难熔高熵合金激光增材制造的发展：材料性能与制造工艺调控技术（特邀）

李涤尘[1,2*]，张航[1,2**]，蔡江龙[1,2]
[1]西安交通大学机械制造系统工程国家重点实验室，陕西 西安 710049；
[2]西安交通大学机械工程学院，陕西 西安 710049

摘要 难熔高熵合金具有超越传统合金的优异性能，强度和硬度更高，高温性能和耐蚀性更优异，在航空航天、核工程、武器装备等领域具有广阔的应用前景。难熔高熵合金发展面临着两个难点：常规真空电弧熔炼方法制备的难熔高熵合金存在成分偏析严重、研发周期冗长、材料尺寸受限等难题；难熔高熵合金的硬度很高，难以实现复杂结构的成形和加工。因此，现有的冶金、成形、加工等技术面临挑战。通过激光增材制造实现材料与结构一体化成形是突破现有问题的发展方向，国内外学者在此方面进行了大量探索。本文对难熔高熵合金激光增材制造的发展现状进行了综述与分析，介绍了难熔高熵合金复杂构件从材料到制造的研究进展，阐述了高熵合金的研发途径、增材成形工艺和缺陷调控、难熔高熵合金在不同温度下的力学性能，以及增材制造工艺面临的挑战和取得的进展，最后总结了难熔高熵合金增材制造未来的应用方向和发展趋势。

关键词 激光技术；激光增材制造；难熔高熵合金；合金开发；一体化制造
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1 引 言

2004 年，我国学者叶均蔚突破传统材料设计思路，提出了一种“多主元”合金的设计新理念[1]，该合金又被称为“高熵合金”（HEA）。一方面，它激发了人们对多主元合金广阔组成空间的不断探索；另一方面，高熵合金是典型的“浓固溶体”，其所具有的特殊无序固溶体相结构使其具有大晶格畸变、高构型熵、扩散迟滞效应和“鸡尾酒”效应等四大效应。在这些特殊效应的作用下，高熵合金有望突破传统合金的性能极限，集超高硬度、高强度、大延展性、杰出的热稳定性、良好的耐磨性和耐蚀性、良好的抗氧化性等于一体[2-9]。目前研究的高熵合金可以分为过渡元素高熵合金、难熔高熵合金、共晶高熵合金等。近年来，高熵合金成为材料研究领域的一大热点，具有重要的研究价值与应用前景。

难熔高熵合金（RHEA）是由高熔点元素 W、Ta、Nb、Mo、Hf、Re 等组成的高熵合金，其特点是强度高和密度大[10-11]。相对于常规高熵合金而言，其在高温下仍能保持高强度，而且具有良好的热稳定性。Senkov 等[12]于 2010 年首次设计了 WNbMoTa 与 WNbMoTaV 两种难熔高熵合金，WNbMoTaV 合金的硬度高达 5360 MPa，WNbMoTa 在 1600 ℃时的压缩强度为 405 MPa[12-13]。在纳米尺度下，WNbMoTa 难熔高熵合金的屈服强度超过了 10 GPa[14]，被认为是极具潜力的新型金属材料，引起了新一轮高性能金属研究热潮。

高熵合金含有大密度、高熔点元素，通常采用真空电弧熔炼而成，但真空电弧熔炼易出现成分偏析，而且难以成形大尺寸、复杂结构的零件[12,15-18]。此外，难熔高熵合金大多延展性较低，二次成形和加工比较困难，难以适用由材料向构件发展的长流程制造模式。激光增材制造技术是一种高能激光束点对点的数字化成形工艺，能够成形熔点高、结构复杂的零件，同时，其大通量的试验优势可以实现材料的快速开发和迭代。激光增材制造主要分为激光粉末床熔融（LPBF）和激光定向能量沉积（LDED）。在 LPBF 技术中，高能激光束按照三维 CAD 切片模型中规划好的路径，对粉末床上的金属粉层进行逐层扫描，扫描过的金属粉末通过熔化、凝固达到冶金结合的效果，最终获得模型所设计的金属零件。其特点是所制作的构件精密，适合小尺寸精密件的制造。LDED 技术将高能量激光束作为热源，在激光四周进行同步送粉形成熔池，同时按照计算机模型所规划的路径进行成形全覆盖，进而实现逐层

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通信作者：*dcli@mail.xjtu.edu.cn；**zhanghangmu@mail.xjtu.edu.cn

累加成形。LDED可以实现变金属成分的梯度材料制造，适合大尺寸构件的制造。基于激光增材制造技术，开展难熔高熵合材料的研发以及复杂结构样件一体化成形，将会推进难熔高熵合金的快速研发和工程化应用。

