

碳纳米管/铜复合导体的制备、性能与应用研究进展

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摘要 在“双碳”目标驱动下, 航空航天、新能源汽车与先进电子器件对导体材料提出了高强高导协同、高电流承载能力及宽温域可靠服役的多维性能要求。碳纳米管因其准一维结构、超高载流容量、低密度及优异力学性能, 成为构建新一代复合导体的理想材料。近年来, 研究者围绕碳纳米管/铜复合导体的界面结构调控、分级构型设计及先进制备技术开展了系统研究, 在电导率、力学性能、载流等方面取得显著突破。本文综述了粉末冶金、电沉积、物理/化学气相沉积等导体制备方法, 对比分析了不同工艺下复合导体的导电、力学、载流性能, 并阐述了其 在高强结构材料、轻量化导体、高可靠性微电子互连、电极材料等领域的应用潜力。在此基础上, 指出当前研究仍面临碳纳米管分散与结构可控性、碳纳米管与铜的有效界面构筑、宏观结构设计 与性能协同优化、规模化制备与成本控制等方面的诸多挑战。展望未来, 应通过精准界面工程、多尺度结构协同设计与工程化制备技术的深度融合, 发展兼具高导电、高强韧、高可靠性的新一代碳纳米管/铜复合导体, 为下一代高效、轻质、可持续的电气与电子系统提供关键材料支撑。

关键词 碳纳米管/铜, 界面, 电导率, 载流能力, 力学性能

金属导体是现代电力传输与电子系统的核心基础材料, 其性能水平直接决定能源效率与装备可靠性。铜(copper, Cu)凭借优异的电导率(约 5.8×10^7 S/m)、良好的延展性及相对低廉的成本, 成为电力传输、电机绕组、集成电路互连等领域的首选材料^[1,2]。随着高功率电子装备、航空航天推进系统及柔性电子技术的迅猛发展, 传统Cu导体正面临严峻的本征性能瓶颈: 一方面, 密度大且力学强度低, 高电流密度下易发生电迁移失效^[3,4], 大电流承载能力有限; 另一方面, 传统金属强化手段如晶粒细化、位错强化或第二相弥散强化, 虽可显著提升强度, 却不可避免地引入大量电子散射中心, 导致电导率显著下降^[1,5]。这一“强度-导电性倒置关

系”已成为导体材料领域长期未能突破的关键科学难题^[6,7]。

碳纳米管(carbon nanotube, CNT)因其独特的准一维结构和卓越的综合性能, 成为突破上述性能权衡的理想候选材料。理论计算和实验研究表明, 单根碳纳米管的电流承载能力可高达 10^8 A/cm²量级^[3,8], 远超传统金属导体; sp²杂化碳键赋予其超高强度(理论值>100 GPa)与热稳定性(>2800℃)^[9,10]。这些特性使碳纳米管在金属基复合导体中兼具增强相与导电相的双重角色。然而, 受限于管间接触电阻高、结构缺陷多及组装均匀性差等难题, 单一碳纳米管组分难以独立构建低阻、连续的大尺寸导体^[11,12]。因此, 将碳纳米管与Cu

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Zhang J, Liu D, Qiu Y, et al. Recent progress in the preparation, properties, and applications of carbon nanotube/copper composite conductors (in Chinese). Chin Sci Bull, 2026, 71: 6398–6411, doi: [10.1360/CSB-2026-0648](https://doi.org/10.1360/CSB-2026-0648)

复合(CNT/Cu), 形成协同导电网络, 已成为发展高性能复合导体的有效路径^[4,13]。

近年来, CNT/Cu复合导体研究取得了系列进展。(1) 界面工程策略的多元化开发及界面结合强度的提升。大量研究表明, 碳纳米管与Cu之间的界面特性在很大程度上影响着复合导体的力学与电学性能^[14-17]。为解决碳纳米管表面惰性、与Cu界面润湿性差的问题, 研究者开发了硫醇功能化^[18]、Ni纳米颗粒界面锚定^[19]、氮掺杂碳层^[20]以及磁控溅射Cu种子层构建Cu-O-C共价键^[21]等多种界面修饰策略。这些方法有效促进了Cu的均匀成核与致密生长, 使界面结合强度增强。Zou等人报道, 经过修饰的界面, 其结合强度可达3.6 MPa以上^[4], 复合材料抗拉强度可达2.5 GPa^[22], 为高可靠、高载流导体奠定了界面基础。(2) 载流能力与电导率的协同提升。传统粉末冶金法虽工艺成熟, 但受限于碳纳米管分散困难和界面散射, 电导率通常较纯铜下降5%~50%^[23]。相比之下, 电沉积法通过构建碳纳米管连续网络与Cu基体的复合结构, 电导率可达81%的国际退火铜标准(international annealed copper standard, IACS), 复合薄膜的载流能力高达 6×10^8 A/cm², 电阻温度系数(temperature coefficient of resistance, TCR)降至纯铜的1/9, 80℃以上其电导率反超纯铜^[3]。经石墨烯原位包覆协同增强后, 复合纤维比电导率为铜的1.4倍, 比载流能力为铜的2.8倍^[13]。在评估CNT/Cu复合导体的综合性能时, 电导率与载流能力是两个物理本质不同且不可相互替代的关键指标。电导率反映材料本征的电子输运能力, 由载流子浓度、迁移率及电子散射机制决定, 是静态材料属性。载流能力表征导体在失效前所能承载的最大电流密度, 受电迁移稳定性、焦耳热积累及散热条件等动态因素控制。纯铜虽具有极高的电导率, 但其载流能力通常不超过 10^6 A/cm², 且在高电流密度下易因电迁移和热致失效而损坏。CNT/Cu复合导体的独特优势在于, CNT网络可提供额外载流通道、物理阻挡Cu原子扩散路径以及快速导出焦耳热, 从而在电导率尚未达到纯铜水平时, 其载流能力已可实现数量级的提升, 最高达 6×10^8 A/cm²。因此, 本文将对两者分别加以考察, 以全面评价复合导体的工程适用性。(3) 复合结构的多尺度设计与功能化拓展。在粉末冶金法中, 通过构建三维石墨烯网络^[24]与无序多层石墨烯^[25], 实现了极低添加量下的高效强化(抗压强度1.56 GPa)。气相沉积法可借助外延界面与“竹节”状结构降低界面电阻^[26], 也可通过焦耳热驱动气相沉积

实现位点选择性沉积^[27]。本课题组早在2011年就在碳纳米管可纺丝阵列纤维上电沉积Cu, 获得了抗拉强度811 MPa、电导率 1.84×10^5 S/m的轻量化导线^[6], 验证了电沉积法构筑高性能CNT/Cu核壳结构的技术可行性。

