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基底对类金刚石薄膜摩擦学性能的影响

张仁辉,赵 娟

(铜仁学院材料与化学工程学院,贵州铜仁 554300)

摘 要:为了研究不同基底对类金刚石薄膜摩擦磨损性能的影响,采用等离子体增强化学气相沉积方法在高速钢、SiC和304不锈钢基底上成功制备了类金刚石薄膜。采用SEM,TEM,Raman测试手段对膜层的微结构进行了表征:SEM表征结果显示膜层总厚度约为6.5 μm,而且层与层之间有明显的界面;TEM表征结果显示沉积的膜层为无定型结构;Raman光谱分析显示沉积的薄膜存在明显的G峰和D峰,可以确定沉积的薄膜为类金刚石薄膜。摩擦测试结果显示,基底对类金刚石薄膜摩擦磨损性能具有显著影响,对于不同基底,钢球对偶上均存在明显的转移膜,高速钢基底的磨痕宽度最小,而且沉积在高速钢基底上的类金刚石薄膜具有最低的磨损率,摩擦系数约为0.1。采用Raman光谱对不同基底磨痕表面微结构进行了分析,认为高速钢基底具有最低磨损率可归因于其磨痕的石墨化程度低。研究可为制备具有优异摩擦磨损性能的类金钢石薄膜提供参考。

关键词:摩擦学;摩擦系数;类金刚石;Raman;SEM;TEM

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Effect of substrates on tribological properties of diamond-like carbon coating

ZHANG Renhui, ZHAO Juan

(School of Material and Chemical Engineering, Tongren University, Tongren, Guizhou 554300, China)

Abstract: In order to well investigate the effect of different substrates on the friction and wear of diamond-like carbon (DLC) coating, the DLC coatings are deposited on substrates like the high-speed steel (HSS), SiC and 304 stainless steel by using plasma enhanced chemical vapor deposition method. The diamond-like carbon is prepared. The microstructure of the coatings is characterized using SEM, TEM and Raman. The SEM results exhibit that the total thickness of the coatings is about 6.5 μm, and there's apparent interfaces between layers. The TEM results imply that the coatings have an amorphous structure. Raman spectrum exhibits that G and D peaks are observed, which implies that the deposition coatings are diamond-like carbon coating. The results of tribological tests show that the substrates have a significant effect on the friction and wear of the coating. For different substrates, the transfer film is found on the steel counterpart surface, the wear track of the HSS has a lowest width, and the DLC coating that deposited on HSS exhibits the lowest wear and low friction coefficient (about 0.1). The microstructure of different substrates wear track surfaces is analyzed by using Raman spectrum, and the lowest wear of the HSS is attributed to the lower degree of the graphitization. The research provides reference for preparing the DLC coating with excellent tribological properties.

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第一作者简介:张仁辉(1985—),男,湖南辰溪人,副教授,博士,主要从事材料物理与化学方面的研究。

E-mail:zrh_111@126.com

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Keywords：tribology；friction coefficient；diamond-like carbon；Raman；SEM；TEM

众所周知，类金刚石薄膜具有优异的摩擦磨损性能[1-3]，这主要归因于其高硬度和高化学惰性。然而，类金刚石的高内应力限制了其在电子设备与汽车等领域中的应用[4]。研究发现，异质原子掺杂类金刚石薄膜能很好地降低其内应力[5-6]。异质原子掺杂不但能进一步提升类金刚石薄膜的沉积厚度，而且还可以进一步提升类金刚石薄膜的力学性能[7-10]。

近年来，黄金霞等[11-12]采用磁控溅射系统在聚合物基底(PEEK)上成功沉积了类金刚石薄膜，而且系统研究了其在 NaCl 体液中的摩擦磨损性能。一些研究人员[13-15]采用磁控溅射方法在织构化的不锈钢基底上制备了织构化的类金刚石薄膜，其在水环境中显示出优异的摩擦磨损性能。张仁辉等[5-6]采用化学气相沉积方法制备了超厚类金刚石薄膜，制备的薄膜具有优异的力学和摩擦学性能。王永欣等[16]系统地研究了不同基底(Si_3N_4，SiC 和 WC)对类金刚石薄膜的摩擦磨损性能的影响。综上所述，类金刚石薄膜的摩擦磨损性能不但与沉积方法有关，还与沉积的基底类型有关。基于此，本文采用等离子体增强化学气相沉积系统在不锈钢、碳化硅和高速钢基底上成功制备了类金刚石薄膜，并系统地探讨了不同基底对类金刚石薄膜的摩擦磨损性能的影响。

