

## 金属-石墨烯复合涂层研究进展

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**摘 要:** 对石墨烯与各种材料的复合涂层进行了详细的介绍, 主要包括金属-石墨烯复合涂层的制备方式、制备工艺、石墨烯的分散性以及石墨烯的添加对涂层性能的影响。电沉积、化学镀和电刷镀等制备方式都可以获得均匀致密的复合涂层, 石墨烯的加入细化了涂层的晶粒, 使涂层的微观形貌发生了一定的改变。石墨烯作为第二相粒子添加时, 机械超声分散效果较差, 一般通过添加表面活性剂再配合机械超声分散的方式来分散石墨烯, 表面活性剂中的阴离子活性剂与阳离子活性剂配合使用分散效果较好。另外, 还有一种保持石墨烯在溶液中浓度动态平衡的方法也有较好的效果。石墨烯作为第二相粒子加入金属涂层中, 增强了金属涂层的导热、导电、耐磨、硬度和耐腐蚀等方面性能。最后, 分析展望了金属与石墨烯复合涂层的发展趋势。

**关键词:** 石墨烯; 复合涂层; 电沉积; 分散; 性能

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## Research Progress of Metal-Graphene Composite Coatings

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**ABSTRACT:** Graphene is a two-dimensional material composed of hexagonal carbon atoms. Due to its unique physical, chemical and mechanical properties, graphene has been considered as an ideal reinforcement phase of metal materials. Researchers have prepared composite coatings of various metals and graphene. In this paper, the composite coatings of graphene and various materials are reviewed in detail, including the preparation method and processes of the composite coating, the dispersion of graphene and the effect of graphene on the properties of the coating. Preparation methods such as electrodeposition, electroless plating and electric brush plating can obtain uniform and dense composite coatings. The addition of graphene refines the grains of the coating and changes the microscopic morphology of the coating. When graphene is added as the second phase particles, the mechanical ultrasonic dispersion effect is poor. Generally, the graphene is dispersed by adding a surfactant and then combined with mechanical ultrasonic dispersion. Among the surfactants, the dispersion effect of the combination of anionic and cationic surfactants is better. In addition, another method to maintain the dynamic equilibrium of graphene concentration in solution has also achieved good results. The addition of graphene as the second phase particles enhances the thermal conductivity, electrical conductivity, wear resistance, hardness and corrosion resistance of the metal coating. Finally, the development trend of metal and graphene composite coatings are analyzed.

**KEY WORDS:** graphene; composite coating; electrodeposition; dispersion; performance

石墨烯 (Graphene, Gr) 具有独特的二维结构和优异特性, 如高热导率、高透光率和高电子迁移率<sup>[1-4]</sup>, 被用于许多领域, 如传感元件<sup>[5]</sup>、电池<sup>[6-8]</sup>、生物装置<sup>[9]</sup>和涂层的防腐<sup>[10-11]</sup>等。目前, 石墨烯主要的制备方法有机械剥离法<sup>[12-14]</sup>、氧化还原法<sup>[15]</sup>、化学气相沉积法<sup>[16]</sup>、外延生长法等。石墨烯主要是使用氧化还原法进行量产, 氧化石墨烯 (GO) 是石墨烯的氧化物, 其基面含有环氧化物和羟基, 此外还有位于边缘的羰基和羧基<sup>[17]</sup>。氧化石墨烯可以通过去除含氧基团还原成为石墨烯<sup>[18-19]</sup>。根据层数, 可分为单层、双层以及多层石墨烯, 这几种石墨烯具备的性质相差较大。鉴于石墨烯材料优异的性能及其潜在的应用价值, 在众多领域已取得了一系列重要进展, 但石墨烯在实际应用上还有许多困难, 无法生产大面积石墨

烯、分散性差、价格昂贵等都给石墨烯的商用造成了阻碍。

在金属涂层表面技术应用方面, 可将二维材料石墨烯作为第二相加入其中, 获得金属-石墨烯复合涂层, 从而提高涂层的性能<sup>[20-23]</sup>。在复合涂层的研究中, 研究者将石墨烯作为第二相, 形成 Ni-Gr<sup>[24-30]</sup>、Cu-Gr<sup>[31-35]</sup>、Fe-Gr<sup>[36]</sup>、Al-Gr<sup>[37]</sup>、Ag-Gr<sup>[38-39]</sup>、Co-Gr<sup>[40]</sup>、ZnNiFe-Gr<sup>[41]</sup>、Ti6Al4V-Gr<sup>[42]</sup>、PPy-Gr<sup>[43]</sup>、树脂-Gr<sup>[44]</sup>等复合涂层。表 1 总结了近年来金属-石墨烯复合涂层种类、制备工艺、工艺参数以及涂层相关性能。本文针对金属-石墨烯复合涂层研究进行了介绍, 分析了制备的方法工艺、石墨烯的分散方式和石墨烯对涂层性能的影响, 最后展望了金属-石墨烯复合涂层的发展方向。

