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激光选区熔化工艺制备多孔镁合金骨支架的研究进展

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摘 要:镁合金因其与人体骨骼相近的力学性能和可降解特性在人体骨组织支架移植中具有良好的发展前景,且将其制备成多孔结构有利于细胞的生长、增殖及分化。增材制造中的激光选区熔化工艺(SLM)制备多孔镁合金骨支架,在精确控制孔隙率与尺寸的同时,避免了传统铸造等工艺产生的形貌与性能缺陷。综述了多孔镁合金骨支架在临床医用中的可行性并介绍了 SLM 制备流程,通过对增强机制的分析阐明 SLM 工艺镁合金的性能优势。同时根据元素与工艺参数的变化剖析其作用机制与优化方案。最后总结现阶段工艺面临的瓶颈及其作用因素,以此提出改进方向与展望未来发展趋势,助力实现其医疗产业应用。

关键词:选区激光熔化;镁合金骨支架;增材制造;生物材料;稀土镁合金

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Progress of Porous Magnesium Alloy Bone Scaffolds Prepared by Selective Laser Melting

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Abstract: Magnesium alloys with porous structure are promising for human bone scaffold transplantation due to biodegradability and similar mechanical properties, which is also conducive to the growth, proliferation and differentiation of cells. The preparation of porous magnesium alloy bone scaffolds by Selective Laser Melting (SLM) method in additive manufacturing avoids the morphological and performance defects arising from traditional casting and other processes while precisely controlling porosity and dimensions. This paper presents the feasibility of porous magnesium alloy bone scaffolds for clinical applications and describes the SLM process. The enhancement mechanism is analyzed to clarify the performance advantages of the SLM process for magnesium alloys. The mechanism of action and optimization is also analyzed according to the variation of elements and process parameters. Finally, the bottlenecks of the current process and its factors are summarized, and the directions of improvement and future development trends are proposed to realize its medical industrial applications.

Key words: selective laser melting; magnesium alloy bone scaffold; additive manufacturing; biomaterials; rare earth magnesium alloy

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镁及其合金因其良好的生物相容性、低毒性，被广泛用于植入性骨支架器械[1-2]。镁合金与人体皮质骨的杨氏模量和密度相近，可大程度模仿骨骼机械性能，减小应力屏蔽效应。对比钛、铁等金属，镁合金通过生物降解创造出的高 Mg^{2+} 浓度环境，在避免二次手术的同时，增强巨噬细胞的吞噬能力并促进成骨细胞增殖分化[3-6]。此外，镁基材料可显著抑制细菌黏附并促进形成生物保护膜，降低植入部位的炎症风险[7]。因此，镁合金支架已成为金属骨组织移植的理想材料。

然而，密排六方结构(HCP)的镁合金滑移系统有限，导致其冷加工性受到限制，几乎不易塑性冷成型。镁合金在铸造过程中存在明显脆性倾向，成形往往伴随粗晶、缩孔和夹渣等缺陷，难以满足骨科植入物要求。同时，粉末冶金、化学气相沉积和电沉积等方式也无法对多孔镁合金支架的精密孔隙尺寸与定制几何形状进行调控，器件难与受体匹配[8-11]。近年来，增材制造(AM)正以高灵活定制自由度，在设计与创建具有精确孔隙的复杂 3D 多孔结构中潜力巨大，为多孔镁合金骨支架的高精度制备提供新的机遇[12]。此外，AM 工艺无需模具，且无需焊接或铆接，消除了传统加工中所需的长时间、多步骤，有利于批量加工[13-14]。其中，选区激光熔化(SLM)是增材制造制备多孔镁合金骨支架新兴工艺之一[7]。

本文首先对多孔镁合金骨支架和 SLM 工艺进行介绍，通过对微观结构变化的分析综合讨论了 SLM 镁合金产品的性能优势。同时详细阐述了 SLM 工艺参数对镁合金成形过程中影响作用，并归纳近期部分优化参数与典型特征。此外，本文总结了 SLM 工艺现阶段所面临的挑战以及对镁合金制备的限制瓶颈，以此讨论未来 SLM 工艺制备镁合金骨支架的研究方向与性能优化的发展措施，旨在助力早日实现其大规模体内移植应用。

