei. The deposition and properties of TiC/a-C:H films[D]. Shanghai: Shanghai Jiao Tong University, 2007.
- [62] DAI W, KE P L, MOON M W, et al. Investigation of the microstructure, mechanical properties and tribological behaviors of Ti-containing diamond-like carbon films fabricated by a hybrid ion beam method[J]. Thin solid films, 2012, 520(19): 6057-6063.
- [63] 王永霞, 冶银平, 李红轩, 等. 退火温度对 a-C:H 膜结构及摩擦学性能的影响[J]. 无机材料学报, 2011, 26(2): 209-213.
- WANG Yong-xia, YE Yin-ping, LI Hong-xuan, et al. Effect of annealing temperature on the structure and tribological property of a-C:H film[J]. Journal of inorganic materials, 2011, 26(2): 209-213.