尽管上述研究在特定性能指标上取得了突破性进展, 但相关工作在制备方法、界面设计与宏观性能之间的关联机制上仍较为分散。粉末冶金、电沉积、物理气相沉积(physical vapor deposition, PVD)、化学气相沉积(chemical vapor deposition, CVD)、化学镀、分子级混合(molecular level mixing, MLM)等不同制备工艺在碳纳米管分散状态、界面结合模式及最终导体构型上的差异如何定量影响力-电-热综合性能, 仍缺乏横跨多种方法体系的横向对比与规律性总结。为此, 本文将从制备方法出发, 系统梳理粉末冶金、电沉积及气相沉积等主流技术的研究进展^[28,29], 重点分析各工艺在结构构建与性能调控中的作用机制, 并对比不同方法在导电、载流及力学性能方面的差异化特征^[30,31]。在应用层面, 总结各工艺在轻量化电力传输、微电子互连、柔性电子器件及极端环境特种导体等领域的研究进展, 如图1所示。在此基础上, 归纳当前制约该类材料发展的关键问题, 包括碳纳米管分散与界面稳定性、结构可控性及规模化制备等挑战, 并对未来发展方向进行展望, 以期为高性能复合导体材料的设计与工程化应用提供参考。

1 CNT/Cu复合导体的制备方法及其性能

CNT/Cu复合导体的制备方法直接影响碳纳米管的分散状态、界面结合以及复合结构形貌, 从而决定材料的电学和力学性能。不同制备方法在碳纳米管分散方式、界面结合机制以及宏观结构构建方面各具特点。

1.1 粉末冶金法制备及其性能

粉末冶金是制备碳纳米管增强Cu基复合材料的主流固相成形方法, 如图2所示, 其典型流程包括: 碳纳米管预处理(酸化、功能化或金属包覆)、碳纳米管与Cu粉的混合球磨、压坯成形、致密化烧结(如热压或放电等离子烧结)及后续热处理^[32]。该方法的优势在于工艺成熟、适于批量生产, 且可制备大尺寸块体材料。

粉末冶金法制备CNT/Cu复合导体的性能以不明显降低导电性的前提下提升力学性能为主。其强化机

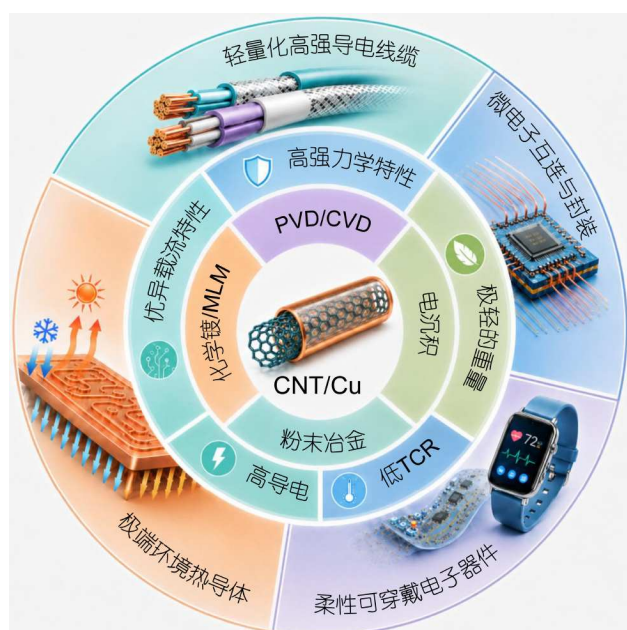


图1 CNT/Cu复合导体的制备、性能及应用

Figure 1 Preparation, properties, and applications of CNT/Cu composite conductors

制主要有载荷转移^[33]、细晶强化和^[34]位错强化^[35]等。载荷转移方面,在Cu-Cr合金中原位生长碳纳米管,界面处形成的 Cr_3C_2 和 Cu_2O 过渡相使载荷转移贡献达70 MPa,占增强总量的84%^[36],高效载荷转移依赖于碳纳米管的均匀分散与强界面结合。细晶强化方面,沿Cu基体晶界处添加3 vol%碳纳米管,通过钉扎效应抑制Cu晶粒长大,Cu晶粒从微米级细化至约544 nm,屈服强度增加5~6 MPa^[37];在 $\text{Al}_2\text{O}_3/\text{CNT}/\text{Cu}$ 复合体系中,晶粒尺寸从9.6 μm 细化至4.8 μm ^[38]。位错强化方面,碳纳米管与Cu基体热膨胀系数差异显著(CNT 约 $1 \times 10^{-6}/\text{K}$,

Cu 约 $17 \times 10^{-6}/\text{K}$),在复合导体界面处产生高密度几何位错,如原位生长CNT/Cu复合导体中位错密度高达 $1.4 \times 10^{15}/\text{m}^2$,较纯铜提高74%,贡献约8~9 MPa的强度增量^[36]。为系统比较CNT/Cu复合导体性能相对于Cu的变化趋势,本文汇总了现有文献中普遍关注的抗拉强度和硬度数据,如图3(a)所示,与碳纳米管复合后的CNT/Cu复合导体抗拉强度和硬度较纯铜和纯铝均有提高,抗拉强度可达154~563 MPa,硬度达79.1~197 HV^[7,39~43]。理论上碳纳米管的增强效率与其本征结构密切相关,管壁数越少、长度越长、晶格缺陷越少,其力电性能越优异。但长碳纳米管易因范德华力团聚形成微米级束状结构,均匀分散时可有效承载,团聚则成为应力集中源,降低强度与延展性。为应对分散与界面挑战,研究者开发了片状粉末冶金(将Cu粉预球磨为片状,使碳纳米管优先附着,抑制团聚并诱导取向分布^[34]),引入Ni^[44]、TiC^[33]、Mo^[45]等中间层改善润湿性,以及等通道角挤压、差速轧制、搅拌摩擦加工^[32]等大塑性变形工艺,这些方法不仅能细化晶粒,还能促进碳纳米管取向排列甚至构建三维网络。尽管如此,相比于纯铜,添加碳纳米管后复合导体的电导率普遍下降,落在53.7%~95.6% IACS区间^[1,33,34,37,38,44,46~52](图3(b))。值得注意的是,Zhang等人采用蔗糖辅助常压快速热退火在Cu粉表面原位生长三维石墨烯状纳米片,在仅0.096 wt%的超低添加量下,实现了电导率超过IACS 3.4%,抗拉强度319 MPa,强化效率达149.7%^[24]。

总体而言,粉末冶金法工艺成熟且易于产业化,但受限于碳纳米管分散均匀性及界面散射问题,该方法在超高电导率和载流能力上仍面临根本性挑战。Zhang等人^[53]通过第一性原理计算与四点弯曲实验发现,石墨烯掺入Cu基体后,尽管电子从Cu向石墨烯转移提高