表 1 金属-石墨烯复合涂层的镀液组成、工艺参数、微观结构、制备方法及其性能

Tab.1 The electrolyte composition, deposition conditions, microstructure and deposition methods of metal-graphene composite coatings

Coating	Bath composition	Parameters	Microstructure evolution	Performance	Method	Ref.
Ni-Gr	Ni(NH <sub>2</sub> SO <sub>3</sub> ) <sub>2</sub> 350g/L, H <sub>3</sub> BO <sub>3</sub> 40g/L, NiCl <sub>2</sub> 10g/L, GO 1g/L	pH=4 $\theta=50\text{ }^{\circ}\text{C}$ CD=5 A/dm <sup>2</sup>	The Gr content is 0.12wt%. Gr changes the preferred orientation of the electrodeposited Ni growing from (200) to (111)	Thermal conductivity increased by 15%, 6.85 GPa 4-fold than Ni layer	DC, ED	[24]
Ni-Gr	NiSO <sub>4</sub> 240 g/L, NiCl <sub>2</sub> 45 g/L, H <sub>3</sub> BO <sub>3</sub> 30 g/L, SDS 0.05 g, Gr 0.1~0.5 g/L	$\theta=50\sim80\text{ }^{\circ}\text{C}$ CD=1 A/dm <sup>2</sup> $t=2\sim8\text{ h}$	A fine grained and intact arrangement of Ni crystals in the composite coating. The average thickness of coating increases with increasing amount of Gr	The hardness increased, 203~228HV <sub>0.2</sub> , the reduce in the friction coefficient for the composite coating	Dipulse ED	[25]
Ni-Gr	H <sub>4</sub> N <sub>2</sub> NiO <sub>6</sub> S <sub>2</sub> 300 g/L, NiCl <sub>2</sub> 30 g/L, H <sub>3</sub> BO <sub>3</sub> 35 g/L, SDS 0.2 g/L, Gr 0.15 g/L	pH=3.74 $\theta=50\text{ }^{\circ}\text{C}$ $P=10\text{ MPa}$ $t=60\text{ min}$	The grain size of Ni-Gr coating is small and compact	The hardness of the coating is 1.27 times that of Ni coating, reaching 756.4HV <sub>0.2</sub> . When the duty cycle of pulse plating is 0.25, the coating has the highest microhardness and the best wear resistance	Pulse ED	[26]