1　多孔镁合金骨支架

在人体内，由于物理应力由骨支架承担，当支架的弹性模量与周围组织之间不匹配时会导致应力屏蔽现象，致使植入物与骨之间的弱界面结合，并缺乏组织生长的生物支持，导致植入支架松动并过早失效[15-16]。镁合金因具备与骨骼相似的力学性能，可有效降低应力屏蔽效应[17]。同时，通过在镁合金支架中创建横截面孔径小于 1 mm 的多孔结构，如图 1 所示，可有效模拟骨的生理海绵结构特性，促进骨组织的向内生长。此外，相互连接的中空空间也能形成血管系统，进而加速成骨过程[18]。然而，当支架的孔径过大或过小时不利于细胞生长，且高孔隙率会导致支架机械强度的降低[19]，精准控制镁合金骨支架的孔径与孔隙率一直是其成形难点。

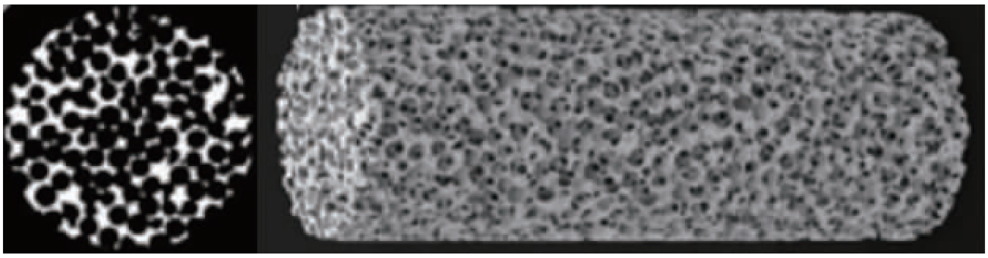

图 1　多孔镁骨支架[4]

Fig. 1　Porous magnesium bone scaffold[4]

2　SLM 镁合金制备工艺

由激光粉末床熔融工艺制备的金属零件往往具有高精度，可满足骨支架精确互联多孔结构的需求[20]。SLM 作为基于激光粉末床熔化的成形工艺，可以制备复杂的层次结构，在高度定制的可生物降解承重骨支架应用中前景无限[21]。在 SLM 工艺中，激光对粉末材料的快速冲击形成瞬态温度场，通过系统固有的快速加热和冷却过程，产生的高温度梯度和高冷却速率使镁合金快速硬化，致使显微组织强化并形成亚稳相，表现为由枝晶定向包裹而成的柱状晶粒以及过饱和导致的固溶强化，这对提高镁合金支架机械性能和耐腐蚀性起着至关重要的作用[11,22-23]。该工艺中，零件是以超薄的厚度逐层制造的，工作系统如图 2 所示。橡胶刷将送料机倒入的镁合金粉末扫到成形区域并形成均匀薄层，随后聚焦的激光束在特定区域熔化粉末层形成焊道。当第一层粉末层上的选定区域完成时，活塞将到达下一次粉末层沉积的规定长度，第二层粉末被激光照射熔化并与先前熔化的区域融合[24-25]。由于

SLM工艺的固有热处理，其中每一层通过后续层的沉积进行周期性重新加热，因此SLM制备的镁合金样品具有独特的沿(0001)强织构生长的细晶粒微观结构，并具有可忽略(<0.1%)的冶金工艺缺陷[26-27]。

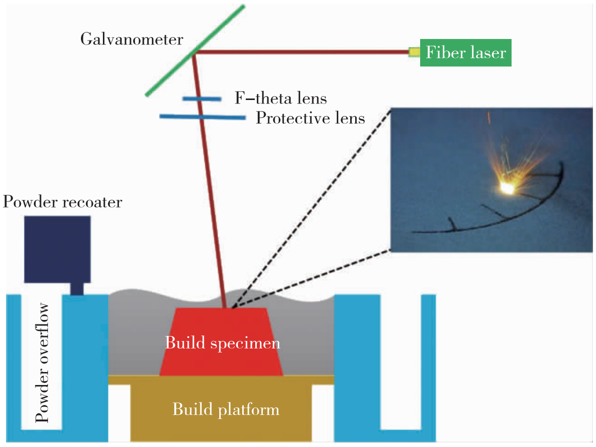

图2 SLM工作系统示意图[28]