1　试验部分

1.1　试验材料及制备

抛光后的硅片，厚度相同(厚度均为 4 mm)的 304 不锈钢，SiC 和高速钢(钢号：W6Mo5Cr4V2(M2))作为类金刚石薄膜的沉积基底，基底在无水乙醇和丙酮中分别超声 40 min，N_2 气吹干后放入等离子体增强化学气相沉积系统，将类金刚石薄膜沉积在硅片上，以便于观察薄膜截面结构、高分辨形貌和拉曼光谱表征。腔体的初始气压抽至 1.0×10^{-3} Pa。基底在 Ar 等离子体中清洗 30 min，气压为 2.1 Pa。在设置的条件下，类金刚石薄膜采用交替沉积的方法沉积在特定的基底上。交替沉积方法的参数如下：a)SiH_4(25 sccm)，CF_4(22.5 sccm)，C_2H_2(150 sccm)和 Ar(100 sccm)，气压为 4.0 Pa；b)SiH_4(25 sccm)，CF_4(22.5 sccm)，C_2H_2(100 sccm)和 Ar(100 sccm)，气压为 2.8 Pa。沉积电压统一设定为 800 V，频率为 1.5 kHz，占空比为 30%。为了增强膜基结合力，将厚度约 200 nm 的 Si 中间层沉积在基底上。

1.2　试验方法

采用 TX-200V 光学显微镜观察磨斑形貌；采用场发射扫描电子显微镜(FESEM，JSM-6701F)表征膜层的截面形貌；采用高分辨透射电子显微镜(Tecnai™ G^2 F30，FEI，USA)表征膜层的微观结构；采用拉曼光谱(LABRAM-HR800)对膜层的微观结构进行表征，波长为 532 nm，扫描范围为 800～2 000 cm^{-1}；测试时间为 60 s；膜层的硬度由纳米压痕仪测定(NanoTest600，Micromaterials Ltd.，United Kingdom)；膜层的摩擦学性能由 CSM 球盘往复滑动摩擦磨损试验机测定；大气湿度为 35%，钢球半径为 6 mm，载荷为 5 N，振幅为 5 mm，频率为 5 Hz，滑动速度为 7.45 cm/s。

2　结果与讨论

图 1 为制备的类金刚石薄膜的截面形貌。图 1 显示，膜层的截面微结构均匀致密，而且层与层之间具有明显的界面，膜层的总厚度为 6.5 μm。图 2 为类金刚石薄膜的高分辨透射电镜图，显示膜层的微结构为无定型结构。

图 3 为类金刚石薄膜的拉曼光谱，类金刚石薄膜的拉曼光谱由高斯分峰法拟合为 G 峰(1 580 cm^{-1})和 D 峰(1 350 cm^{-1})[17-18]。2 个明显特征峰说明所制备的膜层为典型的类金刚石薄膜。峰位在 860 cm^{-1}附近为 Si—O 振动峰[19]，这归因于硅基底的影响。

图 4 为沉积在高速钢、碳化硅和不锈钢基底上的类金刚石薄膜的摩擦系数曲线图。沉积在碳化硅基底上的类金刚石薄膜具有最高摩擦系数，约为 0.22；沉积在不锈钢基底上的类金刚石薄膜具有最低摩擦系数，约为 0.1；沉积在高速钢基底上的类金刚石薄膜的摩擦系数约为 0.13。