图2 粉末冶金法制备CNT/Cu复合导体典型流程图

Figure 2 Synthesis of CNT/Cu composite conductors via powder metallurgy

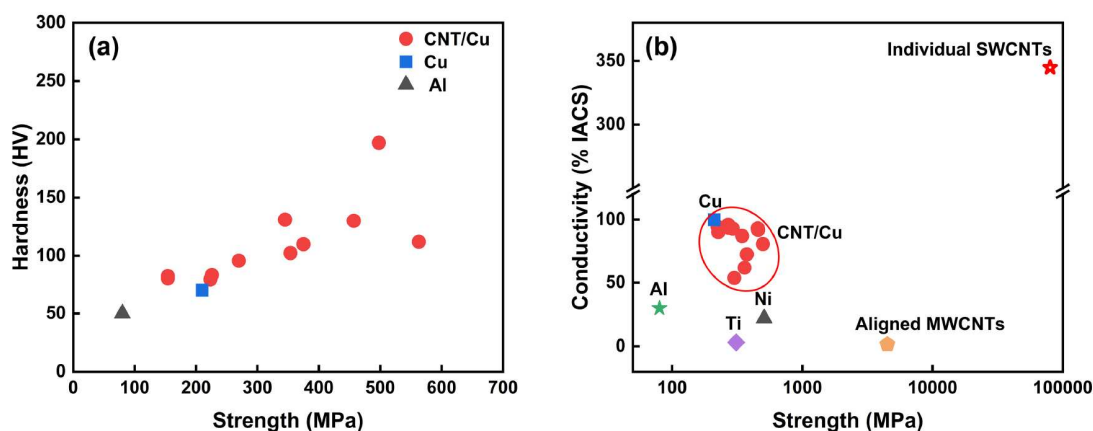


图3 粉末冶金法制备的CNT/Cu复合导体性能对比。(a) 抗拉强度和硬度的对比图; (b) 抗拉强度与电导率的对比图

Figure 3 Performance comparison of CNT/Cu composite conductors via powder metallurgy. (a) Tensile strength versus hardness; (b) tensile strength versus conductivity

了石墨烯的载流子浓度, 但界面散射显著增强, 导致复合材料整体电导率下降。这一发现揭示了粉末冶金CNT/Cu复合材料在追求力学增强时难以避免电导率牺牲的本质矛盾。

1.2 电沉积法制备及性能

电沉积法通过精确调控电解液组分、沉积参数、界面结合及工艺步骤, 可调节Cu在CNT骨架上的沉积, 实现从“核-壳”到“全混合”乃至“限域填充”的结构调控。“核-壳”结构通常通过硫醇功能化^[18]、预沉积Ni纳米颗粒^[19]或磁控溅射种子层^[21]等界面改性手段实现, 图4(a)为电沉积法制备CNT/Cu核壳纤维的流程图^[19]。在CNT表面引入活性位点或过渡层, 形成Cu-S、Ni-C、Cu-O-C等强化学键以降低成核势垒, 如图4(b)所示^[4]。这种致密的包覆结构赋予了材料极高的力学强度, 抗拉强度甚至超过1000 MPa^[18,19,22,31], 同时保持了 10^6 A/cm²量级的优异载流能力^[19,22]。“全混合”结构则多采用两步法工艺, 即先在有机电解质中预沉积Cu种子层实现均匀渗透, 再通过水相电镀使Cu与CNT网络深度交织, 如图4(c)所示^[3]。这种结构有效突破了“核-壳”结构的载流瓶颈, 将载流能力提升至 10^8 A/cm²量级^[3,54], 展现出卓越电子传输潜力。“限域填充”结构则侧重于利用添加剂调控镀液润湿性, 抑制表面过快沉积, 促进Cu向CNT束内部孔隙的深层填充^[55,56], 如图4(d)所示^[57]。该结构在耐高温性能方面表现卓著, 其耐受温度高达1179℃, 已高于Cu的熔点, 体现了优异的高温热稳定性。电沉积法凭借常温常压操作、工艺简便、

易连续化及CNT含量调控范围宽(1.5 vol%~84 vol%)等优势, 为制备高性能CNT/Cu复合导体提供了灵活且高效的技术路径。

电沉积法制备的CNT/Cu复合导体在力学、电学、载流及热学性能方面均展现出优异表现。在力学与电学性能的协同调控方面, 电沉积法制备的CNT/Cu复合导体表现出优异的综合性能, 抗拉强度跨度达318~2540 MPa, 电导率可在35%~97% IACS范围内通过工艺优化进行调控。Chen等人^[18]利用硫醇功能化形成Cu-S配位键并结合亚微米Cu种子层, 使复合纤维抗拉强度达1210 MPa, 电导率保持在69% IACS。Liu等人^[19]通过电化学预沉积Ni纳米颗粒形成Ni-C键及固溶过渡层, 强度达1100 MPa, 电导率为67.2% IACS。Zheng等人^[58]对比了Ni和Cu介质层, 发现Ni镀层力学增强效果最强但电导率下降较大, Cu介质层综合性能最平衡。Wang等人^[59]通过磁控溅射方法引入Al过渡层形成Al-C键, 制备出的复合纤维强度达6.6 GPa, 为原始CNT纤维(812 MPa)的8倍。Dong等人^[20]利用多巴胺热解构建氮掺杂碳层, 电导率为52.8% IACS, 比电导率提升20.7%。Xu等人^[21]利用湿纺单壁碳纳米管表面含氧官能团结合磁控溅射Cu种子层形成Cu-O-C键, 电导率达 $(4.84 \pm 0.3) \times 10^7$ S/m(约85% IACS), 比电导率为 $(1.01 \pm 0.04) \times 10^4$ S m²/kg(较纯铜高56%)。Bazbouz等人^[60]用周期脉冲反向电镀MWCNT/Cu纤维, 电导率为92.3% IACS, 比电导率为 9.38×10^3 S m²/kg(较纯铜高45%)。Park等人^[13]电镀后CVD生长石墨烯, 复合纤维比电导率为 5.6×10^3 S m²/kg。Kim等人^[61]通过热脱氧去除部分

