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柔性硬质纳米复合涂层*

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摘要: 研究了利用磁控溅射方法制备的柔性硬质纳米复合涂层。结果表明柔性硬质纳米复合涂层具有以下优异性能: 是一类具有高硬度、高韧性以及抗裂纹性能的新型涂层; 具有较高的硬度模量比($H/E^* \geq 0.1$, $E^* = E/(1-\nu^2)$)、弹性恢复系数($W_e \geq 60\%$)、压应力($\sigma < 0$)_L, 且少缺陷的微观结构; 生长处于Thornton结构区域相图的T区。磁控溅射非常适合制备纳米复合涂层, 文中将对其制备柔性纳米复合薄膜的机理做深入阐述。涂层生长主要受以下3个参数影响: 涂层生长过程中吸收的能量 E_p , 其包含沉积原子携带的能量 E_{ca} 和轰击离子携带等能量 E_{bi} ($E_p = E_{ca} + E_{bi}$), 基体温度 T_s 和涂层材料的熔点 T_m 。柔性硬质涂层具有广泛的应用前景, 如柔性保护涂层、柔性功能涂层、防脆性涂层开裂的柔性保护涂层以及柔性多层涂层。文中还将详细阐述低温磁控溅射制备柔性纳米复合涂层的原理, 并阐述纳米复合涂层及其性能的发展趋势。

关键词: 硬质纳米复合涂层; 微观结构; 宏观应力; 力学性能; 能量; 柔性; 裂纹抑制; 磁控溅射

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Flexible Hard Nanocomposite Coatings

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Abstract: The article reports on flexible hard nanocomposite coatings prepared by magnetron sputtering. It is shown that the flexible hard nanocomposite coatings represent a new class of coatings which are simultaneously hard, tough and resistant to cracking, exhibit high values of the hardness H and effective Young's modulus E^* ratio $H/E^* \geq 0.1$, elastic recovery $W_e \geq 60\%$, compressive macrostress $\sigma < 0$ and dense, void-free microstructures, and are formed in the zone T of the Thornton's Structural zone model (SZM); here $E^* = E/(1-\nu^2)$, E is the Young's modulus and ν is the Poisson's ratio. The magnetron sputtering, which is a very powerful process used in the preparation of nanocomposite coatings, is described in detail. The basic principles of the formation of the flexible hard coatings are also described in detail. It is shown that the key parameters which determine the formation of these coatings are the energy $E_p = E_{ca} + E_{bi}$ delivered to the growing coating by condensing atoms (E_{ca}) and bombarding ions (E_{bi}) (the non-equilibrium heating), the substrate heating controlled by the substrate temperature T_s (the equilibrium heating) and the melting temperature T_m of the coating material. The flexible hard coatings have a huge application potential. Four examples of flexible coatings are given: flexible protective coatings, flexible functional coatings, flexible over-layer preventing cracking of brittle coating and flexible multilayer coating. Also, the principle of low-temperature sputtering of flexible nanocomposite coatings is described in detail. Finally, trends for future development of these nanocomposite coatings with unique properties are given.

Keywords: hard nanocomposite coatings; microstructure, macrostress; mechanical properties; energy; flexibility; resistance to cracking; magnetron sputtering

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0 引言

硬质纳米复合涂层是新一代涂层的代表^[1-44],典型的代表如二元nc-TiN/a-Si₃N₄硬质复合涂层,其优点主要在于提升涂层的硬度,使涂层获得尽可能高的硬度。镀膜领域通常将硬度 $H > 40$ GPa的纳米复合涂层称为超硬纳米复合涂层。目前主要有两大类二元纳米复合涂层能够提升硬度,硬质相/硬质相纳米复合涂层和硬质相/软质相纳米复合涂层^[10, 41, 42]。需要强调的是两类涂层体系都能够提升涂层硬度,而第二类硬质相/软质相纳米复合涂层还具有其它优异的物理性能和功能特性。

还需要强调的是纳米复合涂层在高于1 000 ℃的条件下还具有优异的热稳定性和抗氧化性能。对最近研发出的两种涂层的研究结果表明,具有高含量(原子数分数)Si(>20%)的nc-TiN/a-Si₃N₄非晶纳米涂层以及由共价键组成的Si-B-C-N涂层,分别在~1 500 ℃和~1 700 ℃的条件下表现出较好的热稳定性和抗氧化性^[34]。另外还需要注意到硬度的提升并不是评价硬质纳米复合涂层的唯一指标。对于许多应用场合,提高涂层的韧性比追求超高(比如 $H > 40$ GPa)硬度更重要。因此,目前柔性涂层的研究主要关注如何能同时提高涂层的硬度、韧性以及弯曲抗开裂性能^[41, 44-52]。这种涂层具有广泛的应用前景,可以将功能涂层制备在不同的柔性基底上,如聚合物箔片、薄片玻璃以及纺织品上,并在柔性电子器件、平板显示以及微型机电装置(MEMS)等领域获得应用。

文中主要阐述柔性纳米复合涂层的研究进展,介绍一类新型的抗开裂柔性硬质涂层,该涂层是采用反应磁控溅射方法制备的,并探讨①涂层微观结构与其力学性能(硬度 H 、等效弹性模量 E^* 、弹性恢复系数 W_e 、宏观应力 σ 以及薄膜生长吸收的能量 E_p)之间的关系;②柔性硬质纳米复合薄膜的生长条件;③脆性涂层裂纹扩展的抑制原理;④4种典型的柔性硬质涂层;⑤低温磁控溅射制备柔性涂层的原理。这里实际的弹性模量 $E^* = E / (1 - \nu^2)$, E 为试验得到的弹性模量, ν 为泊松比。文章最后概述了纳米复合涂层的发展趋势。

1 磁控溅射制备纳米复合涂层

磁控溅射是制备纳米复合涂层的有效方法^[53-80]。目前,磁控溅射技术已经被良好的掌握,直流(DC)和射频(RF)以及直流脉冲和交流脉冲等形式

的磁控溅射都能够被用于制备纳米复合涂层,此处提到的交流脉冲主要为负的半个正弦波。直流磁控溅射通常用来制备金属基或导电涂层,射频及脉冲磁控溅射适用于制备绝缘涂层。涂层溅射过程中的气氛条件可以是纯氩气或氩气和反应气体的混合气体。第一种情况下涂层主要由溅射靶材上的元素组成,当气体为氩气和反应气体的混合气时,该过程被称为反应磁控溅射。