图 5 a)—图 5 c)分别为沉积在高速钢、碳化硅和不锈钢基底上的类金刚石薄膜的磨损表面轮廓。沉积在高速钢基底上的类金刚石薄膜的磨损体积为 1.04×10^{-6} mm^3；沉积在碳化硅基底上的类金刚石薄膜的磨损体积为 1.4×10^{-6} mm^3；沉积在不锈钢基底上的类金刚石薄膜的磨损体积为 2.44×10^{-6} mm^3。

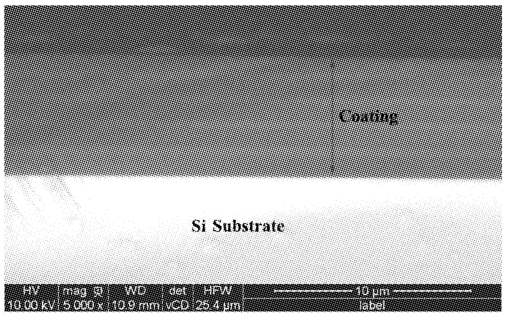


图 1 类金刚石薄膜的截面形貌照片

Fig. 1 Cross-sectional image of DLC coating

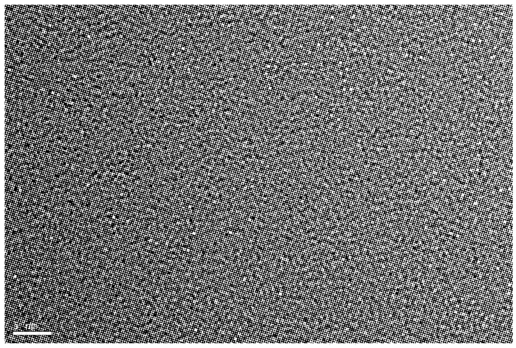


图 2 类金刚石薄膜的高分辨透射电镜图

Fig. 2 HR TEM image of DLC coating

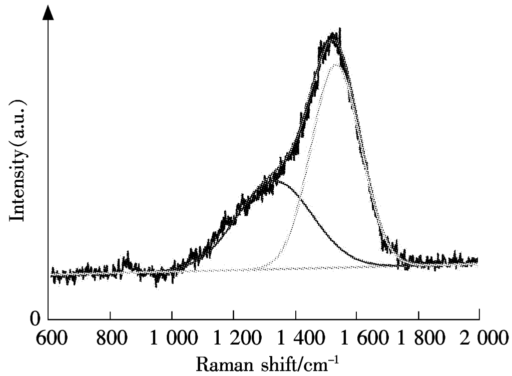


图 3 类金刚石薄膜的拉曼光谱

Fig. 3 Raman spectrum of DLC coating

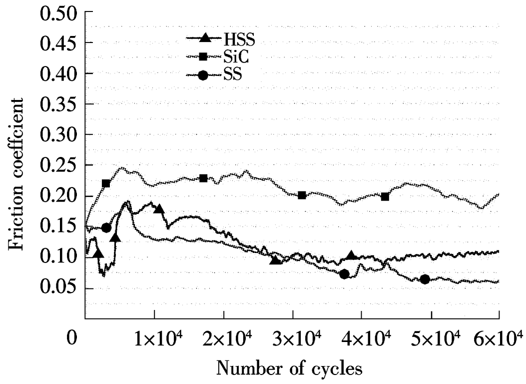
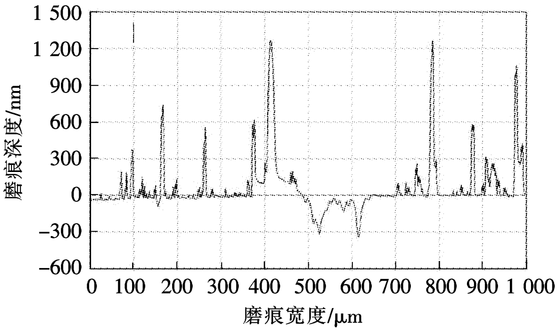
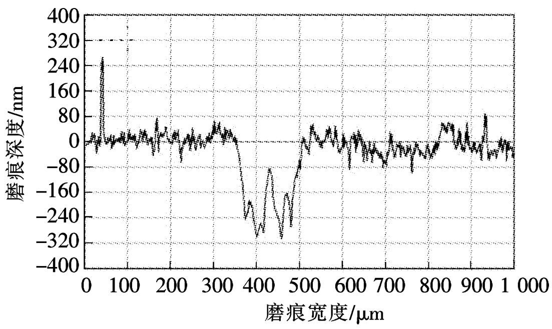


