

激光制备高附着性能的铜基类金刚石膜*

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摘要:提升类金刚石(Diamond-Like Carbon, DLC)膜在被保护基底上的附着能力具有明显的实际应用价值。从微观机理上分析了前期设计的Cu基多层DLC膜有效性的原因。在此基础上,研究了DLC/SiC循环层中两者厚度比例对膜层的附着性能、纳米硬度和耐磨性的影响,以优化结构、进一步提升实际应用所需的膜层性能。纳米划痕和压痕测试结果表明:随着DLC层与SiC层厚度比例的增大,多层DLC膜在Cu基上附着性能逐渐降低,但当厚度比小于2.3时,仍接近厚度400 nm的单层DLC膜在Si基上的附着性能;Cu基多层DLC膜的纳米硬度逐渐提高,同时,耐磨性接近纯DLC膜。

关键词:铜基类金刚石膜;脉冲激光沉积;临界载荷;纳米硬度;耐磨性

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Cu-based diamond-like carbon film with high adhesion prepared by pulsed laser deposition

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Abstract: Improvement for the adhesive property of the DLC (diamond-like carbon) film on the protected substrate has obvious value in the actual application, and the reason for the validity of the Cu-based multi-layer DLC film designed in our former research was analyzed in the view of the micro-theory. Then, in order to optimize the structure of the multi-layer film and improve its performance in the practical application, the influences of the thickness ratio between the DLC layer and SiC layer in the periodic layer on the adhesion property, nano-hardness and wear property were studied. The results of the nano-scratch and nano-indentation tests show that the adhesive property and nano-hardness of the Cu-based multi-layer DLC film decreased and its nano-hardness increased, respectively, while the thickness ratio was maintained in the increasing state. Critical load of the multi-layer DLC film on the Cu substrate could approach that of the single-layer DLC film with the thickness of 400 nm on the Si substrate, when the thickness ratio was below 2.3. Meanwhile, the wear property of the Cu-based multi-layer DLC film was approximately close to that of the pure DLC film.

Keywords: Cu-based diamond-like carbon film; pulsed laser deposition; critical load; nano-hardness; wear property

由于类金刚石(Diamond-Like Carbon, DLC)膜具有高硬度和低摩擦的显著优势,在力学和摩擦学领域受到广泛关注。但是,它不能直接镀制在很多材料上,主要有两个原因:一是其内应力极高^[1-2],尤其是脉冲激光沉积法(Pulsed Laser Deposition, PLD)更是大于2 GPa^[3-4],导致膜层本身不能镀厚;二是与基底材料的理化特性差异大,导致附着性能低^[5],这一点对于金属材料尤为突出。另外,很多金属材料与类金刚石膜的硬度差异极大(1个数量级以上),因此降低了类金刚石膜的高硬度保护作用,在外力作用下也容易

破裂。

膜层附着牢固是其工程应用的基本要求。临界载荷是附着性能高低的表征参数之一,可由纳米划痕(nano-scratch)或微米划痕(micro-scratch)测试获得;两者主要区别在于使用金刚石针尖的尺度差异大,与样品的接触面积差异巨大,导致测试结果差异巨大。所以,划痕测试结果只能在同等测试条件下比较不同样品的附着性能,而不能将不同测试条件下的测试结果相互比较。Constantinou等^[6]采用准分子激光(248 nm)在Si基底上制备出Ag掺杂DLC膜,临界载荷(纳米划

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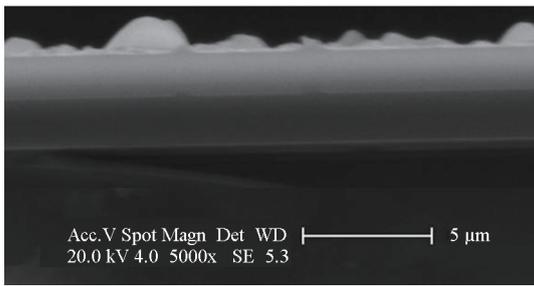
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构的具体情况。图 2(a)所示为 SEM 观察的样品 S3 断面,即多层 DLC 膜的结构;图 2(b)所示为起黏附作用的 Ti 层和独立 SiC 层的局部结构。