难熔高熵合金激光增材制造以其成形能力和性能优势在航空航天、核工程、国防装备等多领域展现出了巨大潜力。例如，在高超声速飞行器制造过程中，激光增材制造可以突破传统多材料组装和成形方法，整体制造大尺寸、复杂结构难熔高熵合金零部件。该工艺的特点在于能够发挥高熵合金耐高温（熔点高于2500 ℃）、比强度高、耐蚀性好、热阻大等物理特性。采用激光增材制造技术替代传统的粉末烧结、焊接、胶接、表面涂层等复杂工艺，可以解决高熔点合金不易成形、加工的难题，同时有望实现成分/性能梯度可变的复合结构，为高超声速飞行器关键部件的一次性快速制造提供了新的技术途径。

发挥难熔高熵合金增材制造技术的优势，缩短制造流程和提高设计制造柔性，是未来制造技术发展的方向，材料设计和机械结构成形的一体化制造将成为先进制造技术未来的一个重要发展方向。基于难熔高熵合金的梯度材料开发和制备是当前的研究热点。与普通的均匀材料相比，梯度高熵合金材料可以实现材料的连续过渡，将各种优异性能集中在同一个零件上，使零件具有适应不同环境的不同功能。因此，本文围绕难熔高熵合金激光增材制造缺陷控制、工艺窗口优化、材料性能强化以及复杂构件一体化制造的研究进展，总结了难熔高熵合金激光增材形性一体化制造的发展现状和主要挑战。

2　难熔高熵合金激光增材制造缺陷的调控机制

激光增材制造金属部件的显微组织缺陷主要可分为裂纹和孔隙两类。对于单相固溶体的脆性难熔高熵合金而言，其稳定的体心立方（BCC）结构相是其在高温下不易软化的关键。但是，这一特性在激光增材成形的高温梯度下极易诱发裂纹、孔隙等缺陷[19-23]。由于熔池形貌的不稳定性，激光增材制造过渡元素高熵合金同样面临着微孔隙等缺陷难以消除的问题[24-29]。此外，不仅仅是高熵合金，其他金属的增材制造的缺陷控制也是增材制造领域的重要研究方向，也是制约金属增材制造进一步发展的重要因素[30]。因此，对常用金属增材制造中的组织缺陷及控制方法进行研究，对于提升增材制造难熔高熵合金金属部件的力学性能及表面质量具有重要意义。

2.1　裂纹及其调控研究的进展与难点

高熵合金激光增材制造过程中所产生的裂纹主要分为热裂纹和冷裂纹[31]。热裂纹的发生需要同时满足金属熔融液膜缺失和残余热应力存在这两个条件[32]。激光增材制造过程中存在两种主要的热裂行为，即凝固开裂和液化开裂。凝固开裂主要受金属增材制造过程中复杂热循环的影响，一般出现于熔池凝固终止阶段。此时，熔池内部的枝晶正在生长成为完整的晶粒，阻碍了残余液体的流动，从而导致枝晶生长空间被压缩。同时，液膜附近的凝固收缩和热收缩共同产生拉应力/应变，当拉应力超过材料的抗开裂能力时，即发生凝固开裂[33-34]。液化开裂发生在热影响区的加热循环过程中，当热影响区被加热到较高温度时，低熔点相的重熔导致晶界或晶内形成液膜。液膜可能成为裂纹萌生的地方，而热循环过程中产生的较大的热应力会加速裂纹沿晶界扩展。典型的凝固裂纹特征如图1所示[35-37]，其中图1(a)、(b)为最后凝固液膜的不规则树枝状形貌。液化裂纹往往沿晶界发生，没有树枝状特征，如图1(c)、(d)所示。对于冷裂纹而言，由于激光增材制造过程中金属的脆性和热循环引起了较大的残余应力，其发生在相对较低的温度下，而且没有金属液体的填补作用。因此，冷裂纹在晶界处不会显示出任何暴露的枝晶或液相痕迹。相反，它们更直，形态干净，而且经常伴有尖锐的扭结。这些冷裂纹的长度可能比熔池尺寸大得多，它们可以沿着预先存在的热裂纹扩展。