Fig. 2 Schematic diagram of SLM system[28]

3 SLM镁合金性能与增强机制

SLM工艺的物理行为包括吸收、反射、辐射和传热，粉末颗粒在此经过熔化、聚结、相变等过程[29]。由于熔体在成形过程中过热，几乎无法发生均匀形核。异质形核在母材和液态金属晶粒间的固液界面上增强[30]。晶粒生长由向熔池中心竞争的外延开始，当移动的激光束照射到镁合金粉末时形成熔池，在激光束离开该区域后，从衬底或前一层中外延生长的部分熔化晶粒局部凝固。温度梯度相对较低的熔池表面附近倾向发生等轴凝固，且随着冷却速率的升高易导致柱状枝晶形成[31]。

3.1 机械性能

在SLM激光照射下，高凝固速率抑制了α-Mg晶粒的充分生长，阻碍固液界面的热力学平衡，致使镁合金的微观结构细化[32]。根据Hall-Petch公式，细晶粒可以提供更高的显微硬度[33]。此外，在SLM制备的WE43合金中具有不同长度的分层沉淀物，包括类共晶网络的富Nd沉淀物的长条带、微小的富Y沉淀物和大的Zr-Y氧化物，致使其机械性能显著高于传统铸造镁合金[34]。细晶粒尺寸和细分散氧化物导致SLM制备的镁合金出现上屈服点和下屈服点现象[35]。在SLM制备Mg-xSn合金时，除Hall-Petch硬化外，分散的Mg_2Sn相主要在晶界析出并可能抑制位错移动，同样导致硬化效应[36]。LIU等[37]通过激光增材技术制备出具有高显微硬度的层状多孔Mg-Ca合金，表现为重叠熔覆线和周期性形貌特征。

3.2 耐腐蚀性能

LI等[3]首次使用SLM制备了基于金刚石单胞的拓扑有序多孔WE43合金支架，并讨论了其耐蚀机制。镁基质作为阳极在腐蚀初始时溶解，片状第二相析出，同时，阴极反应产生氢气创造出局部的碱性环境，镁表面形成$Mg(OH)_2$保护层。随着$Mg(OH)_2$在氯离子环境中转化为$MgCl_2$以及第二相颗粒周围表面形成可溶性较低的沉淀物，沉淀物的形成和溶解之间平衡。然而，$MgCl_2$的形成会加速裂纹扩展[18]。此外，由SLM制备的WE43相较于铸态WE43阴极活性更强。由于合金主要元素的分布决定基体和第二相颗粒的阳极和阴极动力学，当Y等元素被限制在固溶体中时，基体的溶解速度降低，耐腐蚀性能增强[26]。PAWLAK等[38]验证了经SLM制备的AZ31B合金在0.9%NaCl溶液和多电解质盐水溶液中的耐蚀性均高于传统轧制板材形式的材料。为进一步提高耐腐蚀性，YANG等[39]将具有化学惰性的介孔二氧化硅(MS)通过SLM技术均匀掺入ZK60合金中，在镁基体中形成良好的黏合界面，并促进$Mg(OH)_2$在表面的沉积以形成致密钝化层，进而防止Mg基体的腐蚀。

