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Microstructure of Electrodeposited Copper Foil: Discussion on the Mechanism Model of Three-Dimensional Electrocrystallization

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电沉积铜箔的微观组织结构
——三维电结晶模式中的电结晶机理探讨

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摘要: 电沉积铜箔随着印刷线路板和锂离子电池的大量应用而越来越受到重视,产业规模仍在发展中。相对于电镀设备的制造和电沉积工艺的开发,但有关电沉积的机理方面的研究较少。本文总结了电沉积铜箔的制造过程并分析了不同电沉积铜技术中各电镀参数的差异,指出电沉积电流密度在铜箔形成过程中的重要作用。通过展示和比较不同电沉积铜箔的微观组织结构, 讨论了电沉积中各影响因素对铜箔微观组织结构以及对其宏观机械性能的影响。从前人研究结果中发现电沉积条件和镀液组分对铜箔微观组织形貌及其宏观机械性能有重大影响,但电解铜箔的晶粒大小、织构等微观组织结构参数与其宏观机械性能间无法建立起有效的关联,这对以镀层的微观组织结构为桥梁来建立电沉积条件对铜箔宏观机械性能的理论框架带来极大的困扰。前人试图通过研究铜箔电沉积机理来解决这一难题。经典金属电沉积理论认为提高过电位能够增加瞬时成核数量并降低晶粒平均尺寸,但无法解释结晶中择优取向等问题。渡边辙发现电沉积与冶金的相似性,认为电沉积金属的微观组织结构与金属熔点相关,但其"微观结构控制"理论还存在一些缺陷,例如无法解释添加剂对晶粒的细化作用等。笔者建议可从价键及能带理论角度重塑电沉积机理与铜箔宏观性能间的关系, 既通过建立铜箔电沉积过程中金属键形成与铜显微组织结构的理论联系,探讨其对铜箔宏观特性的影响。

关键词: 过电位; 电流密度; 铜晶粒; 铜箔织构; 物理性能

1 引 言

金属电沉积是一种通过电流作用还原溶液中金属离子, 并沉积到基体表面形成具有一定特性的金属层的方法, 广泛应用于机械、化工、电子、航空航天等领域, 是现代工业中不可或缺的制造加工技术[1,2]。电沉积铜箔制造是一种具有鲜明技术特点的连续金属电沉积方法, 近年来随着铜箔应用下游的电子电路和锂离子电池的快速发展而受到学术界和产业界越来越多的关注[3,4]。对电沉积铜箔技术的研究和开发主要集中在通过调控有机、无机添加剂来改变镀层微观结构,进而获得更薄、更大抗拉强度或延展性等功能性的铜箔,在应用技术开发层面有大量论文和报告发表[5-7]。

然而, 与电沉积铜箔相关的电化学基础理论的研究和发展相对滞后。经典电沉积(结晶)理论体系中的络离子阴极放电、添加剂吸附延迟放电等理论无法解释酸性硫酸铜镀液中添加剂的界面电化学作用机制, 也无法建立添加剂及电沉积参数与镀层微观结构间的因果联系, 大部分添加剂的研发工作还依赖于全面试验法[8,9]。另一方面,经典理论体系[10]试图从沉积过电位角度协调沉积速率与沉积层微观结构的关系, 而忽视了表征反应速率的最关键参数——电流(密度)在其中的作用。最后, 电沉积过程中的能量转换过程也没有得到详细分析。

本文拟将经典电沉积理论和近年来的一些研

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究成果结合笔者的个人见解，就铜箔电沉积过程中电流密度的作用做出一些初步探讨。这一探讨不仅适用于铜箔制造技术中的理论问题，也是对金属电沉积即电结晶过程中电子的行为和作用的新的诠释。虽是一孔之见，仍愿作引玉之砖抛出，以供同行参考。