在原始金属粉末中加入少量微纳米颗粒是解决某些高熵合金成形困难和裂纹敏感问题的通用且有效的成分设计方法[38]。例如，Si、TiB$_2$、Al$_2$O$_3$、TiN、TiH$_2$和TiC等颗粒会被用来解决高脆性合金的热裂问题[39-45]。这类抑制开裂的颗粒满足与金属基体相无热膨胀差异的特性，并且与基体相具有良好的化学相容性和黏附性[46]。因此，开发出同时满足以上条件的微纳米颗粒（以抑制缺陷的形成），是难熔高熵合金研发的重要方向。Wang课题组[47]通过在Al$_6$Mg$_{0.2}$Sc$_{0.1}$Zr高熵合金中加入质量分数为1.3%的Si元素，有效抑制了LPBF过程中热裂纹的产生，同时细化了组织。此后，他们通过将合金成分进一步细化，开发出了一种新型高熵合金——Al$_{8.0}$Mg$_{1.3}$Si$_{0.5}$Mn$_{0.5}$Sc$_{0.3}$Zr[47]。该合金具有极细小的微观结构、高密度层错结构以及独特的9R相。在固溶强化、晶界强化、纳米粒子强化、高密度层错强化的共同作用下，该合金的抗拉强度和断后延伸率分别可达497 MPa和11%；时效热处理后，其抗拉强度提升至550 MPa，断后延伸率根据时效条件的不同在8%～17%之间。

此外，在不改变粉末原料的情况下进行工艺优化和后处理同样可以避免激光增材制造过程中的开裂情况。Xu等[48]发现通过改变扫描策略可将合金组织从较大的柱状晶粒转变成较小的等轴晶粒，从而成功地抑制热裂纹。Stopyra等[37]提出可将$0.4<d/w<0.5$作为避免LPBF制造热裂纹的最佳窗口，其中d/w表示熔池的深宽比。但是，最佳工艺参数不能完全消除热裂纹。粉末床预热有助于降低凝固速度，使凝固更均

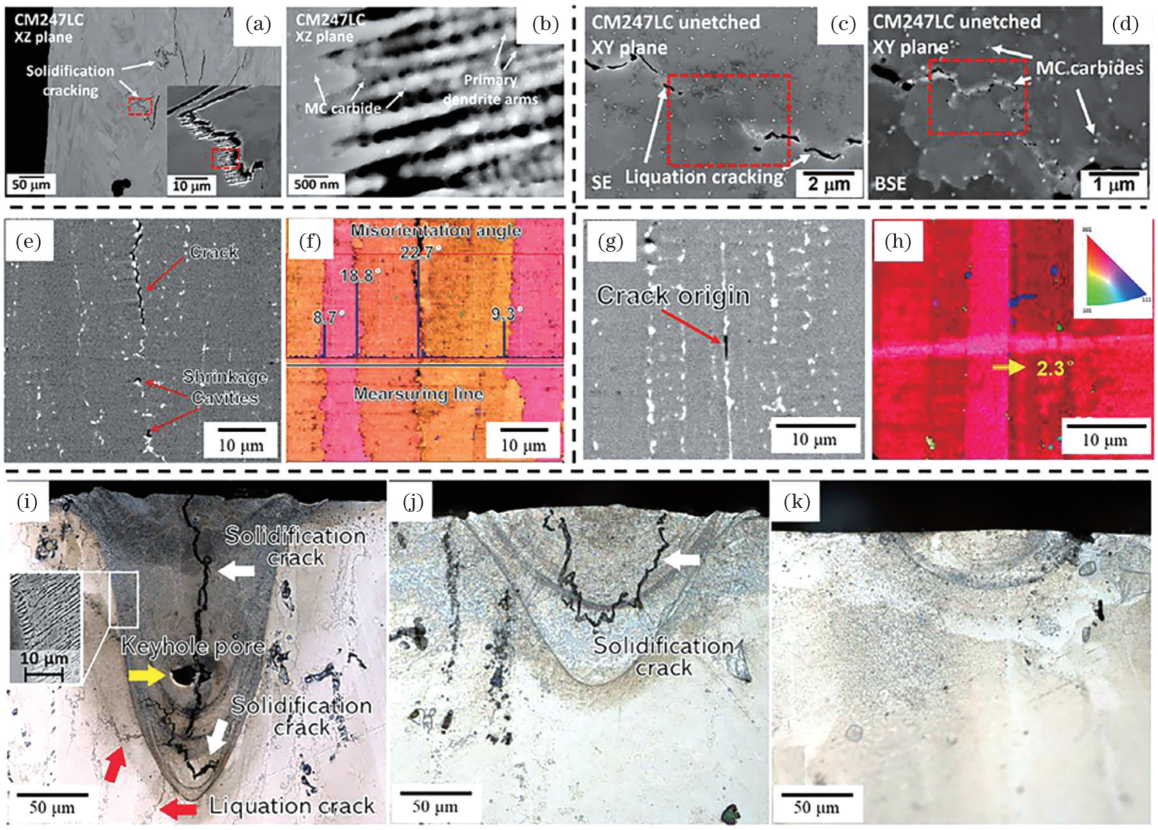

图 1 典型的热裂纹[35-37]。(a)(b)具有不规则树枝状形貌的凝固裂纹;(c)(d)无树枝状特征的液化裂纹;(e)(f)凝固裂纹;(g)(h)液化裂纹区域的形貌及位错图;(i)~(k)LPBF 制造的 AA7075 合金的单道显示出不同的熔池形状和热裂纹敏感性