续表 1

Coating	Bath composition	Parameters	Microstructure evolution	Performance	Method	Ref.
Ni-Gr	NiSO <sub>4</sub> 150 g/L, NiCl <sub>2</sub> 30 g/L, H <sub>3</sub> BO <sub>3</sub> 25 g/L, Na <sub>2</sub> SO <sub>4</sub> 12.5 g/L, Gr 0.1~0.4 g/L	pH=4~6 $\theta=50\text{ }^{\circ}\text{C}$ CD=2 A/dm <sup>2</sup> $t=4\text{ h}$	With the increase of Gr content, the micro bumps on the surface bulge and gather, and the quality of the layer is improved	The coating with 0.4wt% Gr has the best friction and wear performance, the friction coefficient is 0.61, which is 31% lower than that of Ni coating, and the wear rate is $1.9\times 10^{-4}\text{ mm}^3/(\text{N}\cdot\text{m})$ , which is 65% lower than that of pure nickel coating	Pulse ED	[27]
Ni-Gr	CH <sub>3</sub> CONH <sub>2</sub> 37.4wt%, CO(NH <sub>2</sub> ) <sub>2</sub> 28wt%, NH <sub>4</sub> NO <sub>3</sub> 34.6wt%, NiCl <sub>2</sub> 0.05 mol/L, H <sub>3</sub> BO <sub>3</sub> 30 g/L	$\theta=50\text{ }^{\circ}\text{C}$ CD=1 A/dm <sup>2</sup> $t=4\text{ h}$	With the addition of Gr, the grain size of Ni in composite coating is finer than that of pure Ni coating.	The hardness of Ni-Gr coating is 427HV, while the hardness of pure Ni coating is only 265HV. The average friction coefficient of Ni-Gr coating is 0.14, which is much less than 0.43 of pure Ni coating, and the wear rate of Ni-Gr coating is more than 90% lower than that of pure Ni coating.	DC, ED	[28]
Ni-Gr	NiSO <sub>4</sub> 250 g/L, CH <sub>3</sub> COONH <sub>4</sub> 45 g/L, (NH <sub>4</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> 50 g/L, Gr 0~0.6 g/L	$V=12\text{ V}$ $t=5\text{ min}$ Speed=10~12 m/min	Gr has different forms in the coating, and there are certain impurities adsorbed on the surface. The addition of Gr refines Ni grains, the coating has high density, and there are no pores and cracks	The addition of Gr improves the hardness of Ni coating. When the Gr is 0.5 g/L, the hardness of coating is the highest, reaching 570HV	Brushing ED	[30]
Cu-Gr	CuSO <sub>4</sub> 200 g/L, H <sub>2</sub> SO <sub>4</sub> 50 g/L, PAA 25 mg/L, GO/RGO/TRGO 0.1~1 g/L	pH=1±0.02 CD=8 A/dm <sup>2</sup> Pulse frequency= 5 kHz Duty cycle= 30% $t=20\text{ min}$	The existence of GO in Cu is mainly needle like structure. The morphology of Cu-RGO and Cu-TRGO appears denser than that of Cu-GO coating	The tensile strength is 1.4 times, reaching 2.11 GPa. With the addition of 0.5 g/L GO, the coating obtained the best hardness and wear resistance	pulse ED	[31]
Cu-Gr	CuSO <sub>4</sub> 250 g/L, H <sub>2</sub> SO <sub>4</sub> 130 g/L, GO 0.2/0.5/0.8 g/L, PAA 50 times GO-content	$\theta=25\sim 55\text{ }^{\circ}\text{C}$ CD=5~20 A/dm <sup>2</sup>	Gr presents a flake shape with wrinkles on the surface of the coating	The tensile strength of the composite coating reached 60MPa. In hydrochloric acid, Cu-Gr coating shows stronger corrosion resistance than pure Cu foil	DC ED	[32]
Cu-Gr	CuSO <sub>4</sub> 10 g/L, Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> 15 g/L, NaH <sub>2</sub> PO <sub>2</sub> 28 g/L, H <sub>3</sub> BO <sub>3</sub> 30 g/L, NiSO <sub>4</sub> 1 g/L, GO 20~100 mg/L	pH=9~9.5 $\theta=65\text{ }^{\circ}\text{C}$ $t=1\text{ h}$	The Gr acts as the effect of nucleation and increases the possibility of refining the grain size to obtain a dense coating	The tensile strength of Cu-Gr is 4.2 times that of Cu coating, reaching 3.46 GPa. In HCl solution, Cu-Gr showed stronger corrosion resistance than pure Cu foil	Electroless	[33]
Cu-(CNTs+Gr)	CuSO <sub>4</sub> 250 g/L, H <sub>2</sub> SO <sub>4</sub> 130 g/L, CNTs 0.05 g/L, GO 0.025 g/L	CD=10 A/dm <sup>2</sup> $\theta=25\text{ }^{\circ}\text{C}$	The synergistic effect of CNT and Gr makes the coating more compact and the interfacial bonding strength improved.	Cu-(CNT + Gr) has the lowest corrosion current density, the largest linear polarization resistance and the largest positive potential	DC ED	[34]
Cu-Gr	CuSO <sub>4</sub> 16 g/L, EDTA·2Na 65 g/L, NaKC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> 500 g/L, 2, 2'-Dipyridyl 1 g/L, K <sub>4</sub> Fe(CN) <sub>6</sub> 1 g/L, CH <sub>2</sub> O 16 g/L	$\theta=50\text{ }^{\circ}\text{C}$ pH=12.5~13 $t=30\text{ min}$	Gr becomes the nucleation center of copper particles and promotes the nucleation of copper	The addition of Gr improves the hardness of Cu coating. When the content of Gr reaches 3%, the hardness of the coating reaches the maximum, reaching 65.3HV, and also shows the best friction performance	Electroless	[24]
Fe-Gr	FeCl <sub>2</sub> 350 g/L, NH <sub>4</sub> Cl 30 g/L, MnCl <sub>2</sub> 5 g/L, SDS 0.1 g/L, Saccharin 0.1 g/L, GO 0.1~0.5 g/L	pH=1~2 CD=1 A/dm <sup>2</sup> $t=30\text{ min}$	Fe-Gr coating is closely combined with Fe substrate and has good adhesion.	The hardness of Fe-Gr coating is twice that of Fe coating, reaching 248HV. The corrosion resistance is 3.75 times that of pure Fe layer	DC ED	[36]