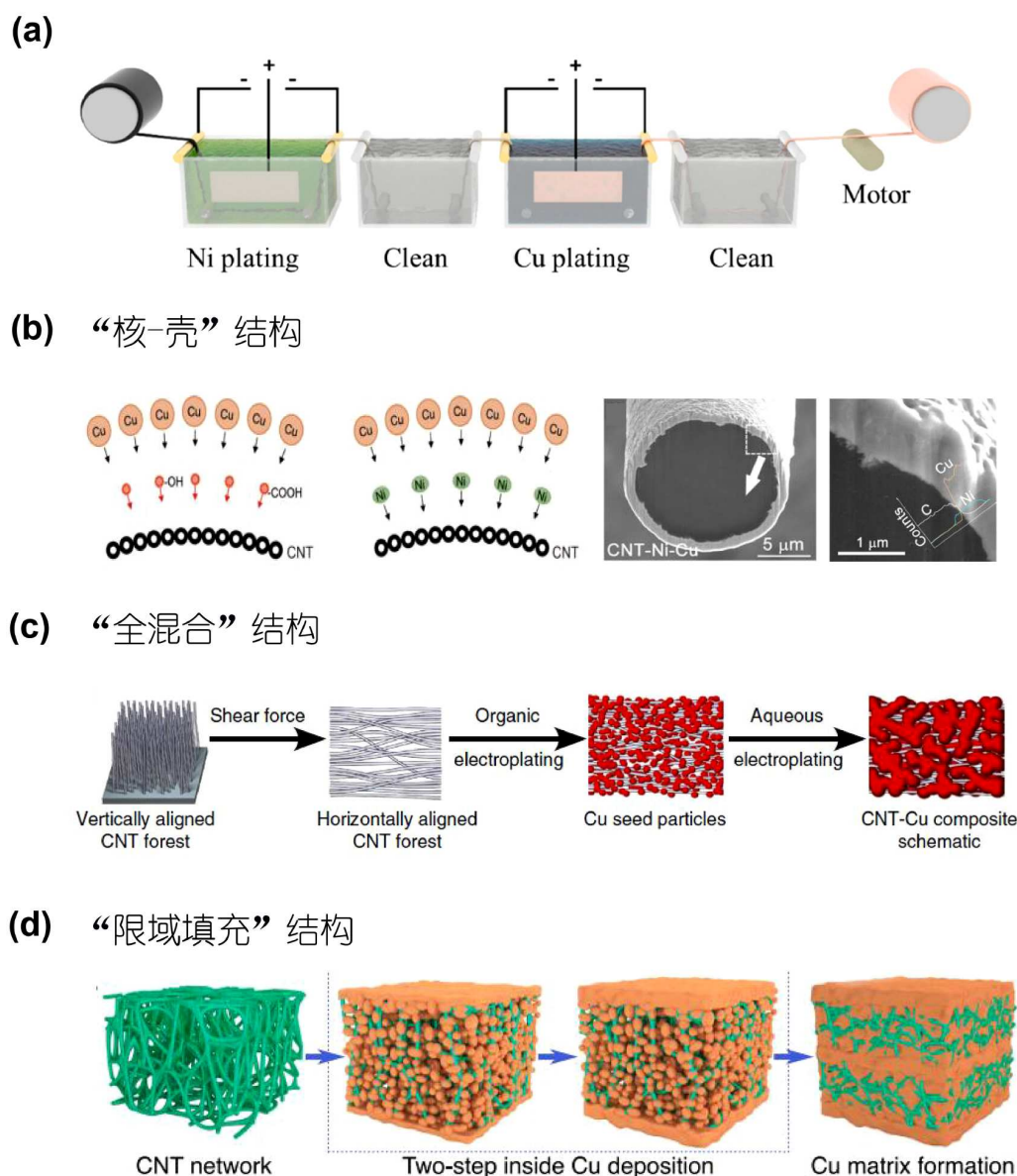


图 4 (a) 电沉积法制备CNT/Cu核壳纤维典型流程图^[19]; (b) CNT/Cu三种沉积方式的示意图及界面SEM图^[4]; (c) CNT/Cu复合导体的制备过程, Cu种子在碳纳米管表面成核生长示意图^[3]; (d) CNT/Cu复合导体在两步电沉积和热压过程中微观结构演变示意图^[57]

Figure 4 (a) Preparation process of CNT/Cu core-shell fibers via electrodeposition^[19]; (b) schematic of three deposition modes for CNT/Cu and their interfaces^[4]; (c) fabrication process of CNT/Cu composite conductors: schematic of copper seed nucleation and growth on the CNT surface^[3]; (d) schematic of the microstructural evolution of CNT/Cu composite conductors during two-step electrodeposition and hot pressing^[57]

含氧官能团, 复合膜垂直电阻从57.5 Ω 降至0.6 Ω , 水平电阻从30.8 Ω/sq 降至0.12 Ω/sq . 此外, 酸处理引入的羟基、羧基等含氧官能团可与Cu形成Cu-O-C键, 能在抗拉强度提高两倍的同时保持>90% IACS的电导率^[62~64]. 载流能力方面, 为系统比较电沉积法制备的CNT/Cu复合导体载流的提升情况, 本文汇总了文献中关于载流及电导率的研究数据, 结果如图5所示. 综合

文献研究可知, 部分CNT/Cu复合材料的电导率虽然仍略低于纯铜, 但载流能力优势极为突出, 相较于纯铜普遍提升几倍乃至一个数量级^[22,29,65,66]. 在典型研究成果中, Subramaniam等人^[3]制备的全混合膜载流性能最为优异, 高达 $6 \times 10^8 \text{ A}/\text{cm}^2$, 在100 MA/cm^2 的直流电流密度下可稳定运行超1200小时, 测试周期内电阻率的变化小于10%. Liu等人^[19]在碳纳米管纤维与Cu的界面处

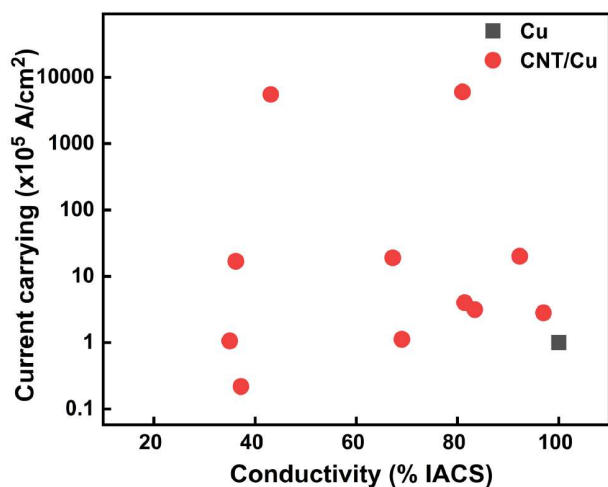


图5 CNT/Cu复合导体的电导率和载流对比图

Figure 5 Comparison of conductivity and current-carrying capacity of CNT/Cu composite conductors