Fig. 1 Typical thermal cracks[35-37]. (a)(b) Solidification cracks with irregular dendritic morphology; (c)(d) liquefaction cracks without dendritic characteristics; (e)(f) solidification cracks; (g)(h) morphology and dislocation maps of the liquefaction crack region; (i)–(k) single pass of LPBFed AA7075 alloy shows different pool shapes and thermal crack sensitivities

匀,从而抑制热裂纹[49-52]。Kempen 等[50]在 M2 高速钢的 LPBF 期间,对基板进行了 500 ℃的预热处理。由于热应力降低,裂纹和分层缺陷被消除。Uddin 等[49]在铝合金 AA6061 的 LPBF 过程中,对粉末床进行了 500 ℃预热。采用优化后的工艺参数,他们制备出了无裂纹的 AA6061 零件。另外,热等静压(HIP)等后处理被广泛用于闭合内部裂纹[53-56]。虽然 HIP 可以成功消除微裂纹,提高合金的延展性,但是在 HIP 过程中晶粒会长大,从而导致合金强度降低[41]。此外,Stopyra 等[37]认为 HIP 处理不能有效闭合合金中的长裂纹缺陷。

2.2 孔隙及其调控研究的进展与难点

激光增材制造金属部件中的孔隙缺陷可以分为 4 种类型:1) 未熔合孔隙;2) 冶金孔隙;3) 微孔隙(锁孔);4) 收缩孔隙。它们的典型结构如图 2(a)~(c)所示[32,57-58]。未熔合孔隙缺陷主要是由输入能量较低,所形成的熔池尺寸较小,不能顺利与基体金属形成有效连接而导致的,其尺寸分布在 50 μm 至几毫米之间,且较为常见[59]。冶金孔隙一般呈现为球状或椭球状,在 LPBF 成形件中的尺寸一般为 5~20 μm,在 LDED 成形件中的尺寸通常为 50 μm 以上。该缺陷主要是由金属部件成形过程中所特有的高冷却速率阻碍熔池内部气体逸出,或熔池上方气体被卷入凝固组织而形成的,是金属增材制造过程的一种固有缺陷,无法有效避免。锁孔是焊接过程中普遍存在的汽蚀现象,常与液态金属汽化有关[60]。随着能量密度增大,熔池形状由浅的半圆形向深而窄的形状转变,熔化模式由热传导模式转变为锁孔模式。在锁孔模式的熔化过程中,金属蒸气在锁孔尖端形成球形锁孔。在 LPBF 过程中,锁孔同样是由不稳定的熔化模式引起的[61]。LPBF 锁孔形状各异,孔径在 10~50 μm 之间[62]。但是,通过控制工艺参数,如降低能量密度,可以实现稳定的熔化模式从而消除锁孔[61]。收缩孔隙是由树枝晶区域的残余液体在凝固过程末期收缩而形成的[32,36]。Chauvet 等[32]表征了增材制造制备的镍基高温合金中的收缩孔隙,如图 2(c)所示。收缩孔隙呈圆形,平均直径<5 μm,枝状树干整齐排列。

控制孔隙最有效、最常见的方法是对工艺窗口和工艺参数进行优化。相当多的研究人员使用体能量密度 E 这一综合指标来确定获得全致密金属零件的工艺窗口[63-66]。Saedi 等[67]采用 LPBF 工艺,以 55.5~79.4 J/mm^{3}的体能量密度制备了低孔隙率的 NiTi 合金。Dadbakhsh 等[68]建议 NiTi 合金采用体能量密度为 111~126 J/mm^{3}的工艺窗口进行制备。可见,在不同