图 4 沉积在高速钢、碳化硅和不锈钢基底上的类金刚石薄膜的摩擦系数

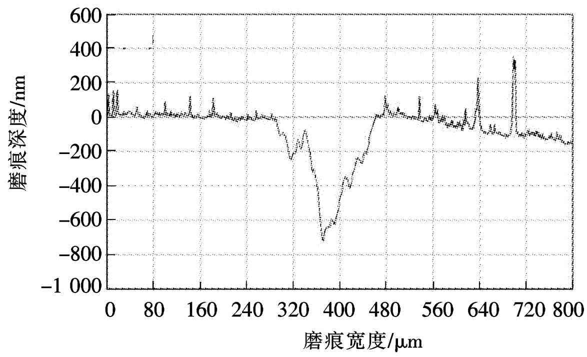
Fig. 4 Friction coefficient of DLC coating deposition on the HSS, SiC and SS substrates



a) 高速钢



b) 碳化硅

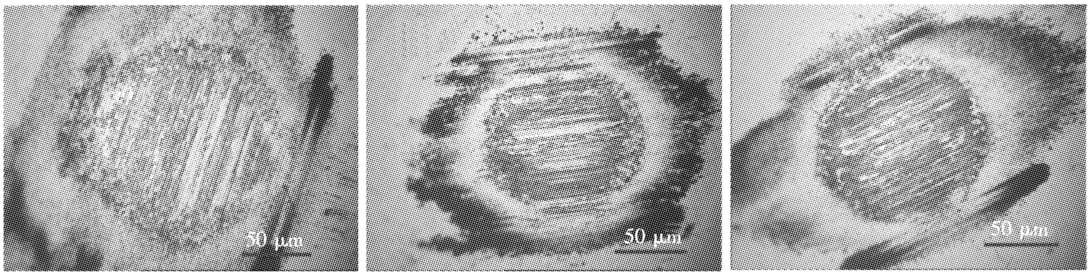


c) 不锈钢

图 5 沉积在不同基底上的类金刚石薄膜的磨损表面轮廓

Fig. 5 Surface profiles across the wear track of the DLC coating deposition on different substrates

图 6 a)—图 6 c)分别为沉积在高速钢、碳化硅和不锈钢基底上的类金刚石薄膜与不锈钢球配副摩擦测试后的磨斑光学形貌照片，显示磨斑上存在明显的转移膜，而且周边有大量磨屑。

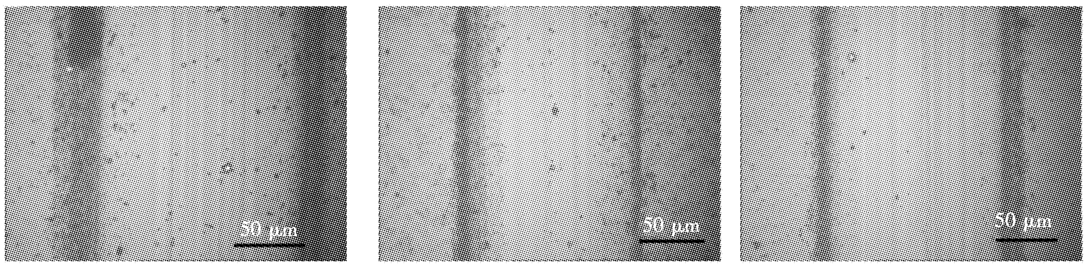


a) 高速钢基底　　b) 碳化硅基底　　c) 不锈钢基底

图 6　类金刚石薄膜与不锈钢球配副摩擦测试后的磨斑光学形貌照片

Fig. 6　Optical micrographs of the stainless steel ball surfaces after the sliding test against DLC coating