续表 1

Coating	Bath composition	Parameters	Microstructure evolution	Performance	Method	Ref.
Al-Gr	THF:PhH 6:4, AlCl <sub>3</sub> 0.75 mol/L, LiAlH <sub>4</sub> 0.25 mol/L, GO 5 g/L, PVP 1.7 g/L	CD=5 A/dm <sup>2</sup> $\theta$ =25 °C $t$ =60 min	Al-Gr coating has higher roughness than Al coating, Gr composition is distributed along a straight line, and the crystal size of Al-Gr coating is smaller than that of Al coating	The hardness of the composite coating is 3.87 times that of Al coating, reaching 290HV <sub>0.1</sub>	DC ED	[37]
Ag-Gr	AgNO <sub>3</sub> 50 g/L, C <sub>4</sub> H <sub>5</sub> NO <sub>2</sub> 100 g/L, K <sub>4</sub> P <sub>2</sub> O <sub>7</sub> 100 g/L, GO 0.4 g/L, PAA 25 mg/L	pH=10 $\theta$ =25 °C CD=1~4 A/dm <sup>2</sup>	The surface of the coating is flat and compact, and black spots can be seen in some areas. The addition of Gr refines the grains of the coating, but has no effect on the thickness of the coating	The addition of Gr improves the corrosion resistance of the composite coating	DC ED	[38]
Co-Gr	CrO <sub>3</sub> 180 g/L, H <sub>2</sub> SO <sub>4</sub> 130 g/L, Cr <sup>3+</sup> 1.8 g/L, SDBS 8 mg/L, Gr 80 mg/L	Pre-CD= 5 A/dm <sup>2</sup> $t$ =2 min $\theta$ =40~55 °C CD=20~50 °C $t$ =10 min	The composite coating is flat with obvious cracks, and there are black substances in the coating which are different from the matrix Cr coating	—	DC ED	[39]
ZnNiFe-Gr	ZnSO <sub>4</sub> 160 g/L, NiSO <sub>4</sub> 140 g/L, Fe <sub>2</sub> SO <sub>4</sub> 150 g/L, Na <sub>2</sub> SO <sub>4</sub> 80 g/L, H <sub>3</sub> BO <sub>3</sub> 10 g/L, CTAB 0.2 g/L, Gr 0~75 mg/L	pH=3.2 CD=1 A/dm <sup>2</sup> $\theta$ =(43±2) °C $t$ =45 min	The addition of Gr improves the compactness of the coating, eliminates the micropores and defects in the coating morphology, affects the abnormal deposition behavior of Zn, promotes the adsorption of Ni and Fe in the coating, and improves the proportion of Ni and Fe in the coating	The addition of Gr improves the corrosion resistance of ZnNiFe coating, and the coating with the highest content of Gr and Ni has the best corrosion resistance.	DC ED	[41]
Ti6Al4V-Gr	Laser cladding powders: Al 6.0~6.75wt%, V 3.5~4.5wt%, Ti Bal., Gr<0.03wt%	Power= 1.5 kW Speed= 7 mm/s Ar flow= 5.0 L/min	A large number of light gray precipitates and acicular martensite are formed in the crystal and grain boundary of Ti6Al4V-Gr. The composite coating forms a good metallurgical combination with Ti6Al4V matrix without cracks and pores.	—	Laser cladding	[42]
CrAlNi-Gr	Laser cladding powders: Cr 65wt%, Al 15wt%, Ni 15wt%, Gr 5wt%	Power= 3.2 kW Speed= 3 mm/s Ar flow= 1.3 L/min Overlap= 12%	Ni and Al form NiAl compound under the action of laser, Gr does not change, the cladding layer is closely combined with the matrix, and there are no obvious defects such as holes and cracks.	Compared with the conventional CrAlNi coating, the wear volume of the composite coating decreased significantly at 25 °C, 250 °C and 500 °C, and the gain mass rate decreased by 91% after high temperature oxidation at 900 °C.	Laser cladding	[45]
Ni-P-Gr	NiSO <sub>4</sub> 30 g/L, NaH <sub>2</sub> PO <sub>2</sub> 25 g/L, Sodium acetate 15 g/L, Sodium citrate 15 g/L	pH=4.5~4.7 $\theta$ =(85±2) °C $t$ =2 h	The surface of the coating is composed of amorphous cell structure, and Gr in a folded shape is embedded in the Ni-P coating.	The addition of Gr improves the hardness of the coating. When the concentration of Gr is 1 g/L, the comprehensive performance of the coating is the best when SDBS and APEO are used as surfactants	Electroless	[46]

Note:  $\theta$ —Temperature;  $t$ —Deposition time; CD—Current density; DCED—Direct current electrodeposition

## 1 制备技术

目前, 金属-石墨烯复合涂层的制备方式主要有

直流电沉积<sup>[24,28,32,34,36-41,47]</sup>、脉冲电沉积<sup>[25-27,31]</sup>、喷射电沉积<sup>[29]</sup>、电刷镀<sup>[30]</sup>、化学镀<sup>[33,35,46]</sup>、激光熔覆<sup>[42,45]</sup>、刷涂<sup>[44]</sup>等。电沉积和化学镀技术具有以下优势: 设备成本相对低, 可镀制形状复杂基体, 沉积温度较低,

