

金属基固体自润滑复合涂层及其制备技术研究进展

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摘 要: 金属基固体自润滑复合涂层具有强度高、耐高温、耐磨损以及易加工等特性, 成为近来研究热点。首先综述了国内外金属基固体自润滑复合涂层的材料体系 (即难熔金属基自润滑复合涂层、软金属基自润滑复合涂层、低温金属基自润滑复合涂层以及高温金属基自润滑复合涂层), 随后分析了金属基固体自润滑复合涂层的润滑机理, 指出润滑膜的低剪切特性是实现减磨润滑的关键。接着介绍了金属基固体自润滑复合涂层的制备技术, 比较分析了烧结、电镀、化学镀、热喷涂、物理气相沉积 (PVD)、化学气相沉积 (CVD)、激光熔覆等技术, 在制备金属基自润滑复合涂层方面的优点和不足。最后总结了目前在关于金属基固体自润滑复合涂层研究中存在的问题, 进而探讨了相应的解决方案, 提出应深入研究金属基体、固体润滑剂与环境三者之间的相互作用机理, 并进一步指出研发新型固体润滑剂、改进现有制备技术、开发新工艺是未来重点发展的方向。

关键词: 固体自润滑复合涂层; 金属基; 材料体系; 润滑机理; 制备技术; 摩擦

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Metal-based Solid Self-lubricating Composite Coating and Its Preparation Technology

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ABSTRACT: Metal-based solid self-lubrication composite coating has recently become a research focus due to its high strength, high temperature resistance, abrasion resistant and easy processing. Material systems of metal-based solid self-lubricating composite coatings were reviewed firstly (i.e., refractory metal-based solid self-lubricating composite coating, soft metal-based solid self-lubricating composite coating, low temperature metal-based solid self-lubricating composite coating, and high temperature metal-based solid self-lubricating composite coating). Lubrication mechanisms of metal-based solid self-lubrication composite coatings were then analyzed, it was indicated that low shear property was the key of antifriction and lubrication. Then preparation technologies of the coatings were introduced. Advantages and disadvantages of such technologies as sintering, electroplating, electroless plating, thermal spraying, physical vapor deposition (PVD), chemical vapor deposition and laser cladding were compared and analyzed. Finally, problems concerning study on metal-based solid self-lubrication composite coatings were summarized, corresponding solutions were discussed, and it was recommended to further study interaction mechanism among metallic substrate, solid lubricant and environment. It was pointed out that research and development of new solid lubricant, improving existing preparation technologies and developing new process were directions to be emphasized in the

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future.

KEY WORDS: solid self-lubricating composite coatings; metal-based; material system; lubrication mechanism; preparation technology; friction

摩擦会导致能量损耗、效率低、温度升高以及性能下降等一系列问题，磨损会造成零件表面形状和尺寸缓慢而连续损坏，使机器的工作性能与可靠性逐渐降低，甚至可能导致零件的突然破坏。有调研表明^[1-2]，2006 年我国因摩擦、磨损而导致的损失约高达 9500 亿元。润滑是降低该危害最为有效的措施^[3-4]，其中油脂润滑是最常见的传统润滑方法，可以降低摩擦，减小磨损。但是油脂润滑具有使用温度范围窄、易变质、不易储存等缺点，此外油脂润滑会污染环境，在要求清洁的环境中，如食品加工设备等，不宜采用油脂润滑。为了降低摩擦、减小磨损，有必要寻求其他的润滑方式。

固体自润滑复合材料具有较宽的使用温度范围，其化学性质稳定，能够在高真空和强辐射等特殊环境中发挥作用，能够实现永久润滑，使用方便且绿色，是解决上述问题最有效途径之一^[5-7]。固体自润滑复合材料有粉末、涂层以及块状三种形式，根据摩擦学观点^[8-9]，磨损发生在工件表面或近表面区域，因此在工件表层制备固体自润滑复合涂层是最经济、有效的方式。固体自润滑复合涂层按其基体类型分为 3 类：金属基固体自润滑复合涂层、无机非固体自润滑复合涂层以及聚合物基固体自润滑复合涂层。无机非固体自润滑复合涂层的强度高，但是不易制备，并且其后期加工的难度较大^[10-12]。聚合物基固体自润滑复合涂层的密度低和抗腐蚀能力强，但是强度较低，且在高温下易于失效^[13-14]。金属基固体自润滑复合涂层因具有优良的综合性能，成为近来研究的热点。