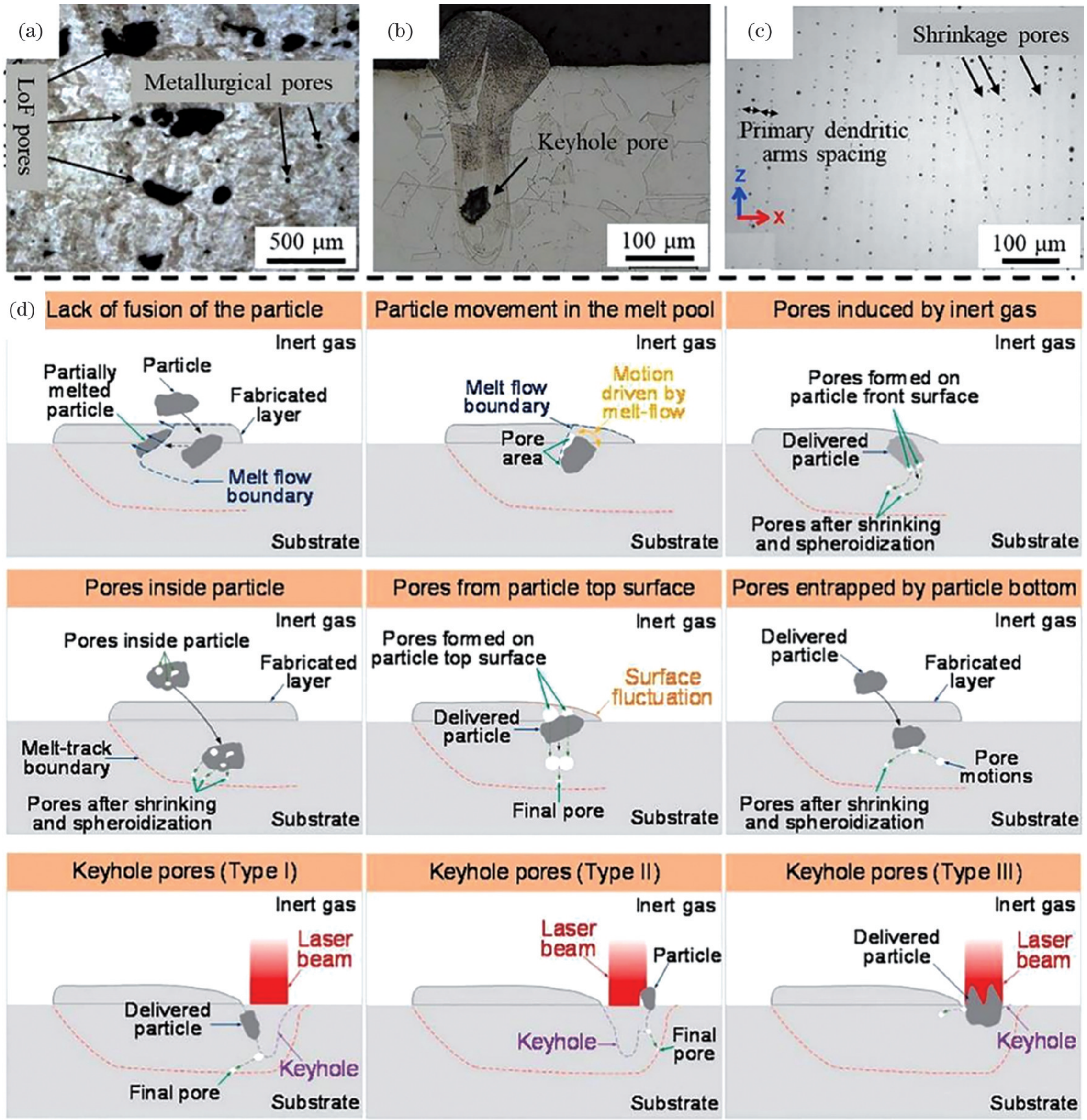

图 2 典型孔隙[32,57-58]。(a)未熔合孔隙和冶金孔隙;(b)锁孔;(c)收缩孔隙;(d)LDED工艺中孔隙的形成机理示意图

Fig. 2 Typical pores[32,57-58]. (a) Unfused and metallurgical pores; (b) keyhole pore; (c) shrinkage pores; (d) schematic diagrams of pore formation mechanism in LDED process

的文献中,由体能量密度定义的工艺窗口差异较大。因此,体能量密度的可靠性和有效性仍然需要进一步深入研究。需要指出的是,即使是采用相同的能量密度也无法保证成形零件孔隙率的稳定性。这是因为忽略了其他的重要因素,如激光光斑尺寸和材料性质等[67,69-70]。因此,为了获得一个最优的工艺窗口,需要开发修正的能量密度公式,或者需要识别单个工艺参数及其相互作用对零件孔隙率的影响。

在难熔高熵合金的激光增材制造过程中,消除裂纹的主要途径是进行成分优化从而使合金具有一定的韧性,而消除孔隙缺陷的主要途径是进行工艺优化。NbMoTaW 系列难熔高熵合金虽然具有极高的耐高温性能,但压缩应变大都不足 2%。高能激光束能产生 10^5 K/s 的温度梯度,热应力远大于材料本身的断裂强度,因此裂纹缺陷很容易产生。在这种情况下,工艺窗口的优化只能减少裂纹,并不能彻底消除裂纹[71]。只能通过控制脆性元素含量和添加低熔点元素来提高合金的韧性,进而抑制裂纹缺陷。在本研究领域,消除裂纹缺陷是研究热点,亦是研究最难点。孔隙缺陷可以通过熔池搭接的优化和最优能量密度的选择进行部分消除[72],到目前为止还未有人通过 HIP 的方式完全消除孔隙缺陷。裂纹缺陷对于合金的室温力学性能和高温力学性能都是致命的,通过抑制裂纹缺陷才能展现合金的真正性能。同时,孔隙缺陷也制约着合金的疲劳性能。因此,大多数难熔高熵合金激光增材制造的研究都聚焦在裂纹缺陷的控制上。