反应磁控溅射的重要性在于其生成的涂层中不仅包含溅射靶材中的元素,还含有反应气体中的元素,利用这种方式能够制备氮化涂层、氧化涂层、碳化涂层、硼化涂层、含氯涂层以及它们的复合涂层。然而反应磁控溅射具有两个缺点,一是具有滞后效应(Hysteresis),二是会在靶材的表面出现打弧现象。这两个缺点会导致靶中毒,因而需要减小其影响以获得缺陷较少的涂层。滞后效应可以通过增大反应气体的抽速 S_{RG} 来改善,使其超过设备泵系统的某一临界抽速^[55]。打弧现象上由于溅射制备绝缘涂层时,绝缘材料不易被刻蚀的区域容易产生电荷聚集,进而发生打弧。通常有两种方式来避免打弧现象发生:①利用磁场控制使靶材均匀刻蚀(目前仍未能很好掌握);②释放绝缘层上不易被刻蚀区域的积累电荷^[56, 80]。当采用脉冲磁控溅射时,若脉冲结束时靶材上为正电压,则能够有效避免打弧现象发生。当双靶脉冲磁控溅射设备在双极模式下溅射时,能够有效避免打弧^[63, 77, 80]。图1所示为双靶磁控溅射的原理图,磁控阴极的电压周期性的由负变为正,当

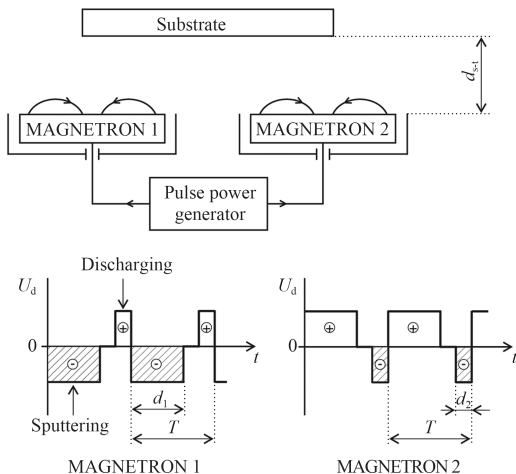
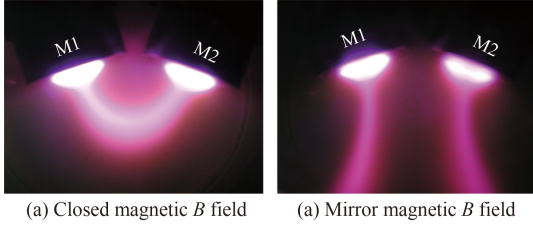


图1 对称双极直流脉冲双靶磁控溅射示意图^[80]

Fig. 1 Schematic diagram of symmetric bi-polar dc pulsed dual magnetron sputtering^[80]

阴极电压 U_d 为负时,靶材材料被溅射出来。反之,阴极电压 U_d 为正时,由于电子的轰击,可中和聚集在靶材绝缘层上的电荷。如图2所示,磁控溅射靶材上的溅射分布取决于磁场方向^[81]。因此在双靶磁控溅射设备中放置样品时应考虑这一现象。



Conditions: repetition frequency of pulses $f_i=100$ kHz, discharge current $I_d=0.5$ A and nitrogen pressure $p_{N_2}=0.5$ Pa

图2 双靶磁控溅射在双极模式下的电离照片^[82]

Fig. 2 Photos of the discharge of the dual magnetron operated in a bipolar mode^[82]

涂层生长过程中所吸收的能量对其宏观、微观结构、元素和相结构以及物理性能都有影响^[83-88]。其主要包括①基底加热吸收的热能 E_{sh} , ②轰击转化的动能 E_p , 包括轰击离子的能量 E_{bi} 和快速中性粒子轰击的能量 E_{fn} , ③形成化合物过程中吸收的热能 E_{ch} , ④靶材释放的热能 E_{mt} , ⑤吸收等离子体产生的辐射 E_{rad} 。涂层在生长过程中吸收的总能量可以用式(1)^[88]来表示:

$$E_T = E_{sh}(T_s, t_d) + E_p(U_s, i_s, a_D, p_T, t_d) + E_{ch}(t_d, T_a) + E_{mt}(W_d, t_d, d_{s-t}) + E_{rad}(t_d) \quad (1)$$

式中 t_d 为涂层的制备时间, T_a 为退火温度, $p_T = p_{Ar} + p_{RG}$ 为溅射混合气体的总气压, p_{Ar} 和 p_{RG} 分别为氩气和反应气体的分压。 $W_d = (U_d I_d)/S$ 为磁控溅射靶材的功率密度, U_d 和 I_d 分别为磁控溅射的电压和电流, S 为靶材的总面积, d_{s-t} 为基底到靶材的距离。溅射粒子传递的动能 E_p 由两项组成:

$$E_p = E_{bi} + E_{fn} \quad (2)$$

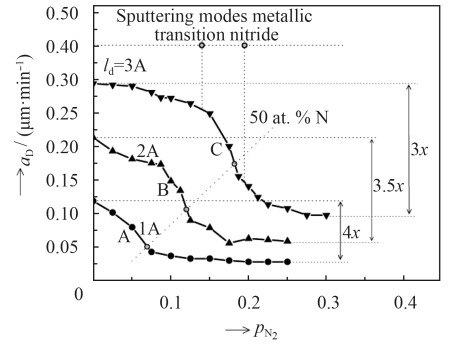
为简化粒子碰撞过程, 假定全部粒子都被离子化, 则 $E_{fn}=0$, 吸收的碰撞能量由式(3)^[84-88]表示:

$$E_p [Jcm^{-3}] = E_{bi} = E_i(v_i/v_{ca}) = e(U_s - U_p)i_s/a_D \approx (U_s i_s)/a_D \quad (3)$$

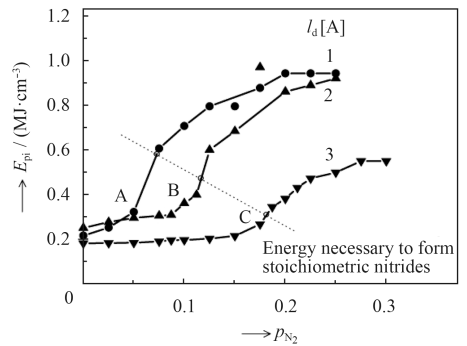
式中 E_i 为单个离子的能量, v_i 和 v_{ca} 分别代表离子流和原子流, e 代表电子, U_s 为基底偏压, U_p 为等离子体电势, i_s 为电流密度, a_D 为涂层的沉积率。尽管式(3)是简化过的, 但其依然非常有用,