2 电沉积铜箔及其发展

铜箔制造主要有压延法和电沉积法两种。随着技术的不断发展，电沉积铜箔在能耗、铜箔厚度、蚀刻特性等方面的优势压倒压延铜箔，占铜箔市场的65%以上。铜箔的电沉积方法制造相较于其他电沉积技术，起步不算太晚。1922年，美国的Edison首先申请了金属箔的连续制造专利；1937年，美国Anaeonde制铜公司开始生产铜箔，电化学制造铜箔进入工业化时代；1955-1970年代，美国Gould公司和Yates公司相继在美国、欧洲、亚洲建厂发展电沉积铜箔业，标志着电沉积铜箔制造及表面处理技术跨入了新阶段[11]。1993年Gould公司推出低轮廓电沉积铜箔标志着电沉积铜箔发展进入到“高性能铜箔”时期，而电沉积铜箔生产中心也逐渐从美国转移到亚太地区。进入21世纪，我国电子电路行业的突飞猛进带动国内标准电沉积铜箔产能快速增长，形成了较为完善的产业链、市场体系和行业规范。同时随着我国成为锂电池制造和应用的重要市场，锂电池用铜箔的制造已经形成规模[12]。据中国电子材料行业协会电子铜箔材料分会统计，当前我国已经成为铜箔的核心生产基地之一，内资电沉积铜箔生产厂家超过30家，产量占全球的60%，并以10%以上的年复合增长速度发展[13,14]，我国铜箔产能产量发展如图1所示。内资厂商技术积累与全球龙头仍有较大差距，产品以中低端为主。近年来，在各方努力下，与之相关的铜箔品类、装备、工艺和电沉积添加剂等的研究和技术开发也不断涌现[15,16]，高端产品的国产化替代进展明显。

目前，电沉积铜箔主要分为电子电路用铜箔和锂离子电池用铜箔两大类。电子电路铜箔发展较早，并且依电子电路产品的需求发展出标准铜箔、反转铜箔、超低轮廓铜箔、超薄载体铜箔等许多种类[17]，主要强调延展性、界面结合力和表面轮廓度等特性[18]，厚度从5 μm到数百μm不等，国内产量最大的是厚度18 μm和35 μm的标准铜箔。如图2所示，电沉积铜箔主要包括制液、电解沉积生箔、后处理和分切包装四个环节，其中电解生箔是制造电沉积铜箔的核心步骤[19]，见图3。

3 电沉积铜箔制备技术和主要影响因素

制液是将空气不断鼓入热的硫酸溶液溶解金属铜形成硫酸和硫酸铜溶液的过程，再通过净化、调整和补充添加剂，得到电沉积铜镀液[20]。主要反应方程式为：

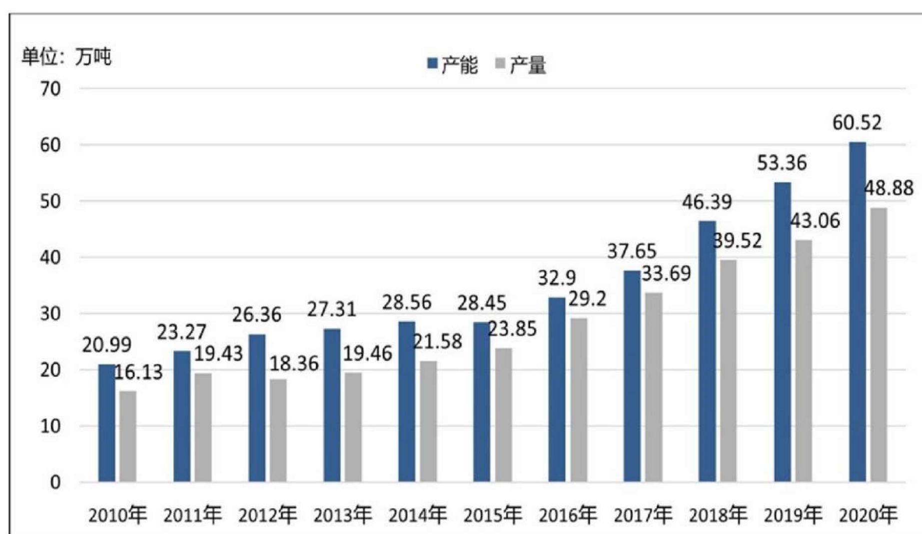


图1 2010～2020年我国电解铜箔产能、产量变化趋势图[14]（网络版彩图）

Figure 1 Trend chart showing production capacity and output of electrolytic copper foil in China from 2010 to 2020[14] (color on line)