1 金属基固体自润滑复合涂层材料体系

金属基固体自润滑复合涂层是通过一定的工艺在基体表面制备的以金属为基体，加入固体润滑剂和附加组元，兼具基体金属性能以及自润滑性能的复合涂层。金属基固体自润滑复合涂层材料体系如表 1 所示。涂层根据金属基体的类型分为四类：以 W、Mo 为代表的难熔金属基自润滑复合涂层^[15-16]，以 Ag 为代表的软金属基自润滑复合涂层^[17-19]，以 Al、Cu 为代表的低温金属基自润滑复合涂层^[20-22]以及以 Ni、Co 为代表的高温金属基自润滑复合涂层^[23-24]。难熔金属基自润滑复合涂层广泛应用于高温和高速的场合，但由于其加工困难、价格高而逐渐被取代。Ag 基自润滑复合涂层具有良好的反射率、电导率、热导率以及延展性等特性，在电子探头和太阳能设备等方面具有独特的优势^[25-27]。低温金属基自润滑复合涂层在温度较低的场合下，具有优良的自润滑效果，当温度升高时，润滑效果降低，高温金属基自润滑复合涂层则与其相反^[28]。金属基固体自润滑复合涂层常用的固体润滑剂大致可分为三大类^[29-30]：1) 无机固体润滑剂，如 Ag、Pb 等软金属，MoS₂、WS₂ 和石墨等层状固体，CaF₂、BaF₂ 和 Al₂O₃ 等金属化合物，Ti₃SiC₂、SrSO₄ 等新型高温润滑剂^[31-33]；2) 有机固体润滑剂，如 PTFE、PE 等高聚物；3) 复合固体润滑剂，如 h-BN+MoS₂、WS₂+Ag+h-BN 以及 MoS₂+Ag 等。

表 1 金属基固体自润滑复合涂层材料体系
Tab.1 Material system of metal-based solid self-lubrication composite coatings

基体材料	固体润滑剂			附加组元
	无机固体润滑剂	有机固体润滑剂	复合固体润滑剂	
软金属：Ag、In、Au、Pb、Sn、Cr、Ni、Cu				
难熔金属基W、Mo，软金属基Ag，低温金属基Al、Cu，高温金属基Ni、Co	层状固体：MoS ₂ 、WS ₂ 、石墨、h-BN、GaS、GaSe 氟化物、硫化物：CaF ₂ 、BaF ₂ 、PbS、CaSO ₄ 、BSO ₄ 氮化物：TiN、CrN、ZrN、BN 碳化物：TiC、WC、CrC 氧化物：Al ₂ O ₃ 、Cr ₂ O ₃ 、TiO ₂ 新型高温润滑剂：Ti ₃ SiC ₂ 、SrSO ₄	Polytetrafluoroethylene(PTFE)、polyethylene(PE)、Polyimide(PI)	h-BN+MoS ₂ 、WS ₂ +Ag+h-BN、MoS ₂ +Ag、h-BN+Ag、石墨+MoS ₂ 、CaF ₂ /BaF ₂ +Ag	增强体如碳纤维、碳纳米管，稀土化合物La ₂ O ₃ ，合金元素Al、Cr

应该注意的是,固体润滑剂在一定范围内才能发挥作用,超出其使用范围会失效,不能起到润滑作用。例如,Slincy H E 等^[34-35]研究表明,MoS₂和石墨等层状固体润滑剂在高于 350 °C 的温度下会发生氧化而失去润滑作用,因此层状固体润滑剂制备的涂层只有在工作温度不高的环境中才能发挥作用。Chen J 等^[36]研究表明,CaF₂在温度大约 400 °C 时会发生韧脆转变,低于 400 °C 时会因变脆而失去润滑作用,因此 CaF₂ 适用于制备在高温环境下服役的涂层。软金属适用的温度范围较宽,但具有易塑性变形、易氧化等缺点^[37-38]。因此,应该根据具体应用选择不同的固体润滑剂。

高温金属基自润滑复合涂层的附加组元有如下几类:碳纤维、碳纳米管等提高涂层强度、硬度以及耐磨性的增强体^[39-40];使涂层具有高硬度、耐高温、耐腐蚀以及抗氧化等特性的元素,如 Al、Cr、S^[41-42]。

2 金属基固体自润滑复合涂层润滑机理

摩擦力是粘着效应和犁沟效应产生阻力的总和。两工件之间产生滑动摩擦一般有以下两种情况:第一种情况,如图 1a 所示,摩擦对偶在软质合金发生相对滑动时,会使软质合金表面产生严重的犁削和擦伤,摩擦力也随之升高,最终导致工件的磨损失效;第二种情况,如图 1b 所示,当摩擦对偶在硬质金属表面发生相对滑动时,根据 Bowden 和 Tabor 固体摩擦理论,可以忽略犁沟效应而只考虑粘着效应对摩擦力的影响。如图 1c 所示,当摩擦对偶与硬质金属之间有一层润滑膜时,Blan 和 Yust^[43]提出了用平均法计算两者之间摩擦力 F 的大小,如公式(1)所示:

$$F = \alpha_m F_m + \alpha_l F_l \quad (1)$$

式中: α_m 为摩擦对偶与硬质金属间的接触面积; α_l 为摩擦对偶与润滑膜的接触面积; F_l 和 F_m 分别为金属和润滑膜的抗剪强度。假设载荷在接触区域均匀分布,摩擦系数 μ 可表示为:

$$\mu = (1 - \chi_l) \mu_m + \mu_l \chi_l \quad (2)$$

式中: χ_l 为摩擦对偶与润滑膜之间的接触面积占

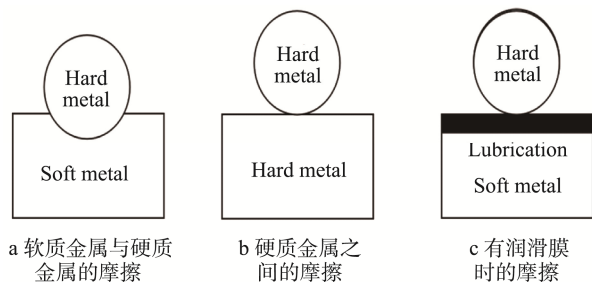


图 1 润滑膜作用原理^[43]

Fig.1 Mechanism of lubrication film^[43].

a) friction of soft and hard metal, b) friction of hard metal, c) friction under lubricated condition

总接触面积的百分比; μ_m 和 μ_l 分别为金属和润滑膜的摩擦系数。从式(1)和式(2)可以得知,在摩擦表面,润滑膜的面积越大、抗剪强度越小以及摩擦系数越低,则摩擦力越小,产生的润滑效果越好。

金属基固体自润滑复合涂层的自润滑原理如图 2 所示^[44]。当未发生摩擦时,如图 2a 所示,固体润滑剂分布在金属基体中,此时,涂层表面与涂层内部基本没有差别。当开始发生摩擦时,如图 2b 所示,摩擦副之间主要以对偶材料与金属基体的摩擦为主,此时摩擦力较大,涂层表面发生挤压变形,导致分布在金属基体中的固体润滑剂暴露在涂层表面,并且温度升高。最后,如图 2c 所示,在摩擦副之间形成一层具有低剪切特性的润滑膜,实现润滑减磨的作用。

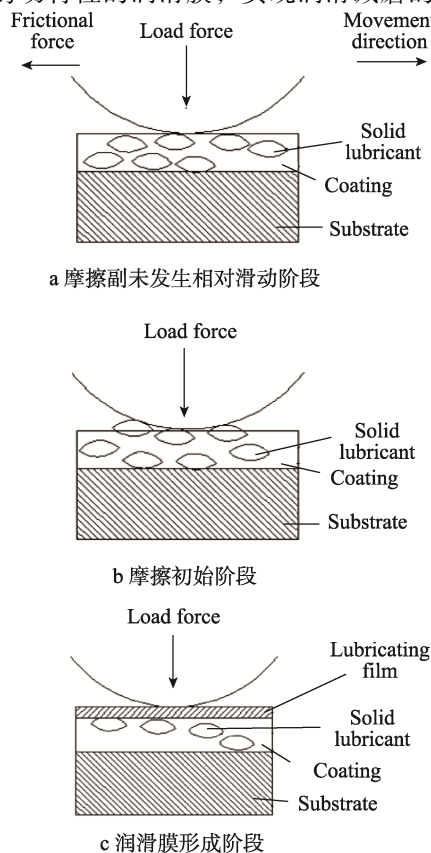


图 2 金属基固体自润滑复合涂层自润滑原理^[44]

Fig.2 Mechanism of metal-based solid self-lubrication composite coatings^[44]: a) stage of no sliding of friction pair, b) initial stage of friction, c) stage of formation of lubrication film

3 金属基固体自润滑复合涂层的制备技术

涂层的制备技术影响着涂层的组织结构,进而决定了涂层的性能。目前制备金属基固体自润滑复合涂层技术主要有^[45]:烧结、电镀、化学镀、热喷涂、物理气相沉积(PVD)、化学气相沉积(CVD)、激光熔覆,其中烧结技术、热喷涂技术、激光熔覆技术应用