因为其包含了测量值 U_s , i_s 和 a_D , 这使得其不仅可以用来计算轰击离子的能量, 还能够用来确定获得一定轰击能量时所需要的达到的等离子体密度。除此之外, 该方程还明确的建立了沉积速率与轰击能量之间的关系, 在反应磁控溅射过程中, 该关系可以用来解释当电离电流 I_d 不变的条件下, 沉积率 a_D 会随反应气体气压的升高而降低。如图3所示, 等化学计量数和过化学计量数的氮化涂层 $Ti(Fe)N_{x \geq 1}$ 在制备过程中所吸收等能量要高于低化学计量数的涂层 $Ti(Fe)N_{x < 1}$, $x = N/(Ti+Fe)$ 。需要注意的是轰击能量对涂层的微观结构和宏观应力有重要影响, 其关系将在第3部分详细讨论。

轰击能量 E_{bi} 主要受3个参数影响: 基底变压 U_s , 电流密度 i_s 和涂层的沉积速率 a_D 。基底偏压应当为负值, 且绝对值小于50 V以避免涂层制备过



(a) Deposition rate, a_D



(b) Energy, E_{bi}

Conditions: the films were sputtered using a DC magnetron equipped with a TiFe (90/10 at%) alloy target of 100 mm in diameter at (1) $I_d=1$ A, $i_s=0.5$ mA/cm², (2) $I_d=2$ A, $i_s=1$ mA/cm², (3) $I_d=3$ A, $i_s=1$ mA/cm², $U_s=100$ V, $T_s=300$ °C, $d_{s-t}=60$ mm and $p_T = p_{Ar} + p_{N_2} = 0.5$ Pa

图3 $Ti(Fe)N_x$ 薄膜的沉积率 a_D 和薄膜生长通过轰击离子传递的能量 E_{bi} 与氮气气压 p_{N_2} 之间的关系^[80]

Fig. 3 Deposition rate a_D of $Ti(Fe)N_x$ films and energy E_{bi} delivered to them during their growth by bombarding ions as a function of p_{N_2} ^[80]

程中缺陷的产生。基体的电流密度 i_s 通常应当大于 1 mA/cm^2 以确保涂层的生长过程。沉积率 a_D 的选择通常取决于制备哪种涂层,呈柱状晶生长的多孔涂层中通常为拉应力,致密缺陷少的涂层中通常为压应力,制备多孔涂层需要在低轰击能量条件下进行,相应的制备无缺陷的涂层需要在高轰击能量条件下生长,具体将在第3部分详细讨论。

然而在磁控溅射过程中获得高轰击能量 E_{bi} 并不容易。电流密度 i_s 和沉积速率 a_D 的大小与电源功率 P_d 以及基底和靶材间距 d_{s-t} 的大小关系密切。降低沉积速率 a_D 可以提升轰击能量 E_{bi} ,功率 P_d 不变的条件下,通过增大基底和靶材之间的间距能够降低沉积率,两者间有如下关系 $a_D \sim 1/(d_{s-t})^2$ 。然而当基底和靶材间距增大意味着样品被置于低电流密度区域,其结果反而是降低了轰击能量 E_{bi} 。因此,有必要提高溅射气体的离化率,可以通过采用单独的离子源来提高溅射气体的离化率。如图4所示,独立的离子源通常为热应激电子束、空心阴极放电或两者的复合。这些溅射系统能够有效

提升轰击能量 E_{bi} 来制备新型先进纳米复合涂层。近年来,高功率脉冲磁控溅射方法(HIPIMS)得到了快速发展^[89-102]。高功率脉冲磁控溅射过程中,作用在靶材上的功率密度($W_t=U_d I_d/S$)非常高,通常在约 100 W/cm^2 到几 kW/cm^2 之间不等,与此同时,其作用周期非常短($\tau/T \leq 0.1$),在脉冲作用过程中,其沉积率 a_D 和溅射原子的离化率(大于90%)都非常高。这意味着高功率脉冲磁控溅射能够替代阴极弧溅射过程,但不会产生宏观的大颗粒,这正是高功率脉冲磁控溅射的主要优势。然而,在一个脉冲过程中,过高的沉积率 a_D (几百纳米)会导致沉积过程中的轰击能量 E_{bi} 降低。目前,高功率脉冲磁控溅射过程中轰击能量 E_{bi} 对涂层性能的影响还未得到很好的理解,全世界许多的实验室中都在紧锣密鼓地开展相关的研究。低温条件($T_s \leq 100\text{ }^\circ\text{C}$)和低压条件($p \leq 0.1\text{ Pa}$)制备纳米复合涂层的磁控溅射方法还需要进一步研究^[74],许多的实例表明,只有研发新型的磁控溅射系统才能制备出具有特殊性能的新兴纳米复合涂层。

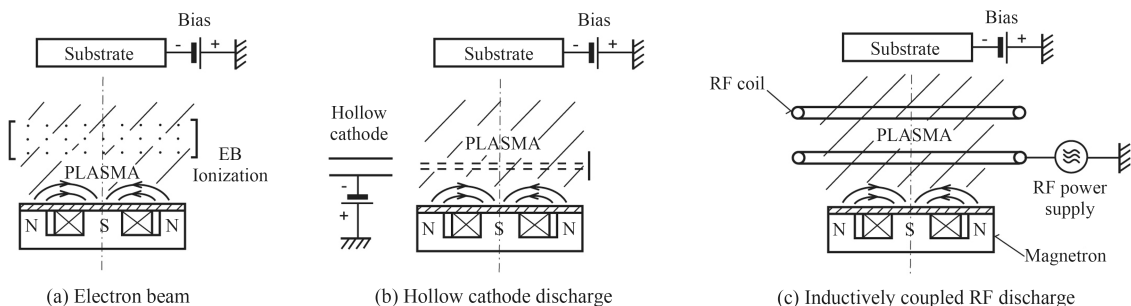


图4 带有溅射气体辅助离化装置的磁控溅射^[80]

Fig. 4 Magnetron with additional ionization of sputtering gas^[80]

2 柔性硬质纳米复合涂层及其表征

Hooke定律可以用来解释柔性硬质涂层的成形机理。 $\sigma=\varepsilon \cdot E$ 式中 σ 为应力(载荷), ε 为应变(变形), E 为杨氏模量。如果希望制备得到的涂层在高弹性形变 ε 条件下不失效,则需要相应的降低杨氏模量 E ,即需要研发在一定硬度条件下杨氏模量更低的材料,然而其并不容易实现。材料的力学性能可以由其应力应变曲线来表示,脆性材料、韧性材料和柔性材料的应力应变曲线是不同的,其示意图如图5所示。