目前,难熔高熵合金增材制造过程中激光强烈的

热作用所导致的裂纹和孔隙缺陷是工艺研究的重点和难点。为了消除裂纹和孔隙缺陷，可从两个方面加以解决：一是通过合金设计进行材料优化，增强材料韧性，从而抑制裂纹产生，减少孔隙形成；二是进行工艺仿真和工艺优化。

3　激光增材制造难熔高熵合金材料的快速研制

相对于真空电弧熔炼等传统的材料成形手段，激光增材制造在快速开发难熔高熵合金上具有明显优势。将几种粉末进行机械混匀或者预制合金粉，然后将激光高能束流作用于粉末，通过形成瞬态的温度在3000 ℃以上的金属熔池，同时借助激光冲击力的作用，能够完全实现金属元素的充分混熔。因此，将W、Nb、Mo、Ta、Zr、Hf、V等元素自由混合并使之充分互溶，能够得到高性能的难熔高熵合金。因此，国内外研究人员已经将激光增材制造作为难熔高熵合金的快速开发手段，从而为难熔高熵合金的高通量实验开发奠定了基础[73-76]。

采用2个或2个以上送粉器的LDED技术可以快速实现难熔高熵合金材料组分及其配比的筛选。Moorehead等[74]结合LDED成形技术研发出了一种高效的材料开发方法。如图3所示，在激光成形设备的4个独立的粉仓中分别放入Nb、Mo、Ta、W粉末，通过调整粉仓中螺旋滚轮的转速来调整送入激光熔池的粉末流量，从而实时改变材料配比和成分，实现复合材料的快速成形。研究人员采用此方法进行了不同成分配比的NbMoTaW合金的LDED成形，通过调整螺旋滚轮转速等参数，基本实现了高熵合金相的形成以及成分设计比例与实际测试比例的精准映射。Nb、Mo、Ta、W各元素的成分误差均在10%以内，且成分分布均匀，如图4所示。

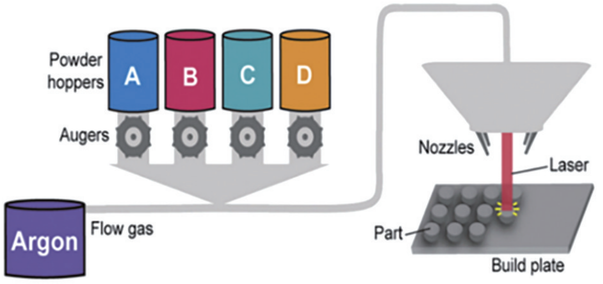

图3　高通量成形原理[74]

Fig. 3　Principle of high flux forming[74]

Dobbelstein等[75]首次采用元素粉末原位合金化方法制备了难熔的TiZrNbTa高熵合金。他们采用5种预混合粉末进行Nb到Zr粉的增量代替，通过每层4次重熔的方式在钼基体上成功地构建了无裂纹的单壁结构。该结构具有从$Ti_{25}Zr_{50}Ta_{25}$到$Ti_{25}Nb_{50}Ta_{25}$的明确成分梯度，结构的中间部分有近乎等原子的TiZrNbTa。此外，他们对图5中的5个区域分别进行了组织和性能分析。结果表明：$Ti_{25}Nb_{50}Ta_{25}$与$Ti_{25}Zr_{25}Nb_{25}Ta_{25}$的组成为单相BCC固溶体，微观结构为粗大晶粒。通过建立此种小型壁结构可以高效地实现元素组成空间的探索，从而极大地提高材料的筛选效率[76]。