引入Ni作为锚定点,有效强化界面结合强度,所制备的复合纤维载流能力达 1.9×10^6 A/cm². Li等人^[22]先通过氯磺酸对碳纳米管纤维进行致密化处理,再采用Ni纳米颗粒进行界面改性,制备的复合纤维载流能力为 1.68×10^6 A/cm². Bazbouz等人^[60]结合无酸湿法纺丝与周期脉冲反向电镀工艺制备多壁碳纳米管/Cu复合纤维,实现了优异的载流性能,可达 2.0×10^6 A/cm². Xu等人^[21]通过磁控溅射Cu种子层再电镀Cu,制备的纤维载流达 3.14×10^5 A/cm². Liu等人^[57]通过两步电沉积法制备的CNT/Cu复合薄膜载流达 4.0×10^5 A/cm². Daneshvar等人^[31]用硫醇功能化碳纳米管,再化学镀Cu,制备的纤维载流达 1.04×10^5 A/cm². 在热学性能方面,复合导体兼具低TCR和优异的高温稳定性. Subramaniam等人^[3]的全混合膜TCR低至 7.5×10^{-4} /K(仅为纯铜的1/9),且在80℃以上电导率反超纯铜. Chen等人^[18]的硫醇功能化纤维TCR约为纯铜的一半. Zou等人^[4]引入Ni缓冲层后,TCR降至纯铜的28%,并在90%载流下稳定运行100 h. Xu等人^[21]制备的纤维TCR为 1.68×10^{-3} /K(约为纯铜的一半). 在高温耐受性方面, Liu等人^[19]的Ni锚定纤维在300~500℃下电导率仅下降9.7%(纯铜则下降40%). Liu等人^[57]的网络限域结构复合膜耐受温度高达1179℃(高于纯铜熔点),热导率达418 W/(m K). Tao等人^[67]用不同种类镀液,通过抑制Cu在CNT表面沉积,使Cu进入碳纳米管薄膜内部,制备出优异性能的CNT/Cu复合薄膜. Park等人^[13]制备的石墨烯协同纤维热导率进一步提升至598 W/(m K). 此外, Arai等人^[55,56]利用PEG、

Cl⁻、JGB协同作用实现单步均匀填充; Yehezkel等人^[68]通过电位控制构建了Cu-CNT-Cu三明治结构,适用于大容量锂电集流体,展现出良好热稳定性.

电沉积CNT/Cu复合导体的突出优势在于其在高电流密度、高温、循环载荷等极端条件下的稳定性,这源于电-热-力多场耦合下的协同效应. 一方面,碳纳米管网络及CNT-Cu界面物理阻挡Cu原子扩散路径,显著提高电迁移激活能;另一方面,碳纳米管的高热导率(~ 3000 W/(m K))可快速导出局部热量,抑制热积累,有效延缓热致失效. 因此,电沉积法制备的CNT/Cu复合导体在载流能力上展现出远超纯铜的潜力. 综上所述,电沉积法通过界面化学键合、空间限域填充及协同散热等机制,实现了CNT/Cu复合导体的宽范围性能调控,是高性能复合导体走向应用较有潜力的制备技术.

1.3 气相沉积法制备及性能

气相沉积技术包括PVD和CVD,能在材料构建过程中同步实现界面生成与结构调控,具有界面纯净度高、微观形貌可控的优势^[69,70]. PVD(磁控溅射、电子束蒸发)在高真空下将金属原子沉积于CNT表面形成核-壳结构,沉积厚度可精确调控^[2,71],但沉积速率低、设备昂贵,难以实现复杂三维结构的均匀覆盖. CVD通过气态碳源在催化剂作用下裂解,原位生长CNT或沉积金属,可形成强化学键合界面,但通常需600~900℃高温,可能引发基体烧结或氧化,催化剂残留及工艺参数耦合影响性能稳定性.

在力学性能方面,研究者通过PVD沉积Cu膜并结合轧制致密化与拉拔处理,使复合纤维的抗拉强度从258 MPa提升至515 MPa^[72]; CVD原位生长CNT(如在Cu-Cr合金粉上以Cr为催化剂)结合放电等离子烧结,制备的复合材料抗拉强度达402.1 MPa^[73]; 焦耳加热CVD结合电镀Cu所得复合导体抗拉强度为92 MPa^[27]; 预压成形Cu-Cr合金粉形成三维多孔结构,经CVD原位生长CNT构建三维互连网络后,抗拉强度达421.2 MPa(提高47.6%)^[74]. 在电学性能方面,研究者通过磁控溅射在碳纳米管薄膜上沉积纳米晶Cu层,退火后形成共格外延界面,复合薄膜电阻率降至 $6 \mu\Omega$ cm(约28.7% IACS),远低于纯Cu薄膜的 $11 \mu\Omega$ cm^[26]; CNT纤维经PVD镀Cu及轧制后,电导率达 1.37×10^7 S/m(约23.6% IACS)^[72]; CVD原位生长CNT结合放电等离子烧结,复合材料电导率达90.9% IACS^[73]; 焦耳加热CVD利用CNT绳线高电阻节点的局部焦耳热,精准沉积Pt纳米

颗粒(~ 5 nm)后电镀Cu, 所得复合导体比电导率达 5.8×10^3 S m²/kg, TCR为 3.12×10^{-3} /K(低于纯铜)^[27]; 三维互连网络结构复合材料电导率达84.6% IACS^[74].

气相沉积技术通过原位界面调控可获得高质量的CNT/金属界面, 在微电子互连、薄膜器件等小尺度应用中具有不可替代的优势. 但PVD沉积速率低、设备昂贵; CVD高温易损伤基体、催化剂残留难以消除. 在宏观导体制备中, 单纯依赖气相沉积难以兼顾性能与成本, 更适合作为界面调控研究手段或与电沉积协同使用.

1.4 化学镀与分子级混合法制备及性能

鉴于碳纳米管与Cu基体间存在界面结合弱、润湿性差的问题, 研究者采用化学镀在碳纳米管表面构建金属包覆层, 形成“核-壳”结构, 以强化界面并提升综合性能^[5,44,75~77]. Shakibhamedan等人^[78]通过化学镀Cu包覆CNT, 再经球磨与放电等离子烧结, 显著提升了复合材料的硬度(128 BHN, 较纯铜提高151%)、剪切强度、电导率(80% IACS)和热导率(342 W/(m K)), 同时将热膨胀系数降至约12.7 ppm/K. Daneshvar等人^[31]则通过硫醇功能化碳纳米管实现无钯化学镀Cu, 构筑了强共价S-Cu键合界面, 所制纤维状CNT/Cu复合导线展现出超高比强度(抗拉强度达1 GPa, 为商用Cu线的5倍)和优异载流能力(1.04×10^5 A/cm², 约为铜的2倍), 且TCR降低近50%. 该方法界面结合牢固、性能协同提升显著, 但工艺繁琐、成本较高, 主要适用于纤维或粉末

前驱体, 适合高可靠性微互连、可穿戴电子及极端环境导体等高端应用的制备.

MLM通过溶液化学手段实现碳纳米管与金属前驱体在分子尺度的均匀复合^[35,38,46,51,79~82]. Liu等人^[83]采用喷雾热解结合MLM制备CNT/Cu复合粉体, 使纳米Cu颗粒作为“桥梁”锚定于界面, 经放电等离子烧结获得晶粒细小(≈ 0.9 μ m)、碳纳米管沿晶界均匀分布的致密块体, 兼具高强度(344 MPa)与良好塑性(伸长率19.6%), 界面载荷传递效率高达87.3%. Xiong等人^[84]在MLM过程中引入Ti元素, 烧结时原位生成Ti₈C₅纳米相钉扎CNT/Cu界面, 抗拉强度进一步提升至512 MPa. MLM技术分散均匀性好, 可实现细晶强化与界面强结合的协同, 但依赖复杂溶液处理与专用设备(如喷雾热解), 高温烧结能耗较高, 适用于需兼顾强度、塑性与导电性的高端结构功能一体化部件.