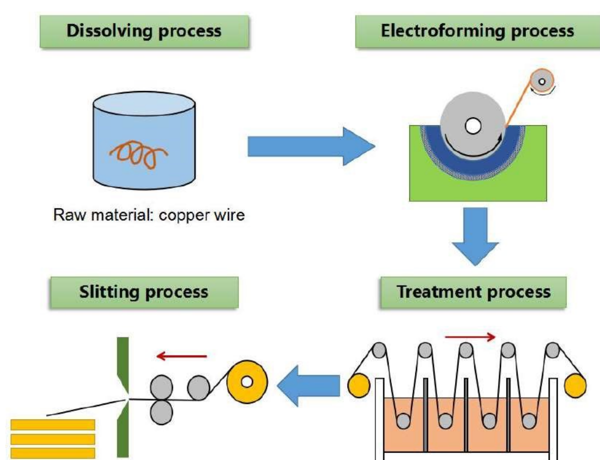


图 2 电解铜箔生产流程图(网络版彩图)

Figure 2 Electrodeposited copper foil production flow chart (color on line)

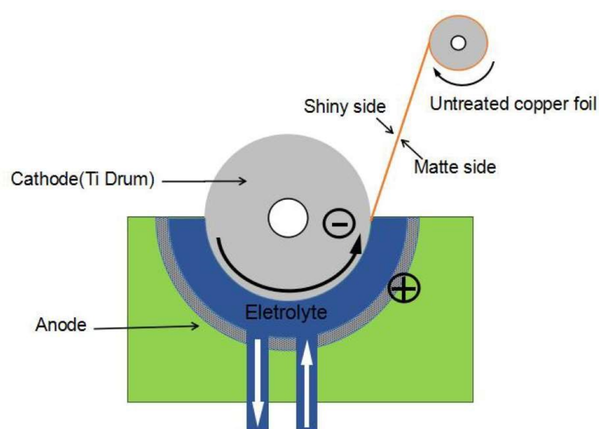
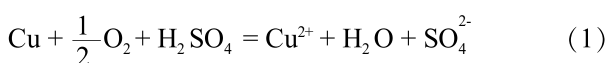


图 3 电解生箔原理图(网络版彩图)

Figure 3 Schematic diagram of production of electrodeposited raw copper foil (color on line)



$$Cu + \frac{1}{2}O_2 + H_2SO_4 = Cu^{2+} + H_2O + SO_4^{2-} \qquad (1)$$

电解生箔一般采用辊式连续电解方法，以 Ti 合金制成的辊筒为阴极基底，电解过程中辊筒部分浸入镀液中并保持辊筒连续转动，铜不断还原沉积在辊筒表面形成致密的铜层，在辊筒转至与镀液脱离后铜层被从基底上剥离、收卷，生箔机和钛合金阴极辊实物见图 4。如表 1 所示，电解生箔的镀液以及主要电镀参数和常规酸铜电镀有较大差异[21,22]。所获生箔一面转印了 Ti 辊光滑平整的表面，称为光面；而面向溶液一面轮廓粗糙且没有光泽，称为毛面，见图 5。生箔再经过打磨、电镀 Zn、

图 4 生箔机和钛合金阴极辊实物图(网络版彩图)

Figure 4 Photographs of electrodeposited copper raw foil machine (left) and Ti drum cathode (right) (color on line)

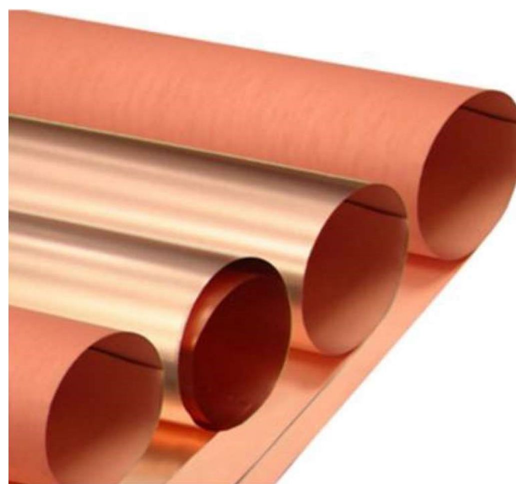


图 5 电解铜箔实物图(网络版彩图)