涂层的厚度、成分和微结构可精确控制<sup>[48-51]</sup>。利用复合电沉积或化学镀技术可以制备出许多具有特殊功能的复合镀层。由于能显著改善镀层的性能,到目前为止,复合涂层制备技术仍然是材料表面技术领域的研究热点之一。激光熔覆是一种高能量表面改性技术,利用高能密度的激光束使涂层与基材表面薄层一起熔凝,在基体表面形成冶金结合的熔覆层<sup>[42]</sup>。刷涂是将涂料刷在基体表面,经过自然干燥或是烘干得到稳定涂层。将石墨烯通过机械分散或表面活性剂分散在水性树脂中,加入固化剂后,涂刷在钢材表面,可获得树脂与石墨烯复合涂层<sup>[44]</sup>。

采用电沉积技术主要制备 Ni-Gr、Cu-Gr、Fe-Gr 等复合涂层,可获得较好的效果。Kuang 等<sup>[24]</sup>在氨基磺酸镍镀液中加入氧化石墨烯 (GO),利用电沉积制备了 Ni-Gr 复合镀层,研究表明:复合镀层内石墨烯含量为 0.12% (质量分数) 时,镀层择优生长取向由(200)晶面演变成(111)晶面。Chen 等<sup>[25]</sup>采用双脉冲复合电沉积技术制备了 Ni-Gr 复合镀层,研究发现,石墨烯使镀层表面形貌更加致密,最佳温度为 60 ℃,石墨烯添加量为 0.4 g/L。Xue 等<sup>[26]</sup>在超临界 CO<sub>2</sub> 条件下,采用脉冲电沉积技术制备了 Ni-Gr 复合镀层,涂层择优取向由(200)晶面改变为(111)晶面,且复合镀层表面光亮,表面粗糙度较低,晶粒尺寸较小。Wan 等<sup>[27]</sup>通过脉冲电沉积制备了 Ni-Gr 复合镀层,发现随着复合镀液中 Gr 含量的增加,涂层表面的微凸体凸起,并聚集,镀层质量提高。Xiang 等<sup>[28]</sup>通过电沉积在有机溶剂中制备了 Ni-Gr 复合镀层,Gr 掺入为 Ni 颗粒的生长提供了更多的成核位点,使晶粒尺

寸变小,镀层中石墨烯含量达到 23.9%。

Maharana 等<sup>[31]</sup>分别将不同浓度的 GO、化学还原氧化石墨烯 (RGO) 和热还原氧化石墨烯 (TRGO) 加入 Cu 镀液中,通过脉冲电沉积制备涂层,获得的 Cu-GO 涂层中的 GO 呈现针状形式分布,RGO 和 TRGO 的涂层比 GO 涂层更加致密,且当 RGO 和 TRGO 的添加量为 0.5 g/L 时,镀层致密均匀,质量最好。Song 等<sup>[32-33]</sup>通过直流电沉积和化学镀制备了 Cu-Gr 镀层,研究了不同工艺参数下镀层的微观组织变化和力学性能。研究发现,GO 的最佳添加量为 0.5 g/L,此时镀层晶粒致密紧凑,且在此添加量下,电流密度为 10~20 A/dm<sup>2</sup> 时,镀层晶粒小,镀层结合力好,且石墨烯在镀层中均匀分布。不同 GO 添加量下的复合镀层 SEM 形貌如图 1 所示,可以看到不同 GO 添加量下的镀层晶粒尺寸差异较大。石墨烯的比面积较大,Cu 离子以石墨烯为中心形核共沉积,提高了基体表面的形核率,使得晶粒细化,涂层致密。但石墨烯浓度过高时易产生团聚,难以实现镀层晶粒细化。Song 等<sup>[34]</sup>将碳纳米管 (CNTs) 和石墨烯 (Gr) 通过电沉积的方法引入到铜基体中,制备出了 Cu-(CNTs+Gr) 复合镀层。在制备过程中,GO 既是被还原的对象,也是 CNTs 的表面活性剂。由于 Gr 的加入,铜的表面织构的择优生长取向由(111)晶面转变为(220)晶面,并且由于 CNTs 和 Gr 的协同作用,Cu-(CNTs+Gr) 复合镀层的力学性能、耐腐蚀性和导电性都得到了提高。卢晓通等<sup>[35]</sup>通过化学镀制备了 Cu-Gr 复合镀层,制备完成后,将镀层分离,和电解铜粉烧结在一起,制成铜-石墨烯复合材料,石墨烯的加入