最为广泛。

3.1 烧结技术制备金属基固体自润滑复合涂层

烧结技术是将均匀涂覆在基体表面的料浆经高温烧结形成表面涂层的工艺方法。用烧结技术制备金属基固体自润滑复合涂层具有固体润滑剂分布均匀、工艺简单、成本低以及应用广泛等优点,但是其制备的涂层与基体为机械结合,结合强度低,表面质量差,因此不适用于制备高压、重载以及腐蚀环境中的金属基固体自润滑复合涂层。段文博等^[46-47]采用感应烧结技术制备出润滑相细小且分布均匀的Ni基自润滑复合涂层,研究表明,涂层组织均匀、细小、致密,其孔隙率为5%左右。Shi等^[48]采用放电等离子体烧结技术制备了Ni₃Al基自润滑复合涂层,研究表明,涂层的摩擦学性能取决于h-BN润滑剂的含量,在从室温到800℃范围内,当h-BN的质量分数为15%且添加质量分数为5%的TiC时,涂层具有相对较低的摩擦系数以及磨损率。

3.2 热喷涂技术制备金属基自润滑复合涂层

热喷涂是利用火焰、等离子电弧等热源将喷涂材料加热至熔融或半熔融状态,使其沉积到经过预处理的基体表面,形成具有特定功能涂层的沉积技术,是制备金属基固体自润滑复合涂层的有效方式之一。目前主要应用的热喷涂技术有等离子喷涂和火焰喷涂。该技术制备的涂层中存在气孔、微裂纹以及夹渣等缺陷,可以采用火焰重熔、激光重熔和炉内重熔等后处理方式消除或部分消除缺陷。Zhang等^[49]用大气等离子喷涂技术制备了添加固体润滑剂Ag或Ag-Mo的Ni基高温固体自润滑复合涂层并研究了其润滑机理,研究表明,温度低于600℃时,Ag形成一层润滑薄膜,产生润滑作用;温度为600℃时,Ag、Mo与O₂发生反应,生成具有层状结构的Ag₂MoO₄薄膜,产生润滑作用;当温度在600℃以上时,部分在磨损区域的Ag₂MoO₄发生融化,形成摩擦系数更低的液态薄膜,产生润滑作用。徐海峰等^[50]采用等离子喷涂技术制备了NiCrBSi-Mo涂层,研究表明,用热喷涂技术制备的NiCrBSi-Mo涂层中,Mo与NiCrBSi结合良好,产生了良好的润滑效果,但是含有较多的孔隙,并且孔隙率随Mo含量的增加而增加。Niranatlumpong等^[51]采用大气等离子喷涂技术制备了NiCrBSi-Mo涂层,研究了Mo含量对涂层摩擦磨损性能的影响,研究表明,Mo的存在可以起到润滑减摩效果,但当Mo含量超过一定量时,会导致涂层开裂与剥落。

3.3 激光熔覆技术制备金属基自润滑复合涂层

激光熔覆技术是将涂层材料以一定的方式放置

在基体表面,采用激光加热的方式使之和基体表面薄层同时熔化,并快速凝固后形成冶金结合的表面涂层的工艺方法。激光熔覆技术效率高,制备的涂层与基体为冶金结合,结合强度高,由于局部加热,因此对基体的材料要求较低,在制备金属基固体自润滑复合涂层方面优于其他技术,近年来,广泛地应用于金属基固体自润滑复合涂层的制备^[45,52]。Lu等^[53]用激光熔覆的方法在Ti6Al4V合金上制备了Ni基固体自润滑复合涂层,研究表明,激光熔覆技术制备的Ni60-10% h-BN自润滑复合涂层具有良好的高温润滑效果。

应用激光熔覆技术制备金属基固体自润滑复合涂层时,会使CaF₂、Ag等熔点低的固体润滑剂因氧化、分解而失效。针对这一问题,Liu等^[54]用激光熔覆技术制备固体自润滑复合涂层前,采用化学镀Ni-P包覆CaF₂及WS₂固体润滑剂,研究表明,涂层中均匀分布着CaF₂颗粒,说明包覆方法能有效地降低CaF₂的分解。

4 问题与展望

综上所述,金属基固体自润滑复合涂层在材料体系、润滑机理以及制备技术方面取得了相应的研究成果,并且成功地应用于机械、电子以及航空航天等诸多领域。然而,目前仍存在一些急需解决的问题:

1) 固体润滑剂的使用温度范围有限,目前还没有一种能够在很宽温度范围中使用的金属基固体自润滑复合涂层。因此,开发新型固体润滑剂,扩大涂层的使用温度范围是目前急需解决的问题。

2) 金属基固体自润滑复合涂层没有完整系统的理论体系,目前主要以现象解释为主,接下来应深入研究金属基体、固体润滑剂与环境三者之间的相互作用机理,用以指导涂层材料的设计及其制备。

3) 目前金属基固体自润滑复合涂层主要以传统的涂层制备技术为主,具有一定的局限性,为进一步提高涂层质量、开发新的涂层体系,制备技术的改进以及新工艺的开发也是一个极其重要的发展方向。

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