Figure 5 Photograph of electrodeposited copper foil (color on line)

Cr、Sn 等金属或涂布树脂等后处理来修整表面轮廓、抗氧化和提高结合力等[23,24]，最后经清洗烘干，分切和包装完成生产。

锂电铜箔作为锂离子电池的负极集流体具有较高的电导、热导和抗拉强度，但对铜箔的延展性要求较低[25]。为提高电池的重量及体积能量密度，锂电铜箔发展方向主要是降低厚度，主流锂电铜箔厚度已经从 9 μm 降至 6 μm，并向 4.5 μm 过渡。锂电铜箔生产流程与上述电子电路铜箔生产流程相同，但添加剂配方更接近于常规电镀铜配方，电解电流也略低于电子电路铜箔，生箔无需进行其他后处理直接应用于电池制造。

可见，电沉积铜箔与常规酸性电镀铜在镀液组成上有一定差异性，但在施镀温度和沉积电流

表 1 电解沉积电子电路铜箔和常规酸铜电镀的主要操作参数比较[21,22]

Table 1 Comparison of operating parameters in electrodeposited copper foil and conventional electrolytic copper productions[21,22]

Main operational parameter	Electrodeposited copper foil	General acid copper electroplating
Concentration of inorganics Cu^{2+}(g·L^{-1})/H_2SO_4(g·L^{-1}) /Cl^-(mg·L^{-1})	65 ~ 100 / 90 ~ 140 / 40	15 ~ 50 / 50 ~ 250 / 60
Additives	Natural reagent: collagen, gelatin, etc.	Artificial reagent: PEG, SPS, JGB, etc.
Temperature (℃)	55 ~ 80	18 ~ 30
Current density (A·dm^{-2})	35 ~ 130	1 ~ 3

密度上有显著差异[26-28]。特别是铜箔电沉积的电流密度远远高于酸性镀铜规定的电流密度。如此高密度的电子流在铜箔连续电沉积中的影响机制是什么？这是一个值得探讨的问题。

铜箔生产过程中,除沉积电流密度外,需要重点管控的工艺参数有钛阴极辊表面状态[29]、基础盐的浓度[30]、添加剂浓度[31,32]、温度和溶液搅拌强度[33]等。实践中发现 Ti 阴极辊表面颗粒度大小和平整性不仅影响铜箔光面的轮廓度，还能影响铜箔光面侧的结晶织构[34,35]。一般将此现象解释为初始沉积铜受基底影响的外延生长，因此在非金属的石墨电极或玻碳电极上无法沉积出致密的铜膜。另一方面钛和铜的晶格结构差异在 20%以上使得铜与钛间相互作用较弱，达到一定厚度的铜箔就能够顺利从钛基底上剥离。除此之外,钛阴极辊在铜箔生产中还充当集流体角色，其电导能力对表面的电流分布和温度(电阻致热)有较大影响[36,37]。

研究还发现,镀液中 H^+ 浓度较高后容易产生还原氢与钛产生合金化作用,破坏钛辊表面平整、光滑的结构[38]。并且镀液中 Cu^{2+}、H^+ 浓度与电流密度、温度间有交互作用，一般从 Cu^{2+} 的界面消耗和传质速率关系的角度来解释。Cu^{2+} 浓度较低时，可能无法保证界面上的消耗，而可能增加阴极极化电位而导致产氢。这时提高镀液温度和镀液对流强度,有助于增强阴极界面上 Cu^{2+} 的补给,据测算镀液温度提高 10 ℃，极限电流密度可以提高10%。提高温度还可以提升铜的溶解度,以便增加镀液中 Cu^{2+} 浓度。因而高电流下的电沉积往往伴随较高的镀液温度。低 H^+ 浓度会造成镀层疏松，提高 H^+ 能够提高镀液电导，但考虑到同离子效应，镀液中盐浓度过于接近饱和浓度会使硫酸铜易受温度微小波动引起结晶,而影响产品品质。

添加剂可增大铜沉积的阴极极化，有利于获得致密的箔层,并提高铜箔的延展性、光亮性和硬度等[39]。一般认为添加剂通过吸附在电极表面阻滞 Cu^{2+} 放电,并能够在铜结晶过程中增加晶核密度,细化结晶。因此,添加剂也被认为是调控铜箔微观结构的主要因素[40-42]。