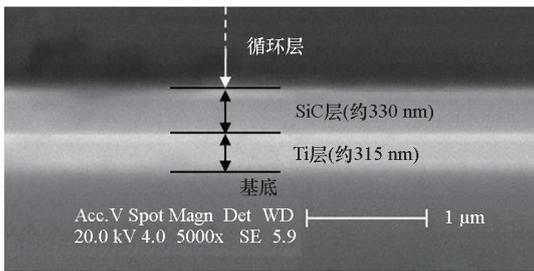
从图 2(b)中可以看出,独立 SiC 层、Ti 层及基底(Si)之间的对比非常明显;但仔细分辨可以发现,Ti 层与基底之间的分界面比较模糊,而 Ti 层与 SiC 层之间的分界面相对要清晰得多,这与金属 Ti 的性质有很大关系。激光等离子体中的粒子携带了高动能,撞击基底(或下接膜层)并扩散,逐渐耗散能量后冷凝成膜。制备 Ti 层初期,Ti 动能粒子向基底内部扩散,形成了模糊的界面;而金属 Ti 却具有阻止外界粒子向其内部扩散的性能^[18],因此 Ti 层在成为黏附层的同时,也是一种障碍层,从而使得 Ti 层与上膜层间的分界面相对清晰。

图 2(b)中循环层中 DLC 层与 SiC 层之间没有明显的区分,其局部经数字图像处理后显示在图 2(c)中,可以大致看出两者间的差别,但分界面仍难辨别。



(a) 多层 DLC 膜结构

(a) Structure of the multi-layer DLC film



(b) 黏附层结构

(b) Structure of the adhesive layers



(c) 循环层结构

(c) Structure of the periodic layers

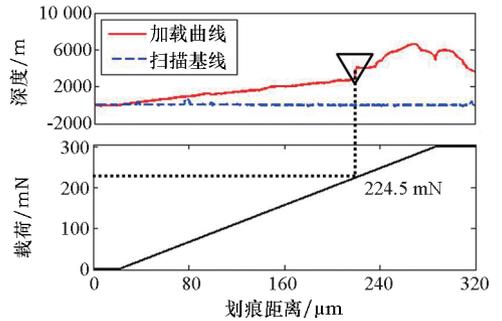
图 2 多层 DLC 膜的 SEM 图像

Fig. 2 SEM imaging of the multi-layer DLC film

2.2 附着性能

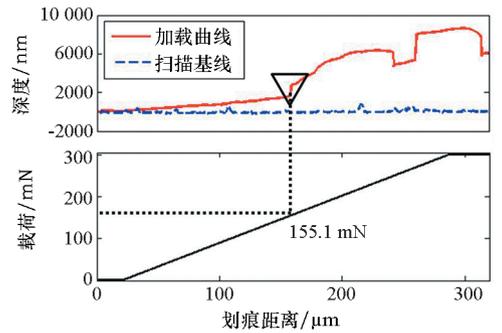
胶粘和重摩擦等测试(依据标准有 GJB2485—1995 和 MIL - 48497A 等)只能定性判断膜层样品的附着性能是否达到某一标准;为了定量测试样品的附着性能,进行纳米划痕测试并比较不同工艺条件下的 Cu 基多层 DLC 膜的临界载荷。