3.3 其他性能

SLM工艺制备的镁合金支架的循环载荷和生物降解在很大程度上相互影响，LI等[40]分别在微观与宏观尺度上解释生物降解对改变疲劳机理的作用机制。微观上，器件中心的生物降解坑充当额外的疲劳裂纹萌生点并以穿晶方式扩展；宏观上，疲劳裂纹在应力集中的器件边缘连接处萌生。即便疲劳寿命提高，裸露的WE43支架仍不适合细胞黏附，WANG等[41]为此分别设计了仿生、金刚石和陀螺结构的多孔镁合金支架，其CAD模型如图3所示，选择机械性能最好的陀螺状支架进行二水磷酸氢钙(DCPD)涂层处理，在抑制了降解速率的同时提高细胞相容性。XU[42]和SHUAI等[43]分别通过SLM制备ZK30-Cu与ZK60-Cu合金，除表现出良好的细胞相容性外还具有较强的抗菌能力。其抗菌机制为合金的降解创造出碱性环境，Cu离子的释放使细胞膜结构遭受破坏，进而使酶变性并抑制脱氧核糖核酸的复制以实现灭菌[42]。这些工作为SLM的设计和制备抗菌镁合金提供了新思路。

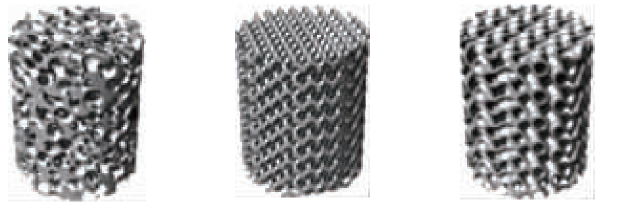

图3　CAD设计模型示意图:仿生、金刚石、陀螺结构[41]

Fig. 3　Schematic diagram of CAD design models: bionic, diamond, gyro structure[41]

4　SLM镁合金成分

当镁含量增加时,由于蒸发产生气孔,伸长率会逐步降低。同时随着固溶体的增加,SLM样品的热导率会略有下降[44]。合金化处理可以有效地提高SLM过程中的沸点和熔点温度范围,从而减少由蒸发带来的损失[30]。稀土元素能够有效削弱镁合金的织构,提高机械性能与生物性能,且稀土元素通常具有较高表面活性,在SLM过程中可以与常规元素结合形成稳定的金属间化合物,抑制晶粒长大同时促进固溶体和沉淀硬化[45-46]。此外,稀土元素合金化可以通过降低塑性变形过程中的临界剪切应力来激活更多的滑移形成位错,引起累积应变硬化并提高抗蠕变性,这些元素的添加有助于开发先进的镁合金用作可生物降解的骨植入物[34,47]。Zr的添加能够细化镁合金晶粒,改善其塑性与耐蚀性。Sr的添加可以提高镁合金抗压强度,改善体外生物相容性并促进体内骨形成[48-49]。在SLM工艺中,Nd的添加可促进金属间相在晶界析出,利于晶粒细化,且Nd_2O_3的形成增加了钝化膜的密度,提高耐腐蚀性能[50]。

WE43合金作为添加Y和稀土元素的可降解生物镁合金,已得到临床验证[37]。采用Gd元素代替部分Y元素可减少由Y_2O_3夹杂物引起的SLM产品的机械性能降低[51]。FU等[52]通过SLM制备了高强度稀土镁合金Mg-15Gd-1Zn-0.4Zr,屈服强度、极限抗拉强度及延展性明显高于传统铸造合金,其强化机制主要来源于细小的晶粒与第二相以及残余应力,此外,合金在时效处理后会通过析出物进一步强化。Zn元素的添加有助于提高合金支架抗氧化性并且加快稀土元素在镁基体的扩散速度[53],且Zn在熔池边界的偏析会形成低熔点共晶相,细晶粒和纳米析出相对镁合金的力学性能起关键作用[54]。WANG等[55]报告在SLM处理的Mg-Y-Sm-Zn-Zr合金微观结构中,未发现显微硬度值较低$Mg_{12}Zn$共晶相以及延伸到晶体中的层状LPSO(Long-Period Stacking Ordered)结构,而是在晶界分布了大量具有较高显微硬度的$(Mg,Zn)_3(Y,Sm)$共晶相,对提升SLM样品的显微硬度具有促进作用。然而在固溶过程中,Zn会促进LPSO结构的形成,且LPSO结构的体积分数随着Zn含量的增加而增加[56]。添加1%Zn在Mg-15Gd-0.4Zr合金中引入额外的γ'沉淀能与β'析出物产生复合强化效应,降低棱柱状β'相的密度并改变其形态,有效强化晶粒内部[57-58]。然而在SLM制备Mg-Zn二元合金中,由于α-Mg和MgZn之间的电偶效应,Zn含量增加会加速降解,并降低合金的致密化。当Zn含量大于1%时,合金出现凝固裂纹[59-60]。