需要注意的是，铜箔工业生产过程中主要采用控电流的模式,而电压(阴极过电位)受太多因素影响而没有受到(也无法)精确控制。日本一些厂商通过多阳极分区控制来调节铜箔电沉积过程中的电压和电流密度,取得了较好的效果[2]。

4 铜箔微观结构分析

5G 应用和新能源车的需求主导了近年来铜箔制造技术的发展方向，如何在保障铜箔机械强度的前提下，尽可能降低其厚度和表面轮廓度是当前最大的挑战[43]。实践中,期望依照金属学分析理论既以金属微观组织结构为桥梁，探索电沉积反应各控制参数和添加剂的界面效应与金属层宏观特性间的关联，构建起电沉积铜箔技术的理论框架。

分析铜箔微观组织结构的主要方法有光学金相分析、X(或中子)射线衍射及电子显微镜分析。图 6 分别展示了电子电路铜箔、锂电铜箔和电子电镀铜的金相显微照片。从俯视图来看,铜晶粒明显低于光学显微镜的分辨能力；制作纵剖面切片并施以微蚀,可以观察到一些粗略的高级结构,但无法分辨晶粒的情况。

X 射线衍射法常常用于分析铜箔的织构,并可以利用谢乐公式计算晶粒的尺寸[54]。但这种分析是基于统计的宏观结果，只能够得到铜箔中一些特定取向所占的体积分数，但不能了解微观的晶粒取向在铜箔中是如何分布的。图 7 展示了文献中采用常规的高角 X 射线衍射法测量得到的不同

表 2 电子电镀铜、电子电路铜箔和锂电铜箔的微观结构差异及分析

Table 2 Microstructural analyses of electronic electroplating copper, electronic circuit copper foil, and lithium battery copper foil

Type	Reference	Average grain size	Dominant crystal plane orientation	Analysis
Acid electroplating copper	[44], [45]	15 ~ 40 nm; > 1 μm	Mostly (111) crystal plane	1. The copper foil with excellent mechanical properties has no absolute correlation with the orientation of the dominant crystal plane. Different dominant crystal planes can obtain high tensile strength (> 400 MPa) and elongation (> 4.0%). 2. Small grain size (tens of nanometers) has high elongation (> 5.0%), but large grains can also obtain copper foil with high elongation.
Electronic circuit copper foil	[11], [33], [46]	0.57 ~ 0.97 μm	(220), (111)	
Lithium battery copper foil	[47], [48], [11], [49], [50], [32]	35 nm ~ 14 μm	(200), (220), (111)	

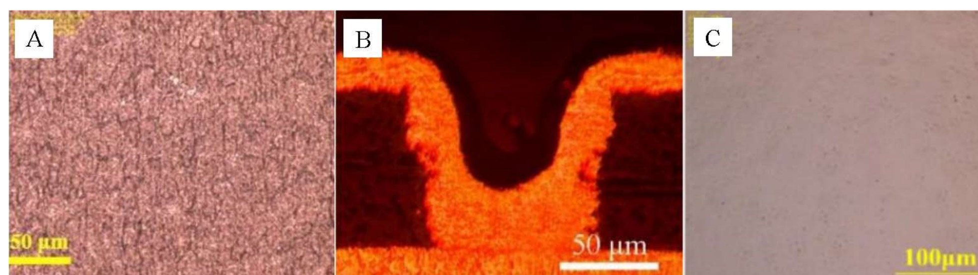


图 6 电子电路铜箔[51](A)、电子电镀铜[52](B)和锂电铜箔[53](C)的金相显微图(网络版彩图)

Figure 6 The surface topographic images of electronic circuit copper foil (A)[51], cross-section of electronic electroplating copper (B)[52], and surface of lithium battery copper foil (C)[53] (color on line)

电沉积铜层的结晶情况谱图，表 3 列出了对这些铜箔织构、晶粒大小的分析。与图 6 中展示的金相显微图比较，利用 X 射线衍射法计算出的铜箔晶粒大小远低于光学显微镜的分辨率，光学金相分析观察到的蚀刻线并不能反映真实的铜箔内结晶状态。