研究中样品的纳米划痕典型测试曲线如图 3 所示。图中,形貌基线已去除倾斜。



(a) 样品 S1

(a) Sample S1



(b) 样品 S4

(b) Sample S4

图 3 铜基 DLC 膜的划痕测试

Fig. 3 Scratch testes of the Cu-based DLC film

图 3 表明,随着载荷的增大,加载曲线的纵坐标“深度”逐渐上升,表示针尖不断深入样品内部,膜层初期发生弹性形变(该段加载曲线近似线性变化);但随着载荷的不断增大,加载曲线在某一位置出现突变(图中倒三角所示),暗示膜层破裂,此后膜层发生了不可逆的塑性形变。膜层破裂的位置对应载荷值,即临界载荷,可以表征膜层的附着性能。加载曲线出现了多次突变,表明内部膜层逐渐断裂,但按“木桶原则”,第一层的断裂即认为整个膜层的失效。根据纳米划痕测试,各样品的临界载荷对比如图 4 所示,其中 X 表示在 Si 基上直接镀制 400 nm 厚 DLC 膜样品,测试条件同其他样品。

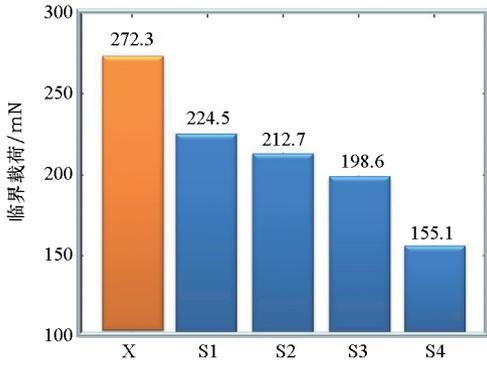


图4 样品的临界载荷对比

Fig. 4 Contrast among the critical loads of the samples

从图4中可以看出,随着DLC层与SiC层厚度比例的提高,Cu基DLC膜的临界载荷逐渐降低。当厚度比小于2.3时,其值接近或超过Si基DLC膜(厚度为400 nm)临界载荷的80%,具备了较高的实用价值。该厚度比例过高(如9:1)时,DLC层厚度过大,其内应力积累严重,这会直接导致膜层在外力作用下的破裂,从而在总体上影响膜层的附着性能。

将Si基DLC膜的临界载荷作为参照,是因为理论上DLC膜与Si的结合最为牢固,这源于C原子与Si原子同族且最为接近,两者之间具有极低的失配界面(mismatch interface),可以形成较强的Si—C原子键。反观C原子与Cu原子,两者之间存在极高的失配界面,因此形成了大量易断裂的弱键;当C原子累积至一定程度时,会引起某一方向上的剪切力过大,导致键的断裂^[5],即膜层脱落。Cu基多层DLC膜的设计就是在Cu基与外层DLC保护层之间添加黏附作用的膜层,并有意识地使两者之间巨大的硬度差异得到过渡,从而增强DLC膜的附着性和保护性。

金属Ti是一种典型的金属与类金属黏结材料,Ti原子在Cu基浅表扩散并以CuTi₂、CuTi、Cu₂Ti等多种较强的金属键存在^[18-21],使Ti层牢固地附着在Cu基上。而SiC被选择作为另一个黏附材料,是因为Ti原子可以取代Si—C中的Si原子,并与其最近的4个C原子产生杂化;该过程填补了Si空位的悬空键,同时对能带结构的影响很小^[22]。因此,SiC层能够与Ti层牢固结合。再次,在DLC层与SiC层的界面中,原子扩散使得DLC层中的C原子与SiC形成稳定的能带结构,增强两者之间的结合^[23-24];同时,一定厚度的SiC层引入也避免了DLC层内应力的不断积累。因此,DLC/SiC循环层在研究中得

到利用。

2.3 机械硬度

纳米硬度是反映膜层抵抗外力作用的机械性能的参数之一,能够表现其抗划伤能力。同等条件下,膜层硬度越高,抗划伤的能力越强。纳米压痕测试是测试薄膜硬度、杨氏模量等机械参数的方法之一。测试中采用经典模块,而非当前流行的动态接触模块(Dynamic Contact Module, DCM)。这是由于金属Cu基底的抛光效果较差(材质太软不易抛光)、表面不是很平坦,厚度为数微米的膜层也不能使样品表面达到适于DCM模块使用的要求。与DCM相比,经典模块具有最大载荷更大、压入深度更深的特点,对厚膜的测试更有优势;虽然精度上略差于前者,但对于研究中的这几个样品的比较已经足够了,在10%膜厚(约400 nm)以内的测试数据仍能保证基本的精度。