1.5 制备方法小结

为系统比较不同制备方法的综合表现, 本文基于现有文献数据, 从性能特征、工艺路径及工程化潜力等多维度对粉末冶金、气相沉积及电沉积三种方法制备的CNT/Cu复合导体展开系统分析. 如图6(a)所示, 粉末冶金法通过固相成形工艺实现碳纳米管在Cu基体中的弥散分布, 其复合材料比电导率较纯铜降低5%~24%^[1,7], 但比强度可提升至纯铜的240%左右^[2,4], 力学增强效果显著; 气相沉积法所得样品的比电导率大多低于纯铜, 而比强度则分布在纯铜的76%~820%之

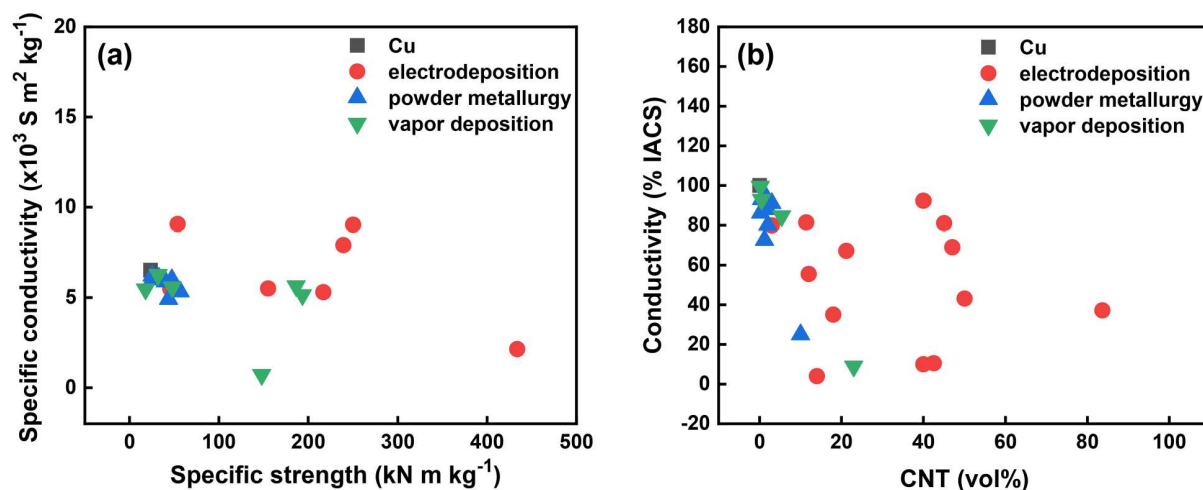


图6 不同方法制备的CNT/Cu复合导体的性能对比. (a) 比电导率与比强度的分布关系; (b) 电导率随CNT体积分数的变化规律

Figure 6 Performance comparison of CNT/Cu composite conductors prepared by different methods. (a) Distribution relationship between specific conductivity and specific strength; (b) variation of conductivity with CNT volume fraction

间^[13,23],数据离散性较大;相比之下,电沉积法展现出更为宽广的性能调控窗口,其比电导率可在较宽范围内调节,部分体系甚至超过纯铜。同时,比强度也覆盖从接近纯铜到数倍于纯铜的区间^[3,6],展现了该方法在多性能协同优化方面的潜力。图6(b)进一步揭示,粉末冶金法与气相沉积法受限于碳纳米管分散难度或高温损伤,碳纳米管含量多低于25%^[1,7],而电沉积法则可在1.5%~84%的宽范围内有效调控碳纳米管的引入量^[3,16,68],为宏观性能的定向设计提供了关键自由度。

表1则进一步更多维度地比较了四种制备方法。粉末冶金法虽工艺成熟、适合批量生产,但电导率牺牲与碳纳米管团聚问题仍待突破;气相沉积法虽可获高纯度界面,但成本高、效率低,规模化应用受限;电沉积法兼具工艺简便性(常温常压操作)、界面原位键合能力及连续化生产潜力,成为最具工程化前景的高性能CNT/Cu复合导体技术路线。然而,其在制备大尺寸块体材料时存在电流分布不均、沉积速率与厚度均匀性控制的挑战,易导致材料性能一致性下降,大规模结构件的工程化应用仍需进一步优化电极设计与沉积工艺参数。此外,化学镀与分子级混合等新兴方法虽通过界面工程强化结合强度,但高成本与复杂流程制约其工业化应用。上述分析表明,各方法在力电性能、工艺成本与规模化潜力间存在显著差异,其选型需依据具体应用场景对性能与成本的综合考量。

2 CNT/Cu复合导体的应用研究

CNT/Cu复合导体在轻量化线缆、微电子互连、柔性电子及极端环境导体等领域展现出优势。典型应用场景总结于表2。

2.1 轻量化高强高导电线缆

航空航天、新能源汽车、电动垂直起降飞行器等领域对线缆的轻量化、高比强度及耐弯曲性要求迫切。在轻量化方面,CNT/Cu复合纤维密度约为3.8~5.9 g/cm³,相较于纯铜实现了30%~50%的显著减重。Bazbouz等人^[60]采用周期脉冲反向电镀法制备的多壁碳纳米管/Cu复合纤维,比电导率高达 9.38×10^4 S cm²/g,较纯铜提升45%,载流能力为纯铜的4~6倍,且具备连续数百米级纺丝的工业化制备潜力。Xu等人^[21]通过磁控溅射引入Cu种子层制备的单壁碳纳米管/Cu复合纤维,比电导率较纯铜提升56%,经5000次弯曲循环后电阻变化率仅2%,非常契合便携式电子设备与无人机供

电系统对轻量化与柔性的严苛要求。在高强高载流性能调控方面,Li等人^[22]结合氯磺酸致密化与Ni界面改性策略,使复合纤维抗拉强度达2540 MPa,载流能力达 1.68×10^6 A/cm²,分别为纯铜的13倍和46倍,在海上风电、新能源汽车等高性能电力传输场景具备应用潜力。此外,Park等人^[13]采用电镀Cu结合CVD生长石墨烯工艺,构建石墨烯协同增强CNT/Cu复合材料,其比电导率可达纯铜的1.4倍,比强度为纯铜的5倍,比载流能力为纯铜的2.8倍,热导率高达598 W/(m K),可应用于电动汽车、无人机及城市空中交通的轻量化电线电缆制造。