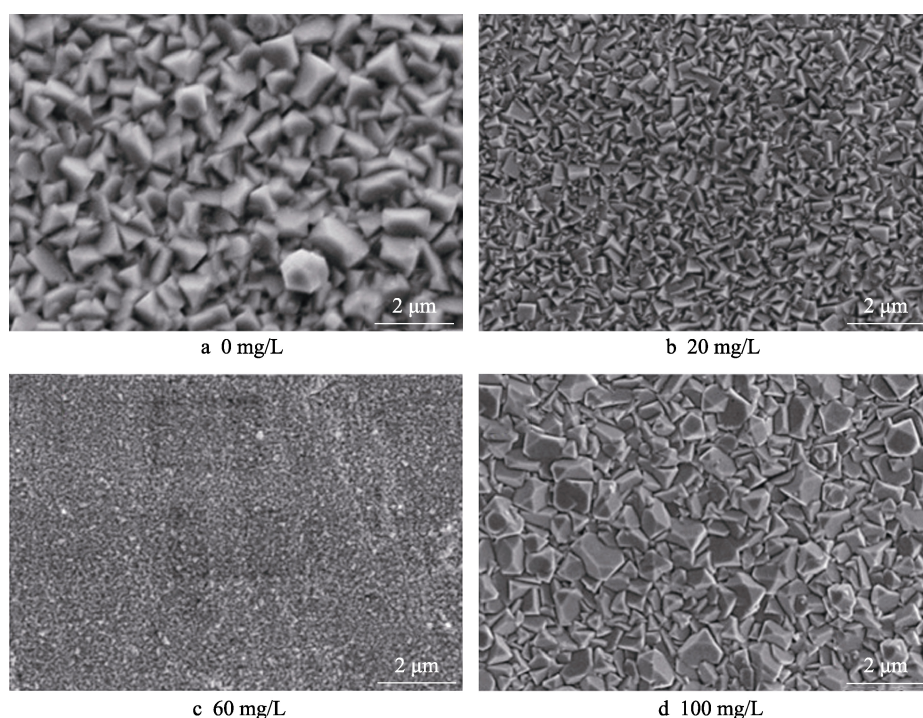


图 1 不同 GO 添加量下 Cu-Gr 镀层的 SEM 形貌<sup>[32]</sup>

Fig.1 SEM images of Cu-Gr coating deposited with different contents of GO<sup>[32]</sup>



提高了铜的形核。这是由于石墨烯表面的褶皱有利于纳米铜颗粒长大,提高了铜含量。

Yang 等<sup>[36]</sup>通过复合电沉积制备出了 Fe-Gr 镀层,发现氧化石墨烯的最佳添加量为 0.4 g/L,复合镀层的硬度和耐腐蚀性能都得到了提高。Li 等<sup>[37]</sup>通过电沉积技术,在四氢呋喃和苯的有机溶剂中制备了 Al-Gr、Al 镀层,Gr 的加入使 Al 晶粒细化。石墨烯纳米片具有较高的比表面积和良好的导电性,使 Al 离子具有丰富的活性成核位点,优先在石墨烯纳米片表面还原,这也导致涂层上出现了较多的石墨烯薄片凸起,

增大了涂层的表面粗糙度。笔者课题组也采用复合电沉积技术在赫尔槽铜阴极片上沉积了 Ag-Gr 复合镀层<sup>[38]</sup>,Gr 的加入细化了镀层的晶粒,使镀层微观形貌致密紧凑(见图 2),但发现石墨烯的加入对镀层的沉积速率没有影响。图 2b 右上角 SEM 图显示出了 Gr 嵌入镀层中,镀层中 Gr 含量为 29.7%。Kumar 等<sup>[41]</sup>通过直流电沉积制备了 ZnNiFe-Gr 复合镀层,Gr 的加入提高了涂层的致密性,提高了合金镀层中 Ni 和 Fe 的占比,减少了微孔和表面缺陷,但对晶粒尺寸没有产生明显的改变。

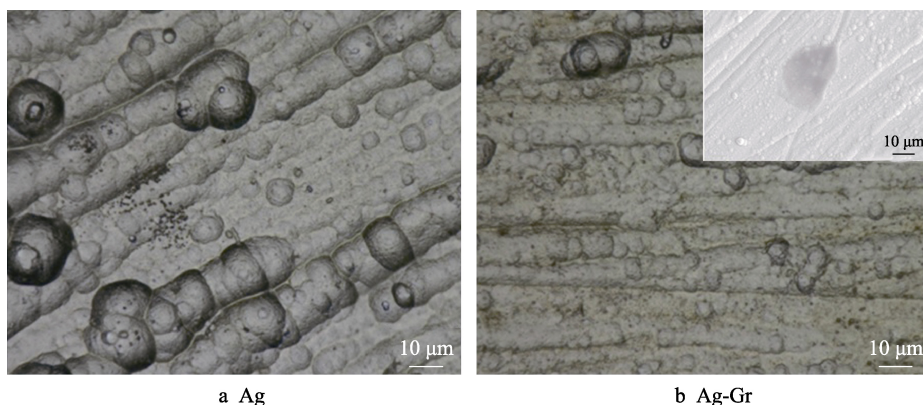


图 2 在 1.39 A/dm<sup>2</sup> 电流密度下沉积的纯 Ag 和 Ag-Gr 镀层的 OM 和 SEM 形貌<sup>[38]</sup>

Fig.2 OM and SEM images of pure (a) Ag and (b) Ag-Gr coatings deposited at applied current densities of 1.39 A/dm<sup>2</sup>