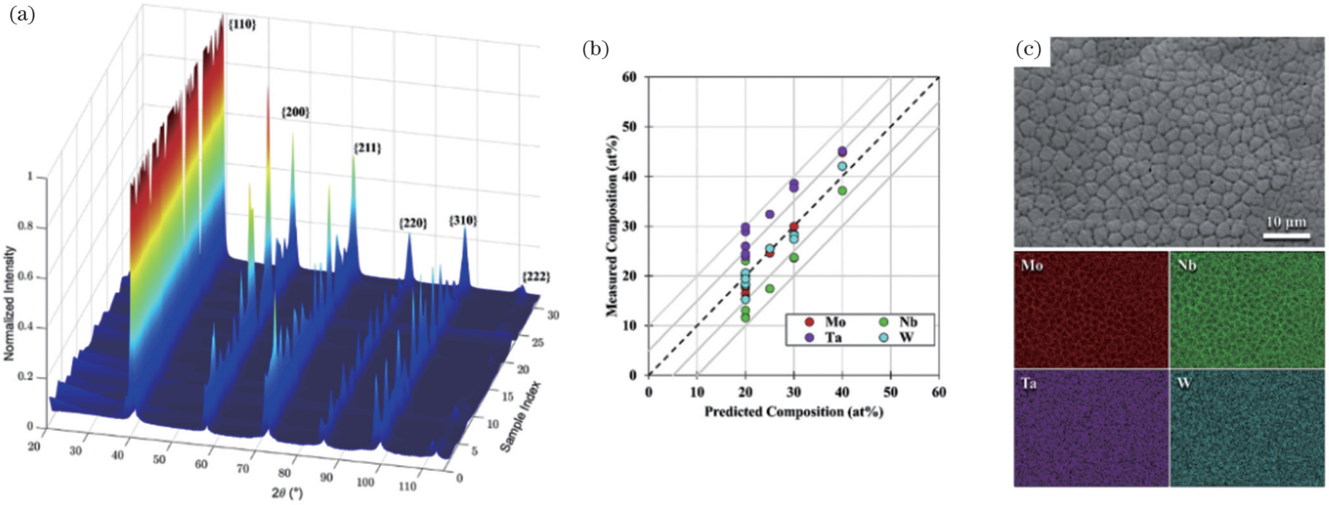

图4　高通量成形的高熵合金相[74]。(a)X射线衍射谱；(b)测量成分与预测成分的对比；(c)SEM图和元素分布图

Fig. 4　High entropy alloy phase with high flux forming[74]. (a) XRD patterns; (b) measured composition versus predicted composition; (c) SEM image and elemental mapping

综上所述，采用机械混粉能够有效动态调控合金组分，从而能够实现多型高熵合金材料设计条件下的大通量快速制造和实验验证，而采用预制合金粉则在较大程度上改善了难熔元素和低熔点元素充分混溶的技术难题，易获得无宏微观偏析的高性能高熵合金材料。目前，W、Mo、Ta、Hf等难熔元素的原材料纯度和粉末球化工艺仍然是行业面临的挑战，高质量球形粉价格昂贵是限制难熔高熵合金工业化应用的一个重要因素。

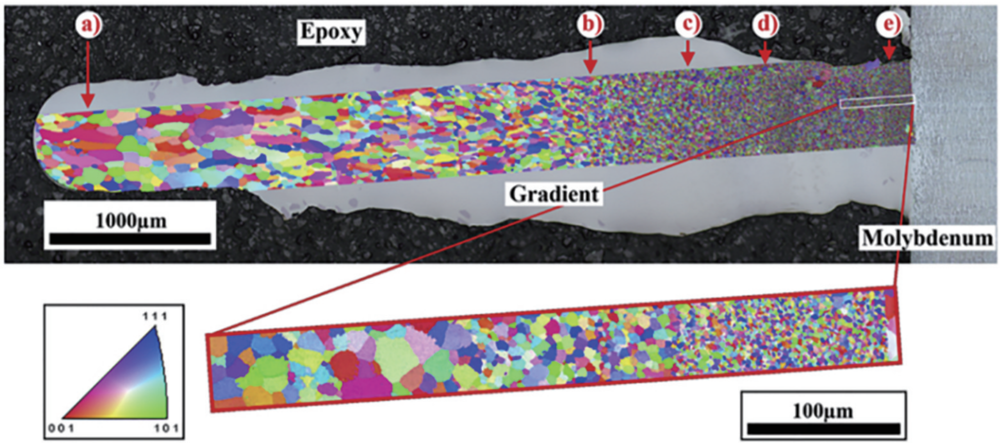

图 5　样件截面的背散射图像以及由背向散射电子衍射(EBSD)获得的焊接结构截面上的晶粒方向

Fig. 5　Backscatter image of sample section and grain direction of welded structure section obtained by electron backscatter diffraction (EBSD)