2.2 微电子互连与封装

随着集成电路制程向5 nm以下节点推进,传统Cu互连面临电迁移失效、焦耳热积累、TCR高等严峻挑战。CNT/Cu复合导体凭借碳纳米管网络对Cu原子迁移的物理阻挡效应、超高载流能力以及与硅匹配的热膨胀系数,为下一代纳米尺度互连提供了新的解决方案。在超高载流与抗电迁移方面,Subramaniam等人^[3]制备的单壁碳纳米管/Cu复合薄膜兼具高载流、低TCR与高稳定性。该团队进一步实现了复合材料的纳米尺度图案化(最小线宽500 nm)与悬浮式多层电路构筑^[29],充分验证了其在三维集成和硅通孔技术中的应用潜力。在各向异性导电与杂散电流抑制领域,Luo等人^[63]制备的单壁碳纳米管/Cu导线电阻各向异性比高达96.5,可有效抑制杂散电流,适用于原子芯片冷磁波导与高功率片上互连场景。在界面层工程调控方面,Frost等人^[86]发现100 Å厚度的Ag层即可实现Cu的均匀镀覆,而Pt种子层展现出最优的抗电迁移性能,为碳纳米管生长后电镀Cu的微电子工艺中耐高温种子层的遴选提供了关键依据。此外,Song等人^[63]制备的4 μm超薄复合箔,电导率达94.5% IACS且兼具优异耐腐蚀性,是高可靠性PCB与锂电池集流体的理想候选材料。综上,CNT/Cu复合导体将在后摩尔时代的先进互连技术中扮演关键角色。未来需重点突破纳米尺度图案化精度、界面接触电阻调控及与CMOS工艺兼容性等核心瓶颈。

2.3 柔性可穿戴电子器件

CNT/Cu复合纤维/薄膜兼具高导电与耐弯折特性,在柔性电子领域展现出广阔的应用前景。在柔性调控方面,Zou等人^[4]引入Ni缓冲层制备的CNT/Cu复合纤

表 1 不同制备方法制备CNT/Cu复合导体性能对比表

Table 1 Comparison of properties of CNT/Cu composite conductors fabricated via different methods

制备方法	结构特征	核心优势	主要局限	典型电导率 (% IACS)	典型抗拉强度 (MPa)	典型载流能力 (A/cm ²)
粉末冶金	碳纳米管弥散分布于Cu晶界或片层间,多呈随机取向	工艺成熟、适于批量生产、可制备大尺寸块体、强化效率高(最高可达149.7%)	碳纳米管分散困难、界面结合弱、高温烧结易损伤碳纳米管、电导率下降明显(5%~50%)	53.7~95.6	218~563	未普遍测试(通常较低)
电沉积	“核-壳”或“全混合”结构,Cu连续相包覆或填充碳纳米管骨架	常温常压操作、界面可控、可连续化生产、载流能力极高、性能调节范围宽	需界面功能化预处理、对碳纳米管骨架均匀性要求高、厚壁填充困难	35~97	318~2540	10 ⁵ ~10 ⁸
物理/化学气相沉积	薄膜或核-壳结构,界面纯净,碳纳米管表面金属包覆或原位生长	界面质量高、结合强(可形成外延或共价键)、结构可控、适合微纳器件	设备昂贵、沉积速率低、难以规模化、高温CVD可能损伤基体	15~45 (薄膜)	100~500 (纤维)	未普遍测试(小尺度下较高)
化学镀/分子级混合 (MLM)	碳纳米管表面金属包覆(化学镀)或分子尺度均匀复合(MLM)	分散均匀、界面结合强、可精确控制成分、强化效率高	工艺繁琐、成本高、废液处理难、主要适用于粉末/纤维前驱体	70~90	300~500	未普遍测试

表 2 CNT/Cu复合导体典型应用场景

Table 2 Typical applications of CNT/Cu composite conductors

应用领域	核心优势	关键性能指标	典型应用场景	代表文献
轻量化高强高导电线电缆	低密度、高比强度、高比电导率、耐弯曲	比电导率 9.38×10^3 S m ² /kg(较纯铜高45%); 电导率35%~97% IACS; 抗拉强度318~2540 MPa; 密度3.8~5.9 g/cm ³	航空航天电缆、新能源汽车高压线束、无人机供电、电动垂直起降飞行器(eVTOL)、海上风电输电	[13,21,22,60]
微电子互连与封装	超高载流、低电阻温度系数、热膨胀匹配、可图案化	载流能力 $10^7 \sim 10^8$ A/cm ² (较纯铜高1~2个数量级); 电阻温度系数低至 7.5×10^{-4} /K(纯铜的1/9); 最小线宽500 nm; CTE与Si匹配	纳米尺度片上互连、三维集成(3D IC)、硅通孔(TSV)、功率逆变器、原子芯片磁波导	[3,29,65]
柔性可穿戴电子器件	耐弯折、超薄、柔性、可拉伸	弯曲10000次电阻不增反降; 最小厚度4 μ m; 180°弯折无剥离; 方阻可低至14 Ω /sq	柔性导线、可穿戴传感器、电热织物、锂离子电池集流体、超级电容器电极、电磁屏蔽层	[4,68,63,56]
极端环境特种导体	宽温域稳定、抗热冲击、抗辐照、耐腐蚀	300~500℃电导率下降仅9.7%(纯铜下降40%); 450次热冲击(-196~150℃) $\Delta R/R_0 < 30\%$; 5 dpa辐照后孔洞<2 nm; 腐蚀电流密度低至 1.36×10^{-6} A/cm ²	深空探测电气互连、核反应堆涂层、高温电机绕组、海上风电电缆、军事装备	[19,63,85]

维, 经10000次弯曲循环后电阻非但未增加反而降低了; Xu等人^[21]制备的复合纤维弯曲5000次后电阻仅增加2%, 均体现出卓越的耐弯折性能。Yehezkel等人^[68]通过电沉积构筑Cu-CNT-Cu三明治结构并将其用作锂离子电池集流体, 首圈放电容量达263~333 mAh/g; Arai等人^[55]制备了碳纳米管增强三维多孔Cu膜, 在超级电容器电极应用中表现出优异的电化学性能; Xing等人^[87]将Cu纳米线与碳纳米管共沉积, 使复合材料垂直热导率提升至10.1 W/(m K), 有效优化了柔性器件热管理能力。在智能织物领域, 研究者用真空蒸镀法在棉织物表面负载CNT/Cu复合层, 使织物的方阻降低92%, 经1000

次弯曲后方阻仅增至初始值的1.8倍, 且在15 V电压下可实现72℃电热升温, 适用于可穿戴加热保暖服饰。尽管性能优异, 该领域的规模化应用仍需解决大面积、卷对卷制备工艺优化以及多模态传感集成等工程难题。

2.4 极端环境特种导体

深空探测、核能系统、高超音速飞行器及海上风电等极端服役环境, 对导体材料的宽温域稳定性、抗热冲击、抗辐照、耐腐蚀性能提出了严苛要求。CNT/Cu复合导体凭借碳纳米管网络的物理屏障作用、低热膨胀系数及优异的化学稳定性, 在极端环境应用中展