电子显微镜拥有更高放大倍率和更好的景深，结合氩离子抛光和聚焦离子束技术(FIB)消除界面应力后，能够较方便在横向截面上选取多点位进行综合分析，是目前研究电沉积铜箔微观组织结构的主要方法[56]。图 8 展示了经 FIB 抛光后在铜镀层中观察到的纳米孪晶相。另外，采用 EBSD 技术能够直接展示晶面取向并投射到极图上对镀层结晶织构进行分析(图 9)。

从上述分析中可以看到，在理论上还未真正建立起完善的电解参数、铜箔微观组织结构和其宏观机械性能的因果关系[58]。其中重要的一方面是对铜箔中夹杂、位错、缺陷等非完整性现象的分析和理解有限[59,60]，另外，常温下铜箔内自发的自退火效应也让研究铜箔沉积条件和微观结构因果关系变得更加困难[57,58,61]。

5 铜箔电结晶机理的探讨

过去的几十年间，大量的实践经验和文献充分证明了铜箔的延展性、微观组织结构和制造工艺参数间存在一定的关系，但对铜箔电结晶机理的探讨还较为欠缺。经典电沉积理论主要从极化

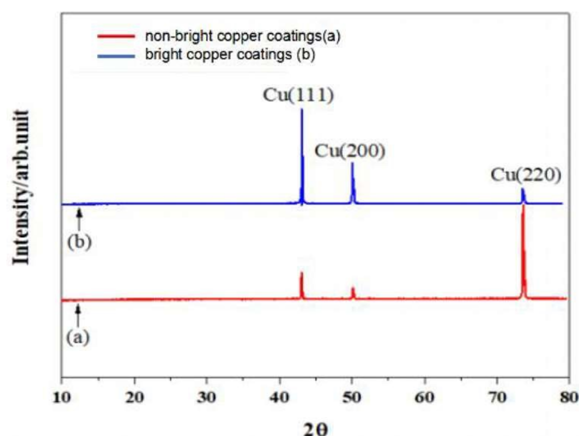


图 7 光亮铜镀层与非光亮铜镀层的 XRD 图[55](网络版彩图)

Figure 7 XRD patterns of bright and non-bright copper depositions[55] (color on line)

表 3 对应于图 7 的光亮镀层与非光亮镀层不同晶面的晶粒尺寸 (nm)[55]

Table 3 Grain size (nm) of different crystal planes of bright and non-bright depositions corresponding to which in Figure 7[55]

Crystal plane	Bright coating	Non-bright coating
Cu (111)	332	628
Cu (200)	223	473
Cu (220)	230	876

过电位的角度来解释电沉积对结晶微观组织结构的调控作用。经典电沉积理论认为,水合或络合的金属离子在阴极还原并脱离水化或络合状态,变成在基底表面迁徙的吸附原子，最终在表面的台阶、棱折等活性位点长入晶格[62]。Vetter[63]等认为晶体生长的过程与放电过电位、扩散过电位、反应过电位和结晶过电位共同组成的沉积过电位有关,沉积过电位的数值决定了镀层的微观结构,称为过电位原理(OT)。高过电位下沉积速率(即沉积电流密度)加快,于是吸附原子浓度增加,促使更多晶核形成，晶粒得以细化。但事实上，OT 理论不好解释镀层的择优取向、非晶和晶态镀层的获得等问题。并且在电沉积铜箔过程中,电沉积反应已经极大偏离平衡位置，过电位和电流密度之间并不一定符合 Tafel 关系，还有可能出现电化学振