图 7 a)—7 c)分别为沉积在高速钢、碳化硅和不锈钢基底上的类金刚石薄膜的磨痕形貌图，显示磨痕周边存在大量磨屑，而且在磨痕内存在不同深度的犁沟。说明膜层的磨损主要归因于磨粒磨损。



a) 高速钢基底　　b) 碳化硅基底　　c) 不锈钢基底

图 7 类金刚石薄膜摩擦测试后磨痕形貌照片

Fig. 7　Optical micrographs of wear tracks of DLC coating

图 8 为原类金刚石表面和不同类金刚石薄膜磨痕内的拉曼光谱图。随着滑动摩擦测试的不断往复，D 峰峰形逐渐变得突出，G 峰峰位不断向高频方向移动，这表明磨痕内的类金刚石薄膜表面已经发生了明显的石墨化[20-21]，而且石墨化程度越高摩擦系数越小，因此，沉积在不锈钢基底上的类金刚石薄膜具有最小的摩擦系数，而膜层的石墨化导致了膜层具有较大的磨损体积。另外，高速钢($W_6Mo_5Cr_4V_2(M_2)$)的硬度为 8.6 GPa[22]，碳化硅的硬度为 31.2～38.3 GPa[23]，304 不锈钢的硬度为 4.6 GPa[24]。图 9 为测试得到的不同基底的类金刚

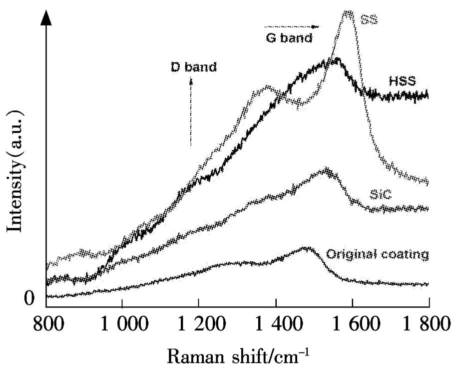


图 8　原类金刚石薄膜、沉积在高速钢、碳化硅和不锈钢基底上类金刚石薄膜磨痕内的拉曼光谱

Fig. 8　Raman spectra of original DLC coating and wear track of and DLC coating deposition on HSS, SiC and SS substrates

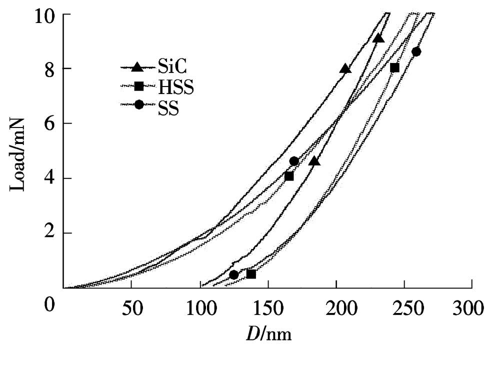


图 9　沉积在高速钢、碳化硅和不锈钢基底上的类金刚石薄膜的纳米压痕曲线

Fig. 9　Nanoindentation load-displacement curve of DLC coatings deposition on HSS, SiC and SS substrates

石薄膜的硬度曲线图。沉积在高速钢、碳化硅和不锈钢基底上的类金刚石薄膜的硬度分别为 9.05,11.4 和 8.97 GPa。高速钢具有较小的磨损体积,这与类金刚石薄膜的硬度和高速钢的硬度接近有关。

3 结 语

采用等离子体增强化学气相沉积的方法在高速钢、碳化硅和不锈钢基底上制备了类金刚石薄膜[25],研究了不同基底对类金刚石薄膜的摩擦磨损性能。结果显示,基底对膜层的摩擦磨损性能具有显著影响,摩擦系数在 0.05~0.25 变化,磨损体积在 $1.04\times10^{-6}\sim2.4\times10^{-6}$ mm^3 变化。沉积在高速钢上的类金刚石薄膜具有最低的磨损体积,摩擦系数约为 0.1。本文只讨论了大气气氛下不同基底对类金刚石薄膜的摩擦磨损性能的影响,未来将重点研究不同基底在水环境和氮气环境下基底对类金刚石薄膜摩擦磨损性能的影响。

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