Zhang 等<sup>[42]</sup>通过激光熔覆技术制备了 Ti6Al4V-Gr 复合镀层,在激光熔覆过程中,Gr 与 Ti 发生了原位反应,生成了羽毛状的 TiC,这导致复合镀层的晶间和晶界处形成了大量的浅灰色析出物,复合镀层与基体之间形成良好的冶金结合。王泽锴等<sup>[46]</sup>通过激光熔覆技术制备了 CrAlNi-Gr 复合涂层,在激光熔覆过程中,只有 Al 和 Ni 发生了化合反应,石墨烯保留了原有的结构,涂层与基体结合紧密,涂层外层主要由 NiAl 和 Gr 组成,扩散层主要由 Cr 和 Gr 组成。

## 2 石墨烯分散性

石墨烯由于其较大的比表面积,极易出现团聚现象。石墨烯在镀液中的分散性对镀层质量起到关键性作用。通过机械超声分散石墨烯效果不佳<sup>[52-53]</sup>,可以通过添加分散剂改善石墨烯的表面活性,提高其亲水性,或使用亲水的氧化石墨烯。其中,表面活性剂有聚丙烯酸(PAA)、十二烷基硫酸钠(SDS)、十六烷基三甲基溴化铵(CTAB)、聚乙烯吡咯烷酮(PVP)等。将表面活性剂和石墨烯一起加入镀液中进行超声分散,配制好镀液后,在电镀时可通过搅拌、鼓气等方法防止石墨烯团聚。还有学者利用 GO 的亲水性和施镀过程中 GO 会发生还原反应生成 Gr 的特性,用 GO 代替了 Gr 进行施镀<sup>[24,32-44]</sup>,在一定程度上解决了 Gr 的分散问题。然而,这种方式产生的石墨烯还是会出现团聚现象<sup>[32-33,36-38]</sup>。另外,利用非离子型和离

子型表面活性剂共同作用可以使体系的表面活性提高,增强石墨烯的分散性<sup>[15,26,46]</sup>。

石墨烯在一些有机溶剂中比在水溶剂中具有更好的分散性,因此可以在有机溶剂中进行复合镀。Li 等<sup>[37]</sup>将石墨烯和 30% 聚乙烯吡咯烷酮加入无水乙醇中,超声 1 h 后,过滤干燥,提高了石墨烯的表面活性,再将处理后的石墨烯加入用四氢呋喃和苯配制的镀液中,进行电镀。Zhang 等<sup>[45]</sup>研究了糖精钠和十二烷基硫酸钠(SDS)、十六烷基三甲基溴化铵(CTAB)、聚乙二醇(PEG)三种表面活性剂对分散 GO 的协同作用,将这三种表面活性剂分别和糖精钠一起作为分散剂,制备了 Ni-GO 复合涂层。研究发现,对 GO 的分散效果为 PEG>CTAB>SDS,添加 PEG、CTAB 制备出的涂层硬度显著提高,添加 PEG 的涂层摩擦系数最低,SDS 对涂层的影响最小,且三种涂层的晶粒尺寸都随着糖精钠的浓度增加而减小。

在石墨棒上加载电压,通过阳极电解剥离的方式可以制备石墨烯<sup>[54]</sup>。Xiang 等<sup>[28]</sup>根据此工艺提出了一种新的金属-石墨烯复合镀层的沉积方法。电沉积过程中,阳极电解剥离产生石墨烯,通过搅拌,部分石墨烯移动到阴极附近,此时阴极附近的金属离子获得电子,并吸附石墨烯,共沉积到阴极上,镀液中的石墨烯含量达成了一个动态平衡,不出现团聚现象。Mai 等<sup>[55]</sup>配制了一种由铜-乙二胺四乙酸([Cu<sup>II</sup>EDTA]<sup>2-</sup>)络合物和 GO 片组成的无表面活性剂胶体溶液,用于电沉积 Cu-GO 复合镀层。该溶液中不含表面活性剂,

溶液中阴离子 $[\text{Cu}^{\text{II}}\text{EDTA}]^{2-}$ 络合物与带负电荷的 GO 片之间由于静电斥力而稳定共存, 有利于 GO 片的电化学还原和均匀分散。