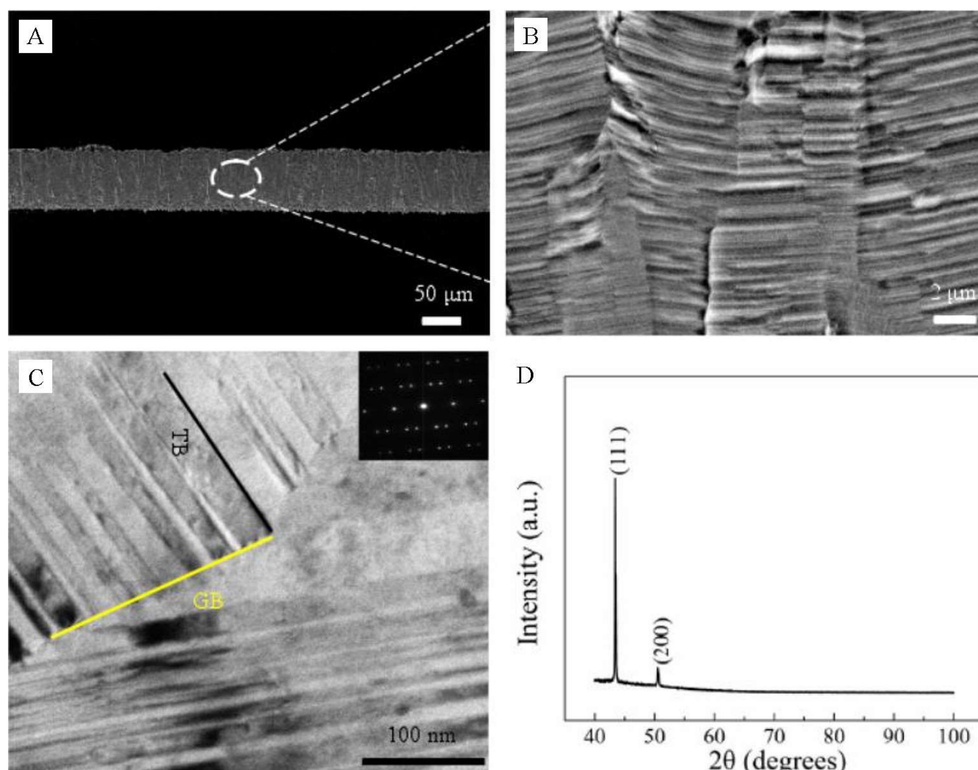


图 8 电解铜箔的截面 SEM 图(A),(B)(A)图选区 5000 倍放大,(C)TEM 图,(D)XRD 图;GB:晶界,TB:孪晶界[57]。

Figure 8 The cross-sectional SEM images (A), and 5000 times magnification of the selected area, (C) TEM image (GB: grain boundary, TB: twin grain boundary), and (D) XRD image of the electrodeposited copper foil[57].

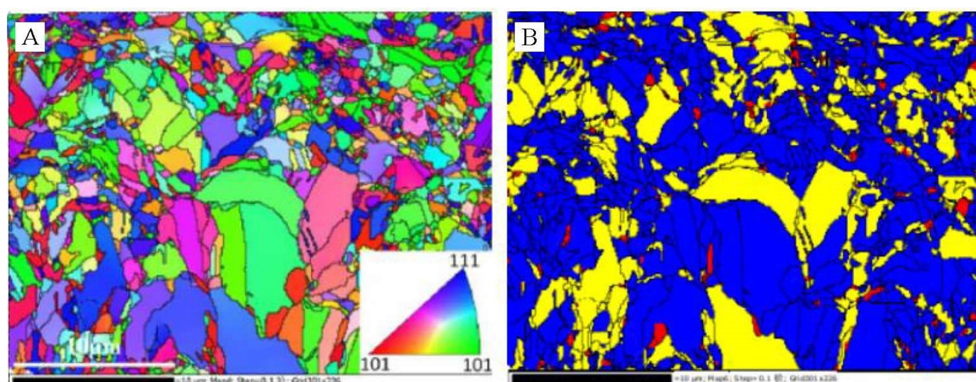


图 9 Cu/CNTs 复合铜箔 EBSD：(A) IPF 反极图，(B) 再结晶组织结构分布图[47] (网络版彩图)

Figure 9 The EBSD images of Cu/CNTs composite copper foil: (A) IPF inverse pole figure, (B) image of recrystallized structure[47]. (color on line)