典型的纳米压痕测试结果“载荷—压入深度”曲线如图5所示。测试针头压到最大压入深度时使用的加载力越大,说明膜层对外力的承受能力越大,也就表明硬度越高;反之,硬度越低。由图5可知,在压入深度为1500 nm的条件下,对样品S1使用的载荷最小,说明其纳米硬度最低。样品S4的硬度最高,这主要是因为样品S4中DLC层的厚度最大,DLC的纳米硬度比SiC的要高得多。因此,随着DLC层与SiC层厚度比例的增大,整个膜层的纳米硬度必然提高。

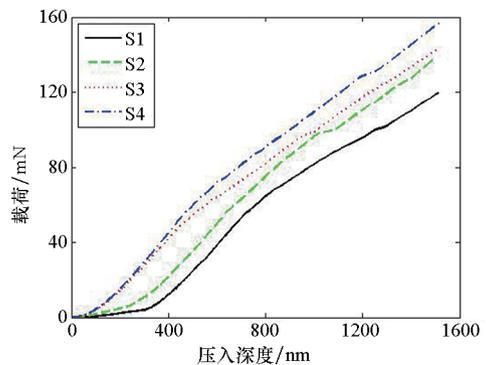


图5 载荷—压入深度曲线

Fig. 5 Curves of load-depth

对样品的“载荷—压入深度”曲线计算后,获得样品的纳米硬度、杨氏模量等参数。对每个样品的纳米硬度取平均,绘于图6中。由图6可知,随着DLC层与SiC层厚度比例的增大,Cu基多层DLC膜的纳米硬度逐渐提高。金属Cu的纳米硬度不足2 GPa,可见设计膜系使其机械性能得到了极大提升。

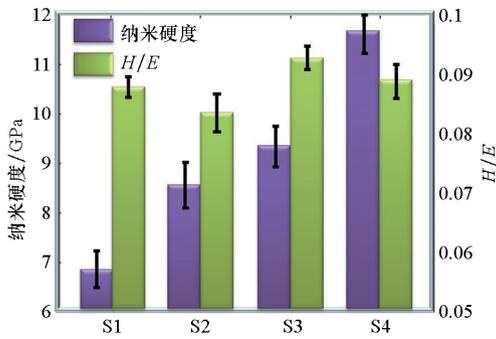


图 6 样品表面磨痕

Fig. 6 Wear trail of the surfaces

除了磨损量参数,膜层的耐磨性还可以由硬度-杨氏模量比(H/E)来表征^[25-26],4个样品的 H/E 也绘于图6中。耐磨性好的DLC膜的 H/E 一般在0.1左右^[25-27],Cu基多层DLC膜的 H/E 在0.085~0.095之间,略低于上述文献的报道值,毕竟与这些报道研究中的Si基或不锈钢基DLC膜相比,Cu基多层DLC膜的 H/E 受到了很多不利因素的影响,如较软的金属基底、较软的SiC层以及较软的金属Ti层。

3 结论

针对金属Cu基底硬度低、硬质DLC保护膜附着性能差的问题,设计制备出Cu基多层DLC膜,使DLC膜层获得了优良的附着性能、机械硬度和耐磨性能。

随着循环层中DLC层与SiC层厚度比例的提高,Cu基多层DLC膜的临界载荷逐渐降低,当厚度比小于2.3时,其值接近或超过厚度为400nm的Si基DLC膜。

随着DLC层与SiC层厚度比例的增大,Cu基多层DLC膜的纳米硬度逐渐提高;同时,表征耐磨性的参数 H/E 接近最佳值0.1。

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