5　SLM工艺参数

SLM器件的微观结构和性能主要受粉末特性和工艺参数影响,其中粉末特性包括流变性、粒径、内部孔隙率等,工艺参数包括激光功率、激光扫描速度、粉末层厚度等[61]。通过调整SLM工艺参数,可以实现多孔镁合金支架所需的孔隙率,并提高机械与耐腐蚀性能[62]。

多孔镁合金的孔隙率和表面形貌取决于激光能量输入,在SLM过程中,粉末表层在激光束的照射下吸收能量并形成相对较浅的熔池,通过热传递将能量转移到粉末底部[63]。能量密度E作为影响表面形貌的关键因素[64],其计算公式如式(1)所示,其中P为激光功率,v为扫描速率,h和t分别代表舱口间距和层厚。当激光能量过低时,由于熔池温度降低,导致镁合金粉末熔化不完全,液体表面张力和粘度增加,液体无法平滑流动,表面因"球化效应"导致粗糙且不均匀,成形质量极差且严重损害疲劳性能。能量输入的补偿可有效克服过快扫描速度下镁合金因无法充分黏合导致的孔隙率增加[65-67],然而能量密度存在临界值,当输入过高时会促进镁粉的强烈蒸发并膨胀吹出熔池,导致粉末层上形成絮状沉积[68-69]。当沉积在较冷的成形区域时,镁蒸汽极可能损坏机器或降低机器寿命[70]。且由于蒸发反冲力形成细长空腔,同时蒸汽中存在的小颗粒会散射激光束并飞溅到透射镜上,阻碍激光束传播导致熔化过程不稳定,最终孔隙率增加[62]。高孔隙率及缺口效应会导致SLM镁合金产品的延展性较低[35]。值得注意的是,激光功率和扫描速度的变化对熔池的显微硬度和化学成分没有影响[71]。

$$E=P/vht \tag{1}$$

WANG等[72]在SLM制备AZ61D时提出“溶质捕获效应”，当液相凝固时，溶质原子被动态的固液面捕获并被固体吸收。如当镁铝合金粉末熔化时，铝溶解在镁基体中，形成Mg-Al液相，而后在凝固时，液相转变为α-Mg固溶体和β-$Al_{12}Mg_{17}$沉淀[73]。激光功率的增加往往伴随更长的冷却时间，这导致“溶质捕获效应”的减弱[74]。合金粉末由于吸收更多能量，熔池温度升高，α-Mg基体中的铝原子被固液面捕获并还原，导致第二相β-$Mg_{17}Al_{12}$的比例大幅增加[72]。弥散第二相在晶界析出时，通过抑制晶粒运动导致强化效应，从而提高合金显微硬度[75]。此外，第二相作为电偶阴极与镁基体耦合并形成许多阳极-阴极位点，导致微电偶腐蚀。同时，第二相在选区激光熔化过程中的快速冷却中被重新分配，削弱非平衡微观结构的不利影响，改善镁合金支架的降解性能[60]。

激光扫描速度决定纳米沉淀行为，进而影响硬度和磨损性能。由于硬度本质上是对金属塑性屈服应力的测量，其变化可通过屈服强度强化机制解释[76]。当增大激光功率p，降低扫描速度v，同时缩小舱口间距h，可减少孔隙度并提高动态强度[34]。WU等[9]设定激光功率为50 W，扫描速度为500～800 mm/s时，可以获得缺陷最小、尺寸精度高的ZK60合金。在此参数下，不仅保证镁不蒸发，同时高激光输入能量可以降低熔融金属的动态黏度，促进熔融金属的充分扩散，改善层间润湿性和固结。YAO等[53]设定激光功率为150 W，扫描速度为800 mm/s，此时热影响区深度达100 μm，Mg-0.5Zn-0.3Ca合金的显微硬度增加15%以上。KRIŠTOFOVÁ等[77]设定SLM功率250 W，扫描速度450 mm/s下，WE43合金的抗压屈服强度和极限抗压强度分别高达208 MPa和395 MPa，在此基准上，抗压屈服强度和极限抗压强度随扫描速度继续增加而降低，当增大功率时，抗压屈服强度降低而极限抗压强度增加。