超硬材料通常都是脆性的,几乎不发生塑性变形,非常小的应变($\varepsilon=\varepsilon_1$)条件下即发生失效。硬质的韧性材料可以同时产生弹性变形和塑性变

形。韧性越高的材料在高应变($\varepsilon_1 \ll \varepsilon \leq \varepsilon_{\max}$)条件下亦不易产生裂纹,能够在高应力 $\sigma_{\max}$ 条件下发生大应变 $\varepsilon_{\max}$ 的韧性材料,其硬度和强度也相应的更高。相反的,塑性材料的应力值 $\sigma < \sigma_{\max}$,应变值 $\varepsilon_{\sigma_{\max}} < \varepsilon < \varepsilon_3$,其强度较低,但具有较好的延展性。硬质韧性材料在曲线0 A之间不发生塑性变形,其弹性系数 W_e 为100%,其对应的硬质弹性涂层的硬度通常在 15 GPa 到 25 GPa 之间,足以满足大部分应用需求。高弹性涂层的主要优点在于其塑性变形小,能够提升其抗开裂性能,这正是柔性硬质韧性涂层受到广泛关注的原因。同时具备高硬度和韧性的柔性涂层代表了新一代先进硬质纳米复合涂层的发展方向。

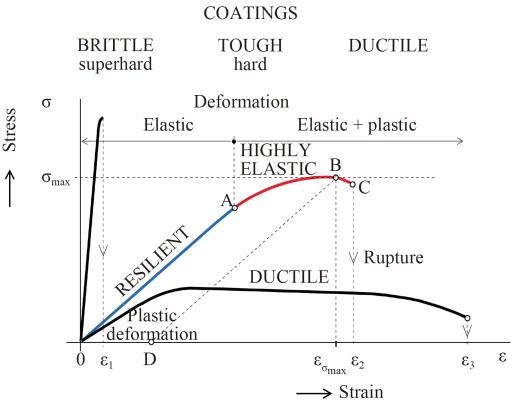


图5 超硬(脆性)、硬质(韧性)、硬质(弹性)以及柔性涂层的应力 σ -应变 ε 关系示意图(弹性涂层为不发生塑性变形的0A段)^[41]

Fig. 5 Schematic illustration of stress σ vs. strain ε curves of super-hard (brittle), hard (tough), hard (resilient) and ductile coatings. Resilient coatings exhibit no plastic deformation (line 0A)^[41]

上述分析为研制新型柔性硬质纳米复合涂层指明了方向，为提高涂层的韧性，需要降低涂层的等效弹性模量 E^* ，提高其弹性恢复系数 W_e 。具备上述性能的涂层已经可以通过磁控溅射方法来制备。与此同时，这些具有高韧性的硬质纳米复合涂层具有以下特性：①不易产生裂纹，② $H/E^* \geq 0.1$ ，③弹性恢复系数 $W_e \geq 60\%$ ，更多的细节可以参考相关文献^[41]。

3 柔性硬质纳米复合涂层的设计

通过研究涂层制备参数之间以及与涂层性能之间的关系，寻找用于制备抗裂纹硬质涂层的通用法则，研究结果表明涂层需要同时具备以下性能^[41, 44]：①较低的等效杨氏模量 E^* ，使得 $H/E^* \geq 0.1$ ，与此同时，弹性恢复系数 $W_e \geq 60\%$ 。②微观结构致密，缺陷少。③涂层整体呈压应力($\sigma < 0$)。

涂层硬度 H ，等效弹性模量 E^* ，弹性恢复系数 W_e ， H/E^* 比值，微观结构，宏观应力，元素及相组成都可通过以下因素来调控。①轰击能量 E_p 和基体温度 T_s ，其中轰击能量由沉积原子携带的能量 E_{ca} 和轰击离子携带的能量 E_{bi} 组成；②涂层材料的熔点温度 T_m ，其受涂层中元素掺杂含量的影响。图6和图7详细描绘了轰击离子的能量与涂层微观结构，宏观应力 σ 以及涂层熔点温度间的关系。

图6采用3D形式展示了涂层微观结构演化与 T_s/T_m 比(热平衡态)和氩气溅射气压 p_{Ar} 之间的关系，也就似与中性粒子对正在生长的涂层的轰击能量 E_p 之间的关系(非热平衡态)。图6所示的薄膜微观结构的演化被称为结构区域模型。1977年

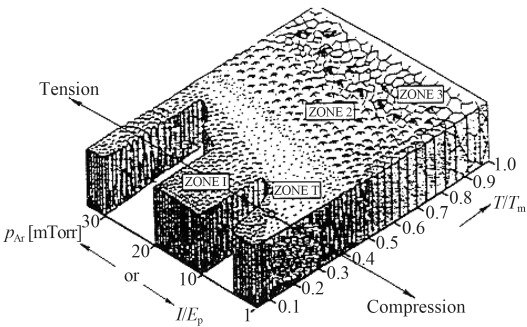
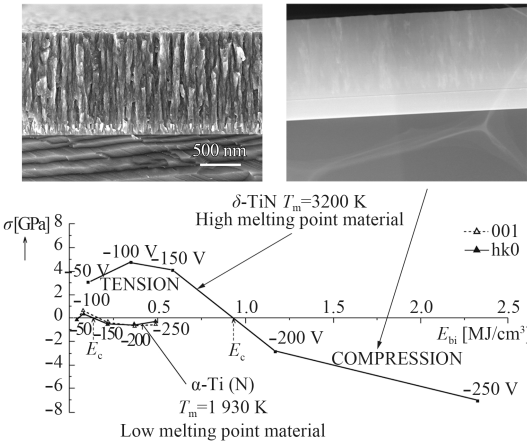


图6 J.A. Thornton提出的溅射制备金属薄膜的结构区域模型^[104]

Fig. 6 Structural zone model (SZM) of sputtered metallic films developed by J.A. Thornton^[104]

Thornton^[104]提出了溅射沉积金属薄膜的结构区域模型，该模型被划分为4个区域：区域1主要由许多锥形微小晶粒组成，晶粒间存在空隙；区域T主要为致密无缺陷的非晶结构，其中嵌有纤维状的晶粒；区域2主要由柱状晶组成，边界由致密的内结晶隔开^[105]；区域3主要由再结晶结构组成。区域1和区域T边界处的宏观应力 $\sigma=0$ ，该边界隔开了不致密的柱状晶区域和致密的非晶区域。区域1和区域T之间截然不同的微观结构使得生长在这两个区域的薄膜性能差异巨大，生长在区域T的薄膜通常会获得一些特殊性能。