国内外研究人员提出了一系列石墨烯的分散方式, 目前看来, 通过一边阳极剥离制备石墨烯, 一边阴极还原制备石墨烯复合镀层的方法比较有效<sup>[28]</sup>, 制备的复合涂层中, 石墨烯的质量分数达 23.9%。但这种方式无法控制石墨烯的掺入量, 镀层的质量不稳定。关于石墨烯的分散需要进一步实验研究。

### 3 复合涂层性能

国内外研究人员对石墨烯-金属复合镀层的性能进行了表征, 主要包括导热、导电、硬度、耐磨和耐腐蚀性能<sup>[56]</sup>。对于不同的金属涂层, 添加石墨烯提高了涂层的某项或是多项性能。这些性能的变化, 一方面是由于石墨烯的加入改变了原涂层的生长方式, 使涂层的晶粒变细小, 镀层变得致密紧凑, 镀层晶粒细化更加有利于提高镀层的硬度和耐磨损性能。另一方面, 因为石墨烯在导电、导热、硬度、润滑和阻隔小分子方面都有远超金属镀层的特性, 所以形成的复合镀层除具有金属涂层自身的性能外, 还具备了石墨烯的一些特殊功能。金属-石墨烯复合涂层的性能见前表 1。

将 Gr 添加到 Ni 镀层中, 提升了 Ni 镀层的各项性能, 导热系数提升了 15% 以上, 硬度最高提升了 4 倍, 摩擦系数最高降低了 60%, 磨损率最高降低了 90%<sup>[24-30]</sup>。将 Gr 添加到 Cu 镀层中, 发现不仅提升了镀层的硬度、耐磨性、弹性模量、拉伸强度等力学性能, 还提升了镀层的导电性和耐腐蚀性能<sup>[31-35]</sup>。除了 Ni 和 Cu, 将 Gr 添加到 Fe、Al、Ag 等镀层中, 也可以提升镀层的力学和耐腐蚀性能。Yang 等<sup>[36]</sup>研究了 GO 添加量对电沉积 Fe 镀层的影响, GO 的最佳添加量是 0.4 g/L, 此时复合镀层的性能最佳。与 Fe 镀层相比, Fe-Gr 镀层硬度提升了 2 倍, 耐腐蚀性增加了 2.75 倍。Li 等<sup>[37]</sup>报道了 Al-Gr 复合镀层的硬度比 Al 镀层提高了 3.8 倍, 摩擦系数降低了 91%。笔者课题组在研究中发现, 0.4 g/L 石墨烯下电沉积制备的 Ag-Gr 镀层的耐腐蚀性能比纯银镀层好<sup>[38]</sup>。

石墨烯不仅在单一金属镀层中改善镀层性能, 在合金镀层中也能提升镀层的力学性能、耐磨损和耐腐蚀性能。Kumar 等<sup>[41]</sup>研究了 ZnNiFe-Gr 复合镀层, 结果表明, 石墨烯的加入提高了 ZnNiFe 涂层的耐腐蚀性能。王泽锴等<sup>[45]</sup>在不同温度下对常规 CrAlNi 涂层和 CrAlNi-Gr 复合涂层进行了摩擦磨损研究, CrAlNi-Gr 复合涂层在 25、250、500 °C 下的磨损体积分别减小了 66%、72%、74%。在 900 °C 高温氧化 60 min 后, 复合涂层的质量增加率减小了 91%。石墨烯的加入, 提高了 CrAlNi 涂层的耐磨性能和抗氧化性能。

大量的研究发现, 将石墨烯添加到单一金属镀层中和合金镀层中, 都能够提升镀层的各项性能, 对这些性能的提升幅度主要取决于石墨烯在镀层中的分布情况, 而石墨烯在镀液中的分散性又决定了石墨烯是否能够均匀分布在镀层中, 所以石墨烯在镀液中的分散性能影响了石墨烯对镀层性能的提升幅度。

### 4 结语

本文对国内外关于金属-石墨烯复合涂层的研究进行了分析, 对这些研究中涂层的制备工艺、石墨烯的分散方式、石墨烯的加入对涂层性能的影响等方面进行了整理归纳。这些研究表明, 二维材料石墨烯作为第二相粒子加入各种金属涂层中, 可以在一定程度上改变金属镀层的沉积效果, 并改善原涂层材料在导热、导电、硬度、耐磨和耐腐蚀方面的性能。未来可以探索更多与石墨烯结合的材料, 并将它们运用到工业中去。但目前, 提高石墨烯的分散性依然是具有较大挑战性的问题, 以现在石墨烯的分散程度, 还无法将之运用到大批量复合涂层的制备中。这还需要后续大量的实验和探索去突破, 如: 寻找到更合适的石墨烯分散剂; 或对石墨烯进行表面改性, 使其更加亲水; 或是采用高速剪切力使其在溶液中均匀分散; 又或者研究新的沉积方式及工艺。

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