荡现象，这也给从过电位角度讨论电沉积过程带来了理论上的困难。

渡边辙通过大量实验认为电沉积和金属淬火过程相似，从金属学研究角度对镀层微观结构进行了解释，提出了微观结构控制原理(TMC)[65]。该理论认为电镀层的微观结构与金属的熔点相关。金属离子在界面放电还原过程中释放出的能量高达几个 eV，足以将原子加热到数万度，界面热量通过电镀液和基底扩散，相当于一个急速淬火的过程，这时高熔点金属固化时间快，倾向于多处形核，导致细晶粒层的形成，而低熔点金属的固化较慢，相应延长了原子的表面扩散距离，于是形成较粗大晶粒。并且镀层纯度越高，晶粒尺寸越大。镀层的微观结构主要取决于元素种类和化学成分而与电镀规范无关。但其理论对金属离子还原释放能量的估值过高，如铜还原所需过电位在 0.4 V 以内，新生原子动能远低于其理论设计的假定。

金属键理论[66]认为金属中自由电子的存在影响了金属的化学性质、熔沸点、金属颜色和金属光泽等。但尚未有文献较为系统地采用价键理论来解释电沉积过程与金属镀层间的关系，金属学中也更重视从原子密堆积的角度考虑金属结晶的问题，而未考虑到电子结构的重组及价键的生成。笔者认为，若以价键理论来研究金属电沉积过程，将能够推动我们对电沉积及金属镀层结构关系的理解。

经典理论主要从过电位角度来考虑晶粒的形成，而在铜箔沉积过程中真正起到影响作用的是电沉积的电流密度。若将电流密度视为金属键形成的速率，并采用量子化学计算的方法分析金属键的能量结构与成键位置的关系，将能够加深我们对金属电沉积过程动力学的理解。另外，金属微观组织结构中的晶界可被视为不连续的价键体系，位错和孪晶相可视为价键的共振结构，残留的添加剂可视为参与价键形成的组分等。通过该模型，能够将铜箔中的不完整与缺陷也统一在同一个理论框架下，对建立微观组织结构与宏观物理性能间的因果关系起到积极作用。

6 总结和展望

经典电沉积理论较难应用于指导电沉积铜箔的生产与技术开发，是当前阻碍铜箔技术发展的瓶颈问题。前人通过实验和理论分析，试图建立更恰当的理论模型和机理解释。笔者通过电沉积铜箔中电流密度的决定性作用以及其对铜箔微观组织结构形成的影响的讨论，提出了从价键形成的角度研究电沉积铜的动力学过程，以及铜箔中组织结构的建议，希望得到学术界同行的认可和积极参与。

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Microstructure of Electrodeposited Copper Foil: Discussion on the Mechanism Model of Three-Dimensional Electrocrystallization

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Abstract: The manufacturing of electrolytic copper foil has attracted more and more attention with the extensive applications of printed circuit board and lithium battery. The industrial scale is still extending. Compared with the developments of electroplating equipment and electroplating process, there is limited research on the mechanism of electrodeposition. This paper summarizes the manufacturing process of electrodeposited copper foil and analyzes the differences of various electroplating parameters in different electrodeposited copper technologies, and points out the important role of electrodeposition current density in the formation of copper foil. By showing and comparing the microstructures of different electrodeposited copper foils, the influences of various factors in electrodeposition on the microstructures of copper foils and the corresponding macroscopic mechanical properties are discussed. From previous research results, it is found that the electrodeposition conditions and the composition of the plating solution have a significant impact on the microstructure and morphology of the copper foil, as well as the macroscopic mechanical properties. It is difficult to establish an effective relationship between the microstructures such as crystallite size and plane and the mechanical properties, which brings great challenge to the theoretical framework of the macro-mechanical properties of copper foils by using the microstructure of the coating as a bridge to establish electrodeposition conditions. Much effort has been tried to solve this problem by studying the mechanism of copper foil electrodeposition. The classical metal electrodeposition theory reveals that increasing the overpotential can increase the number of instantaneous nucleation and reduce the average grain size, however, it cannot explain the preferred orientation in crystallization. Watanabe found the similarity between electrodeposition and metallurgy, and believed that the microstructure of electrodeposited metal is related to the melting point of the metal, but this “microstructure control” theory still has some defects, such as the inability to explain the refining effect of additives on grains, etc. The author suggests that the relationship between the electrodeposition mechanism and the macroscopic properties of copper foil can be reshaped from the perspectives of valence bond and energy band theory. Influence of the macroscopic properties of copper foil can then be discussed.

Key words: over-potential; current density; electronic copper foil; microstructure; physical property