图7所示为宏观应力 σ 与轰击离子能量 E_{bi} 之间的关系。薄膜材料的熔点温度对薄膜宏观应力和微观结构的影响也能够从图中看出来。薄膜的宏



Conditions: $p_1=p_{Ar}+p_{N_2}=5Pa$, $T_s=350\text{ }^\circ\text{C}$, $T_s/T_m=0.32$ and 0.19 for the $\alpha\text{-Ti(N)}$ film and the $\delta\text{-TiN}_{x=1}$ film

图7 溅射制备的 $\alpha\text{-Ti(N)}$ 与 $\delta\text{-TiN}_{x=1}$ 薄膜中的宏观应力 σ 与轰击离子传递的能量 $E_{bi}=U_s i_s/a_D$ 间的函数关系^[24, 106]

Fig. 7 Macrostress σ in sputtered $\alpha\text{-Ti(N)}$ and $\delta\text{-TiN}_{x=1}$ films as a function of energy $E_{bi}=U_s i_s/a_D$ delivered to them by bombarding ions^[24, 106]

观应力 σ 与其微观结构之间也有密切关系,从图7中可以总结出以下几个重要的结论:

(1) 随着轰击离子能力的升高,薄膜中的宏观应力由拉应力($\sigma>0$)变为压应力($\sigma<0$);

(2) 存在轰击离子能量的临界值 $E_{bi}=E_c$,此时薄膜的宏观应力为 $\sigma=0$;

(3) 宏观应力 σ 的大小以及临界离子轰击能量 E_c 的大小与薄膜材料的熔点温度 T_m 有关;

(4) 宏观应力 σ 和临界离子轰击能量 E_c 的大小随薄膜材料熔点温度 T_m 的升高而升高。

临界离子轰击能量 E_c 的大小与以下参数有关,①基底偏压 U_s 和作用在基底上的电流密度 i_s ;②薄膜的沉积速率 $a_D^{[107]}$;③溅射气体的气压 p ;④基底温度 T_s ;⑤薄膜中的掺杂元素及其含量, T_m ;⑥当薄膜沉积率较低时,反应腔体中残留的氧元素和氮元素。临界能量与上述参量的关系可以用函数 $E_c=f(E_{bi}, \text{元素组成}, T_m, p, p_0)$ 表示,其变化过程非常复杂,式中 p 为溅射气体的气压, p_0 为反应腔体中的背底气压。

目前许多的研究表明在区域T生长的薄膜其微观结构缺陷少,呈现微小的纤维状晶粒嵌在非晶基体中,其宏观应力为压应力($\sigma<0$), $H/E^*\geq 0.1$,弹性恢复系数 $W_e\geq 60\%$ 。这表明区域T中形成的薄膜是柔性的,并且当沉积过程中的轰击能量大于临界能量时($E>E_c$),能够有效提升抗裂纹性能。在文中4, 5, 6部分分别列举柔性薄膜的实例。

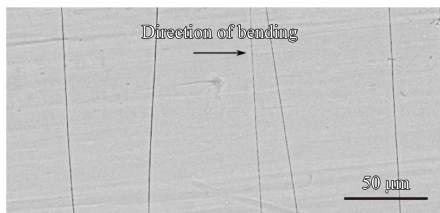
综上所述,为使薄膜在Thornton结构区域模型的区域T中成形,需要在薄膜生长过程中提供足够的轰击能量 E ,使其超过临界能量 E_c 。

4 柔性保护涂层

许多场合下,材料表面容易受到划伤、氧化、腐蚀及冲蚀等损伤,因此有必要制备相应的保护涂层。柔性硬质的涂层在制备过程中需要具有抗开裂性能,以确保柔性的基底在弯曲时涂层不开裂,这即是柔性硬质薄膜所需要具有的性能。

此部分以Zr-Al-O体系为例来探讨柔性涂层的抗开裂性能,该体系中涂层的抗开裂性能由Zr/Al的比值决定,可通过控制涂层的元素成分调整。Zr/Al的比值对Zr-Al-O体系的力学性能具有重要影响,当Zr/Al<1时,涂层体系的 $H/E^*<0.1$,弹性恢复系数,表现出脆性,弯曲过程中易开裂。相反的,当Zr-Al-O涂层体系中Zr/Al>1时,

$H/E^*\geq 0.1$, $W_e>60\%$,表现出较好的抗开裂性能,其结果如图8所示,更多的细节可参考对应的文献^[46, 48]。



$H/E^*=0.06$, $W_e=44\%$, cracks

(a) Brittle



$H/E^*=0.118$, $W_e=75\%$, no cracks

(b) Flexible

Conditions: 3000 nm thick Zr-Al-O coating reactively sputtered at $U_s=U_b$, $T_s=500^\circ\text{C}$, $p_T=1\text{ Pa}$ on Mo strip after bending around steel cylinder of radius $r=12.5\text{ mm}$

图8 脆性和柔性的表面形貌对比^[44, 48]

Fig. 8 Comparison of surface morphology of brittle and flexible^[44, 48]

近期的研究表明,以下的涂层体系也具有较好的抗开裂性能:①Al-Cu-O氧化物/氧化物纳米复合涂层^[45];②Zr-Al-O氧化物/氧化物纳米复合涂层^[46, 48];③Al-O-N纳米复合涂层^[47];④Si-Zr-O氧化物/氧化物纳米复合涂层^[49];⑤Ti-Ni-N氮化物/氮化物纳米复合涂层^[50];⑥Al-Cu-N氮化物/氮化物纳米复合涂层^[51];⑦(Ti,Al,V) N_x 氮化物/氮化物纳米复合涂层^[52]。所有的这些涂层体系都具有高 $H/E^*\geq 0.1$ 和高弹性恢复系数 $W_e\geq 60\%$ 。这表明 $H/E^*\geq 0.1$ 和 $W_e\geq 60\%$ 是评价柔性硬质薄膜的重要指标,细节可参考相关文献^[45-52]。

5 柔性功能涂层

许多功能涂层都是脆性的,在使用过程中容易发生开裂进而失效。因此,非常有必要研究具有抗开裂性能的柔性功能涂层。目前的抗菌涂层中Cr-Cu-O^[103]和Al-Cu-N^[51]涂层体系表现出较好的抗开裂性能,可通过控制元素的成分进行调控。涂层中Cu元素起到杀死细菌的作用,其含量决定涂层抗菌性能。如图9所示,涂层的抗菌效率随Cu含量的增大而提升。