在SLM制备镁铝系合金时，过高激光功率会促进等轴晶粒的粗化。根据固溶体理论，Al可以作为取代原子溶解在α-Mg基体中，由于溶质在快速凝固过程中的保留效应，α-Mg基体中固溶体增加。然而，溶质保留效应随能量密度进一步增大而减弱，导致固溶体减少，最终增加质量损失并降低显微硬度[74,78]。此外，硬度和弹性模量等力学性能与激光能量密度呈反比关系，随激光能量密度增加而降低，此现象与Hall-Petch方程一致[32]。

6 现阶段挑战

现阶段SLM技术面临最严峻的问题为由于速率低、成形尺寸有限，难以满足大规模镁合金零件快速制造的要求[79]。同时在SLM过程中，大部分激光能量由于镁的低吸收而被反射，从而导致效率低下并增加了激光器件击穿的风险。此外，用于SLM的镁合金细粉不仅制备困难且易氧化爆炸[80]。WU等[81]尝试在在AZ31B合金粉末中加入碳纳米管，显著提高了复合材料激光吸收率，且其熔池在大于42 J/mm^{3}的激光输入能量密度时达到完全熔化状态。然而，此时蒸发孔隙率随着温度的升高而呈上升，进而降低致密度。

即便在保护气体环境下，SLM系统中也不可避免存在氧气，固有的快速加热系统会导致氧化活化能降低而加剧镁合金氧化[70]。氧化产物覆盖镁颗粒形成的不可润湿薄膜抑制层间结合，在熔化时变形并聚集在层间的固液界面或激光轨迹上，随熔池形成沿晶界聚集，最终在应力作用下导致裂纹。目前SLM器件的孔隙率仍然高于铸态零件并强度较低[20]，镁合金在SLM冷却过程中易在内部产生残余应力，还需采用等压烧结或热处理以消除应力[11]。

粉末层厚度的把控不当会导致底部粉末不易被激光束穿透熔化，致使各层附着力降低，导致局部应力集中且化学成分不均匀，结合气孔、微裂纹等冶金缺陷，显著降低了镁合金的断裂韧性和延展性，使其塑性较差[30]。此外，SLM工艺由于黏附在物体表面而产生高粗糙度，因此无法通过喷砂或化学蚀刻对自由形状拓扑结构优化以及改善镁合金骨支架的表面质量，还需进行表面机械后处理[38]。

7 展望

镁合金已作为理想体内移植合金材料，通过SLM工艺制备可降解多孔镁合金骨支架具有广泛前景。SLM制备镁合金的力学性能与腐蚀性能提升可归因于微观结构上的晶粒细化与固溶体强化。然而在制备工艺中存在的球化、气孔及裂纹等冶金缺陷，除需对工艺参数进行进一步优化调整外，还需对以下几个方向进行研究。

1）单纯SLM处理的镁合金对于细胞黏附还不够理想，还需进行表面设计或涂层处理，并对耐受极限和细胞毒性进行检查。

2）金属间化合物的微观结构不均匀性沉淀及脆

性网络会降低器件的延展性，还需对 SLM 过程中第二相的析出分布机制及相应的力学性能进行探讨。

3)在多孔镁材料的设计中，平衡机械强度和孔隙率仍是面临的主要问题。在 SLM 工艺参数优化方案中应着重考虑扫描速度与激光功率的变化，以通过最佳能量密度，找到熔化、凝固的合适条件，最终形成兼具表面质量与力学性能的镁合金样品。且由于镁合金具有高热裂纹倾向，还应对其后处理进行探究。

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