现出不可替代的应用优势。在宽温域导电稳定性方面, 多项研究显示, CNT/Cu复合导体的TCR显著优于纯铜。Liu等人^[19]制备的Ni锚定CNT/Cu纤维, 在300~500℃高温下电导率仅下降9.7%(纯铜降40%)。Subramaniam等人^[3]制备的单壁碳纳米管/Cu复合膜TCR极低, 在80℃以上电导率反超纯铜。Zou等人^[4]制备的Ni缓冲层复合纤维TCR为 $1.14 \times 10^{-3}/\text{K}$, 仅为纯铜的1/3.6。在抗热冲击与深空应用领域, Gao等人^[88]在单壁碳纳米管纤维上电沉积Ni中间层, 经450次热冲击(-196~150℃)循环后电阻变化率仅29.8%, 可满足深空探测与航空航天等温度交变极端环境的应用需求。在抗辐照与耐腐蚀性能方面, 磁控溅射制备的CNT/Cu薄膜经 6.25×10^{17} ions/cm² (5 dpa) He离子辐照后, 内部孔洞尺寸仅0.6~1.6 nm, 远小于纯铜薄膜^[85]; 碳包覆层进一步抑制晶界迁移, 使复合材料在400℃、5 dpa辐照条件下仍保持结构稳定, 可作为新型核反应堆结构组件的防护涂层。Song等人^[63]采用GO辅助电沉积制备的复合箔, 腐蚀电流密度低至 1.36×10^{-6} A/cm², 且表面无腐蚀孔洞, 耐蚀性能显著提升。极端环境特种导体是CNT/Cu复合导体最具差异化竞争优势的发展方向。未来应加强高温、辐照、腐蚀多因素耦合环境下的长期可靠性研究, 并着力开发与现有工程体系兼容的接口适配技术。

3 总结与展望

CNT/Cu复合导体的核心价值在于通过界面工程与多尺度结构设计, 突破传统Cu导体中存在的“强度-导电性倒置关系”。主要机制是利用CNT网络的高强度与高载流能力, 结合Cu的高导电性, 通过界面化学键合

(如Cu-S、Ni-C、Cu-O-C)降低电子散射, 并通过空间限域结构抑制电迁移和热失效, 从而实现力、电、热性能的协同优化。不同制备方法因界面调控机制和结构构建能力的差异, 展现出不同的性能特征与应用场景。粉末冶金法工艺成熟、适合批量生产, 但电导率牺牲明显(较纯铜下降5%~50%), 主要用于高强结构部件; 气相沉积法界面纯净、适合微纳器件, 但难以规模化; 化学镀与分子级混合法可实现强共价界面(如S-Cu键)和高均匀分散, 但流程复杂、成本较高; 电沉积法则在常温常压下操作, 通过界面功能化、种子层设计及两步沉积等策略, 实现了从“核-壳”到“全混合”的多种结构可控构建, 其电导率覆盖35%~97% IACS、抗拉强度达318~2540 MPa、载流能力高达 $10^5 \sim 10^8$ A/cm²(较纯铜提升1~2个数量级), 在性能调控范围、界面工程灵活性及连续化生产潜力方面均展现出综合优势, 是当前最具工程化前景的技术路线。然而, 从实验室走向工程应用仍面临碳纳米管均匀分散与结构可控性、界面长期稳定性、宏观结构多性能协同优化以及低成本规模化制备等共性挑战。未来研究应进一步融合理论计算与实验, 深化界面电子输运机制认识; 发展卷对卷电沉积、智能添加剂筛选与在线退火等连续化工艺; 并针对轻量化线缆、微电子互连、柔性电子及极端环境导体等具体应用场景, 开展多因素耦合环境下的服役可靠性研究。可以预见, 随着界面工程与结构分级设计理念的深入, 电沉积法将在推动CNT/Cu复合导体从实验室走向产业化进程中发挥核心作用, 为下一代高效、轻质、可持续的电气与电子系统提供关键技术支撑。

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Summary for “碳纳米管/铜复合导体的制备、性能与应用研究进展”

Recent progress in the preparation, properties, and applications of carbon nanotube/copper composite conductors

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Driven by the global push for carbon neutrality and the escalating demand for lightweight, high-power, and highly integrated systems, emerging sectors—including aerospace, new energy vehicles, and advanced electronics—require conductors that transcend the limitations of traditional materials. These applications necessitate a synergistic combination of high electrical conductivity, high mechanical strength, superior current-carrying capacity, and stability in extreme environments. Carbon nanotubes (CNTs), possessing a quasi-one-dimensional structure, ultra-high intrinsic ampacity, low density, and exceptional mechanical properties, have emerged as ideal candidates for constructing next-generation composite conductors. This review systematically examines the recent advancements in CNT/Cu composite conductors, focusing on interface regulation, hierarchical structural design, and advanced fabrication techniques. This paper comprehensively reviews mainstream preparation methods: powder metallurgy (PM), physical/chemical vapor deposition (PVD/CVD), and electrodeposition. A comparative analysis reveals distinct performance trade-offs. PM, while mature and suitable for bulk production, often suffers from CNT agglomeration and interfacial scattering, typically resulting in a 5%–50% reduction in electrical conductivity compared to pure copper, despite achieving moderate strengthening. PVD/CVD methods offer high interface purity and are ideal for micro/nano devices, yet they face challenges in scalability and high equipment costs. In contrast, electrodeposition has become the predominant strategy due to its ambient processing conditions, ease of continuous fabrication, and exceptional capability for interface and structural control. Advanced electrodeposition techniques, such as “core-shell” and “all-in” mixing structures, have enabled the fabrication of composites with conductivity ranging from 35% to 97% IACS, tensile strengths spanning 318–2540 MPa, and ampacity exceeding that of pure copper by 1–2 orders of magnitude (up to 6×10^8 A/cm²). This review highlights the critical role of interface engineering in overcoming the “strength-conductivity trade-off” inherent in traditional conductors. Strategies such as sulfur/oxygen functionalization, Ni nanoparticle anchoring, and nitrogen-doped carbon layers have been pivotal in enhancing interfacial binding energy and reducing contact resistance. Furthermore, the text outlines the application potential of these composites in four key domains: (1) lightweight power cables for aerospace and electric vehicles, leveraging their high specific strength and conductivity; (2) microelectronic interconnects, utilizing their superior resistance to electromigration and low thermal expansion; (3) flexible and wearable electronics, benefiting from their fatigue resistance and bendability; and (4) specialized conductors for extreme environments, capitalizing on their thermal stability and radiation resistance. Despite significant breakthroughs, the review identifies persistent challenges regarding the scalable manufacturing of high-purity CNTs, the precise control of macroscopic structures, and the cost-effectiveness of production. The paper concludes by advocating for the deep integration of precise interface engineering, multiscale structural design, and engineering-oriented fabrication processes. Future research should focus on developing a new generation of CNT/Cu composite conductors that achieve an optimal balance of high conductivity, strength, toughness, and reliability, thereby providing critical material support for next-generation efficient and sustainable electrical systems.

CNT/Cu, interface, conductivity, current-carrying-capacity, mechanical properties

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