从图9中可以看出，当Cr-Cu-O涂层中Cu的含量(原子数分数)大于20%时，涂层能够起到抗菌作用。然而过高的Cu含量会降低涂层的硬度 H 、等效弹性模量 E^* 、弹性恢复系数 W_e 以及 H/E^* 值，如表1所示。这意味着Cr-Cu-O涂层的抗磨损性能和抗开裂性能都会被降低，特别是当涂层体系被沉

积在柔性基底上时，如图9所示，涂层能够100%的清除E.coli细菌，但从图10和表1中的结果可以看出涂层容易开裂。因此非常有必要研制即具有抗菌性能又能够抗磨损和开裂的涂层。研究表明Cr-Cu-N能够很好的满足上述要求。利用N替换O一方面可以使得10%的Cu就能够100%的杀灭

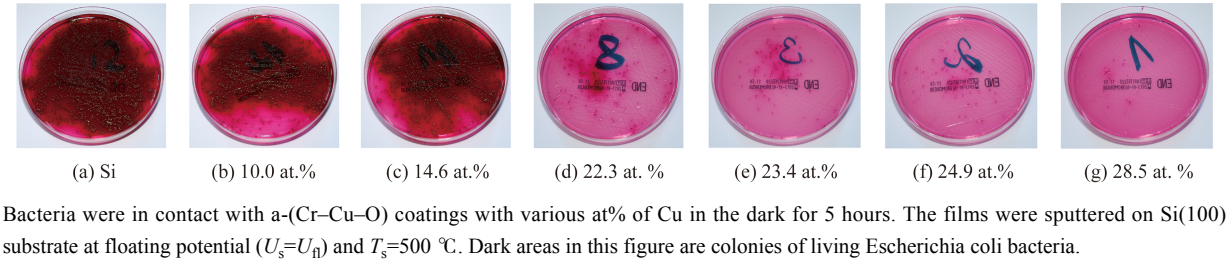


图9 有盖培养皿中利用Endo琼脂培养的大肠杆菌^[103]

Fig. 9 Photos of Petri dishes with Endo agar and colonies of Escherichia coli bacteria cultivated from bacterial suspensions^[103]

表1 溅射制备的Cr-Cu-O和Al-Cu-N涂层的厚度 h ，沉积率 a_D ，制备参数以及物理和力学性能以及其抗弯曲性能评价
Table 1 Thickness h , deposition rate a_D , deposition parameters, physical and mechanical properties of sputtered Cr-Cu-O and Al-Cu-N coatings and the assessment of their resistance to cracking by bending illustrated

Coating	h / nm	$a_D / (\text{nm min}^{-1})$	$T_s / ^\circ\text{C}$	U_{sp} / V	$i_{sp} / (\text{mA cm}^{-2})$	σ / GPa	$n_{Cu} / \text{at}\%$	H / GPa	E^* / GPa	$W_e / \%$	H / E^*	Cracks bending
Cr-Cu-O	2 190	18.3	500	U_{fl}		0.1	19.5	3.2	70	36	0.046	Yes
Al-Cu-N	2 730	63.5	400	-100	1.38	-1.7	9.6	21.9	180	74	0.122	No

Note: i_{sp} is the averaged substrate ion current density over negative pulse of substrate bias U_{sp} ^[44, 51, 103]

E.coli细菌，另一方面可以使涂层的硬度 H 由~3 GPa增至~20 GPa，弹性恢复系数 W_e 由36%增大至74%， H/E^* 由0.046增大至0.122，其宏观应力也由拉伸应力转变为压应力。Cr-Cu-N涂层被制备在55 mm×9 mm×0.15 mm的Mo带上用以测试其抗开裂性能，如图10所示，Mo带绕直径为10 mm的圆柱弯曲，这表明Cr-Cu-O涂层只具有抗菌性能，而Al-Cu-N涂层不仅具有抗菌性能，还能用作柔性涂层。目前最受关注的研究方向是制备具有3种功

能的涂层，使其能够同时具有柔性、透明和导电的功能。

综上所述，虽然开发两种功能或多功能的涂层会有很多的困难，但其依然是可行的，可以通过控制涂层的成分以及涂层制备过程中所吸收的能量来控制其性能^[41, 44]。

6 防脆性涂层开裂的柔性保护涂层

通常情况下，由于功能涂层大多是脆性的，因而很难制备柔性功能涂层。因此有必要研究防止脆性涂层开裂的方法。通常可以通过在脆性涂层表面附着一层弹性涂层，该弹性涂层的 $H/E^* \geq 0.1$ ，弹性恢复系数 $W_e \geq 60\%$ ，且宏观应力为压应力 $\sigma < 0$ ^[49]。

图11所示利用柔性涂层来保护脆性涂层的作用机理，图11(a)所示为脆性的单层Zr-Si-O涂层，其 $H/E^* = 0.08$ ，弹性恢复系数 $W_e = 50\%$ ，宏观应力为拉应力 $\sigma = 0.25 \text{ GPa}$ 。图11(b)所示有两层的涂层结构，其中底层涂层与上述涂层相同，表层为Zr-Si-O涂层具有如下性能， $H/E^* = 0.1$ ，弹性恢复

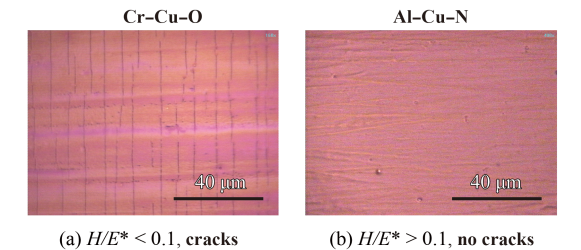


图10 沉积在Mo带上的Cr-Cu-O和Al-Cu-N涂层经过弯曲试验($r=10\text{mm}$)后的表面形貌^[44, 51]

Fig. 10 Surface morphology of Cr-Cu-O and Al-Cu-N coatings deposited on Mo strip after bending around cylinder of radius $r=10 \text{ mm}$ ^[44, 51]

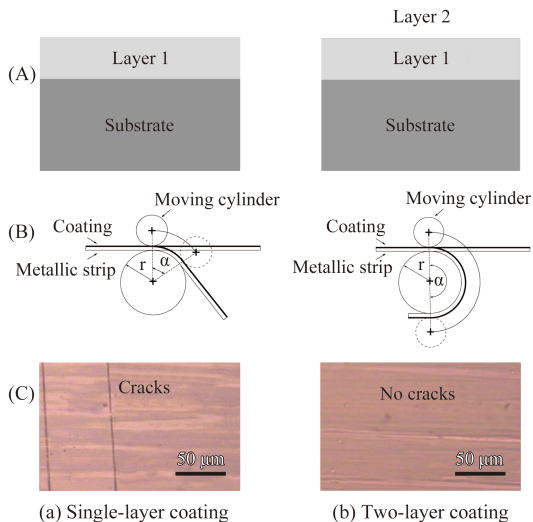


图 11 (A)和(B)分别为涂层/基底的几何结构与Mo带弯曲试验($r=12.5$ mm)的示意图, (C)中(a)和(b)分别为单层和两层Zr-Si-O涂层在弯曲试验后的表面形貌^[49]

Fig. 11 Schematic illustration of (A) coating/substrate geometry, (B) method of bending of the coated Mo strip and (C) photos of surface morphology of single-layer and two-layer Zr-Si-O coating after bending around the cylinder of radius $r=12.5$ mm^[49]

系数 $W_e=68\%$, 宏观应力为拉应力 $\sigma=-1.5$ GPa。两组涂层都是利用溅射镀到钼带($60\text{ mm}\times 10\text{ mm}\times 0.1\text{ mm}$)上, 然后进行弯曲试验, 所用圆柱的直径 $r=12.5$ mm。如图11所示, 和预期的一样, 单层涂层在 $H/E^*<0.1$, $W_e<60\%$ 且宏观正应力 $\sigma>0$, 圆柱的直径 $r=12.5$ mm, 弯曲角度在 30° 左右时, 容易发生开裂, 相反的, 双层结构膜由于其力学性能好, 在 $H/E^*\approx 0.1$, $W_e>60\%$, 宏观压应力 $\sigma<0$, 即使弯曲角度达到 180° 时, 也没有发生开裂现象。

上述结果表明, 通过在脆性涂层表面附着一层弹性涂层, 使其力学性能满足下列要求:

$H/E^*\geq 0.1$, $W_e\geq 60\%$, 宏观应力为压应力($\sigma<0$), 则能够有效的保护涂层不开裂。其中弹性保护层呈压应力状态, 对防止脆性涂层开裂具有重要意义。但还需要开展更多的试验以确定防止脆性涂层开裂的最好方式。

7 柔性多层抗开裂涂层

近期的研究结果表明, 利用多层膜结构控制涂层的宏观应力, 能够有效的抑制厚膜(大于 $10\text{ }\mu\text{m}$)开裂。文中通过研究在钼带上涂有三层和四层的Zr-Si-O涂层在拉伸应力和压应力状态下的抗开裂性能, 探讨该假设的可行性。图12所示为上述涂层在弯曲试验后的表面形貌, 还包括单层和两层的结果。其中拉应力层用L1表示, 压应力层用L2表示, 第一层都为拉应力层L1。每一层的层厚 h_n 及其力学性能如表2所示, n 代表相应的层数。

从图12中可以看出, 涂层的抗开裂性能与涂层中的应力状态密切相关, 当表层涂层中的应力为拉应力时, 涂层发生开裂。相反的, 当表层涂层中为压应力时, 涂层表现出较好的抗开裂性能。此现象对于制备10到 $100\text{ }\mu\text{m}$ 的新型超厚膜具有非常重要的指导意义。还需要注意的是涂层的第一层为非晶结构(利用X射线衍射测得), 而第二层为晶态结构^[44, 49]。基于上述结果, 能够继续开发出许多晶态/非晶双层结构的多层涂层体系, 如图13所示。目前作者的实验室正在开展相关的研究, 可以估计到这种涂层会具有许多优异的性能。

然而此项研究还有许多问题没有答案, 例如压应力涂层最小厚度为多少时, 才能够抑制多层膜的开裂? 经过应力 σ 调控的多层膜其物理性能如

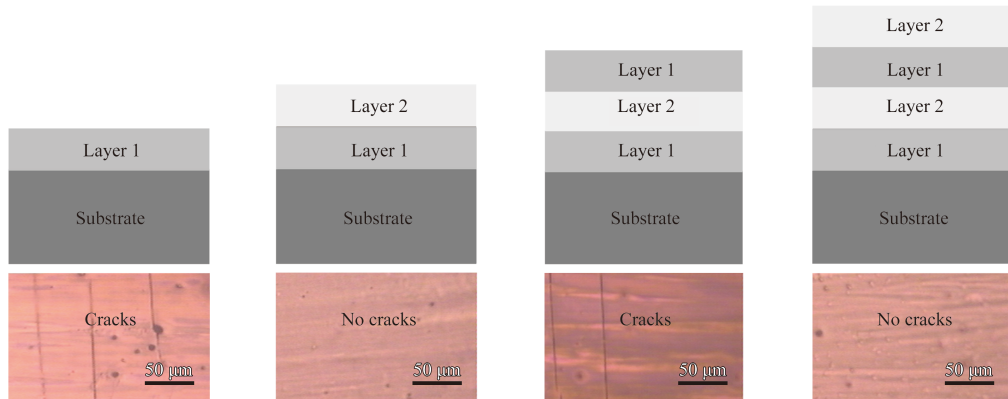


图 12 沉积在Mo带上的(a)单层、(b)双层、(c)三层、(d)四层Zr-Si-O涂层在弯曲试验($r=12.5$ mm)后的表面形貌^[49]

Fig. 12 Surface morphology of (a) one-layer, (b) two-layer, (c) three-layer and (d) four-layer Zr-Si-O coating deposited on Mo strip after bending around fixed cylinder of radius $r=12.5$ mm^[49]

表 2 多层Zr-Si-O涂层的表层力学性能、宏观应力以及弯曲开裂情况。其对应的单层厚度为 h_n ，弯曲试验的基底为Mo带，所用的固定圆柱半径 $r=12.5\text{ mm}^{[49]}$

Table 2 Thickness h_n of individual layers in the multilayer Zr-Si-O coatings, their mechanical properties, macrostress σ in the top layer, and cracks created in multilayer coating during bending of coated Mo strip around fixed cylinder of radius $r=12.5\text{ mm}^{[49]}$

Coating	Content of layers	h_1/nm	h_2/nm	h_3/nm	h_4/nm	h_T/nm	H/GPa	E^*/GPa	$W_e/\%$	H/E^*	Macrostress in top layer	Cracks in bending
Coating A	L1	3 000				3 000	12.6	161	50	0.078	Tension	Yes
Coating B	L1+L2	3 000	3 000			6 000	17.6	165	70	0.107	Compression	No
Coating C	L1+L2+L3	2 500	2 500	2 500		7 500	12.2	149	56	0.082	Tension	Yes
Coating D	L1+L2+L3+L4	2 400	2 400	2 400	2 400	9 600	16.6	157	70	0.106	Compression	No

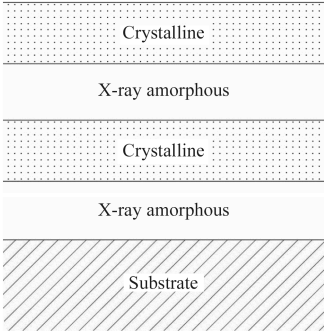


图 13 非晶层和晶体层交替的多层膜

Fig. 13 Multilayer coating composed of alternating X-ray amorphous and crystalline layers

何？宏观在正应力($\sigma>0$)和压应力($\sigma<0$)之间的调控对于多层膜的热稳定性以及热导率会有怎样的影响？涂层/基底间应以怎样的形式结合，以使得涂层的结合力最大？许多问题还有待进一步研究。

8 低温磁控溅射制备柔性纳米复合涂层

如第3部分所讨论的，在结构区域模型中的区

域T中生成的膜具有较好柔性。然而要在区域T中生长涂层，则需要穿过区域1和区域T的边界。如图14所示的二位结构区域相图中，这个边界是 T_s/T_m 以及溅射气压 p 的函数。因此很有必要研究区域1和区域T边界线的控制。实现低温磁控溅射制备在区域T中的薄膜，其关键在于利用非平衡的原子尺度加热(ASH)替代平衡态的基底加热过程(T_s)^[41, 44, 74]。

区域1和区域T的边界位置受到以下因素的影响：①当基体处于负偏压条件时($U_s<0$)^[108-109]的离子轰击能量 E_{bi} ，②快速中性粒子的轰击能量 E_{fn} ，其受溅射气压的影响，随溅射气压 p 的减小而增大。如图14所示，当基底的负偏压 U_s 增大，溅射气体气压 p 降低时，区域1和区域T之间的边界向 T_s/T_m 较低的方向移动，此时基底温度 T_s 较低，甚至可以处于未加热条件(室温 $T_s=RT$)就可以得到区域T的微观机构。需要强调的是，即便在不加负偏压条件下，在较低 T_s/T_m 比值时，也能够使制备的

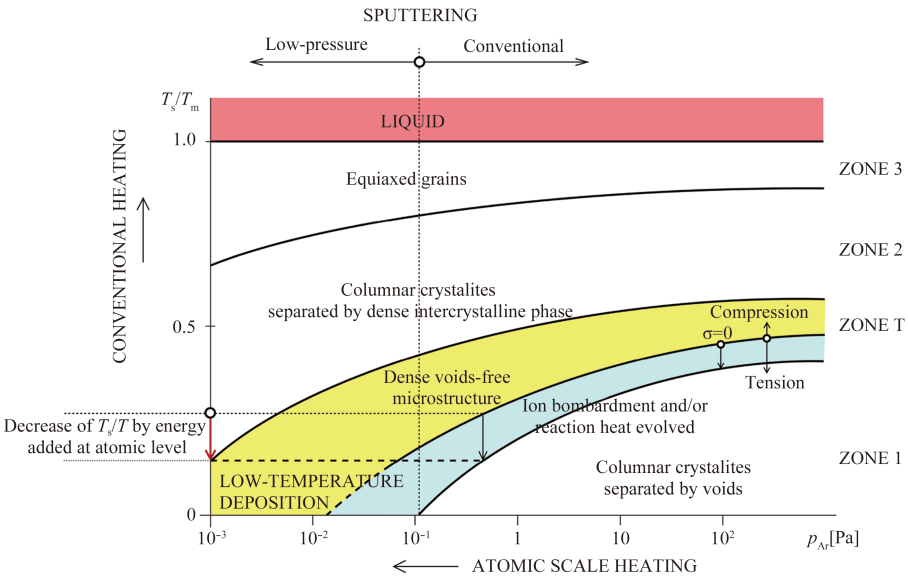


图 14 拓展到低溅射气压区域的Thornton结构区域相图^[74]

Fig. 14 Thornton's structural zone model (SZM) of sputtered films extended to the region of low sputtering gas pressures^[74]

薄膜的微观结构处于结构区域模型的区域T内。如当基底处于浮动电势条件时 $U_s=U_n$,且在较低气压进行薄膜的溅射,如图14所示。然而这需要研制新型的可在低气压下工作的磁控溅射设备,来实现薄膜。更多内容可参考相关文献^[42, 61, 74, 80]。

在 $T_s \leq 100$ °C条件下实现制备处于结构区域相图中区域T的薄膜,对于许多先进的应用领域具有重要意义。特别是对于柔性电子器件,平板显示,微电子机械系统(MEMS),聚合物薄膜以及各种纤维等。可以通过向涂层中选择性的掺杂元素,以使得在低温条件下($T_s \leq 100$ °C),制备得到有纳米晶或非晶态结构、处于区域T的涂层,这是因为元素掺杂能够降低涂层材料的熔点温度,从而升高 T_s/T_m 的大小。

综上所述,在 T_s/T_m 值较小时,当轰击离子的能量 E_{bi} 足够高,或溅射气体气压 p 较低时,是可以在 $T_s \leq 100$ °C条件下制备出处于结构区域相图中区域T中的涂层,使其具有致密,空隙缺陷少,宏观应力为压应力($\sigma > 0$),抗开裂等性能。涂层材料的熔点温度 T_m 对于低温磁控溅射制备柔性涂层过程具有重要作用,其可以决定 T_s/T_m 的大小,并可以通过选择性掺杂来控制其大小。

9 结 论

到目前为止,硬质纳米复合涂层的发展已经有4个重要的里程碑,分别是:①硬质/硬质两相纳米复合涂层,能够有效提升复合体系的硬度;②硬质/软质两相纳米复合涂层,有效提升复合体系的硬度;③在1 500 °C左右时具有高温稳定性和抗氧化性的硬质纳米复合涂层;④具有高韧性的柔性硬质纳米复合涂层,具有良好的抗开裂性能。文中综述了制备柔性纳米复合涂层的准则及其相关应用,然而还有许多的工作有待开展,进一步研制新型的硬质纳米复合涂层,文中将其主要方向总结如下:

(1) 低温磁控溅射制备柔性硬质纳米涂层,使其具有两种或多种功能;

(2) 制备从室温到接近材料熔点温度的大尺度范围内具有热稳定性的单相晶态涂层;

(3) 深入研究涂层性能与薄膜制备过程中吸收的能量或其后续热处理过程的影响;

(4) 研制能在不同实际工况下制备涂层的新型沉积设备。

毋庸置疑,以上内容对于开拓队先进纳米复合涂层制备过程的认知具有重要意义,并能够帮助应用于各种领域的新型涂层体系。

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