4　激光增材制造难熔高熵合金的力学性能

4.1　激光增材制造难熔高熵合金的室温力学性能

目前,针对传统真空电弧熔炼等方式制备的难熔高熵合金进行性能研究的报道比较多[10,77-78],相对而言,增材制造成形的难熔高熵合金的力学性能数据也在不断更新和发展。表 1 总结了增材制造难熔高熵合金的压缩性能[79-89]。Xiao 等[79]采用增材制造技术成形了一种成分均匀、单相且具有良好力学性能的 WTaRe 中熵合金。WTaRe 合金的晶粒尺寸在打印方向上呈现出差异性,垂直和平行于打印方向的截面上的晶粒直径分别为 29.5 μm 和 30.9 μm;其显微硬度值在上述两个方向上分别为(560±25) HV 和(668±8) HV,也具有一定差异。压缩试验表明,WTaRe 合金在平行于打印方向上的抗压强度为(1571±71) MPa,垂直于打印方向上的抗压强度为(1762±40) MPa。Li 等[80]采用激光熔覆沉积法制备了 W_xNbMoTa(x=0,0.16,0.33,0.53)难熔高熵合金。W_xNbMoTa 合金为 BCC 结构的单相固溶体,由于激光熔覆沉积的快速凝固特性,晶粒和枝晶的平均尺寸分别为 20 μm 和 4 μm。随着钨含量增加,合金的维氏显微硬度逐渐提高,分别为(459.2±9.7)、(476.0±12.9)、(485.3±8.7)、(497.6±5.6) HV[80]。Dobbelstein 等[82]采用高通量激光金属沉积方法,通过原位合金化元素粉末制备了五元难熔高熵合金 TiZrNbHfTa 及其四元和三元合金。合金的强度主要受原始粉末中氧、氮含量的影响,而且固溶体的强化作用较小。TiZrNbHfTa 合金的压缩屈服强度可达(1460±30) MPa,抗压强度约为 1900 MPa。Ron 等[83]以混合元素合金粉末为原料,采用 LPBF 制备了 WTaMoNbV 高熵合金,其显微组织、物理性能和电化学行为与传统电弧熔炼工艺制备的同类合金相似。

Ye 等[84]系统研究了 CNTs/$CoCrMoNbTi_{0.4}$ 难熔高熵合金的 LDED 工艺优化、微观组织演变和力学性能。CNTs/$CoCrMoNbTi_{0.4}$ 难熔高熵合金具有多晶结构(BCC、HCP 和 FCC)。由于形成了高密度和超细组织,合金的显微硬度达到 1015 HV0.5,抗压强度达到 2110.5 MPa,压缩应变达到 2.39%。Chesetti 等[85]采用 LPBF 技术成形了 $Al_{10}Nb_{15}Ta_5Ti_{30}Zr_{40}$ 合金,其压缩屈服强度约为 1400 MPa,抗压强度约为 1700 MPa,压缩应变大于 45%。这些性能可能归因于其独特的微观结构——由包含高密度亚晶界的精细晶粒组成,是包含有序 B2 和无序 BCC 固溶体相的纳米级两相混合物。北京航空航天大学的 Su 等[86]采用 LDED 技术制备了 $AlMo_{0.5}NbTa_{0.5}TiZr$ 合金,其显微硬度为(646.4±15.7) HV,室温压缩屈服强度为 2000 MPa,抗压强度为 2368 MPa。

Zhang 等[71]采用 LPBF 成形了 NbMoTaX 系难熔高熵合金。研究后发现,Ti 或 Ni 元素的添加均会对 NbMoTa 合金成形过程中的裂纹产生影响:添加 Ti 元素后,裂纹尺寸减小;添加 Ni 元素虽然消除了微裂纹,但由于主体相的塑性降低,出现了贯穿型大裂纹。此外,将 Ti 和 Ni 元素以等摩尔比加入所形成的 $NbMoTaTi_{0.5}Ni_{0.5}$ 合金缺陷明显减少,并且具有一定的室温强度和高温强度。$NbMoTaTi_{0.5}Ni_{0.5}$ 合金的室温抗压强度可达到 2277.79 MPa,相比于同样工艺成形的 NbMoTa 合金提高了 77.5%。进一步,他们采用 LPBF 成形了无裂纹缺陷的难熔 NbMoTa 系高熵合金 RHEA01,其室温屈服强度和抗压强度分别为 1277.35 MPa 和 1597.62 MPa,硬度为 511.76 HV[87]。该团队采用 LPBF 成形了超高强度、极细晶粒的 NbMoTaTiNi 高熵合金,其室温压缩屈服强度可达 1728 MPa,抗压强度高达 2753 MPa,抗拉强度为 1205 MPa。经 1200 ℃退火后,合金的压缩应变为 33.55%,比退火前提高了 54.3%[88]。他们通过调整

表1 增材制造难熔高熵合金的压缩性能

Table 1 Compression properties of AMed RHEAs

Process	Composition	Compressive yield strength R_{ec}/MPa	Compressive strength R_{mc}/MPa	Compressive strain ε_{tc}/%	Ref.
SEBM	WTaRe (in building direction)	1181±71	1571±71	16.60±1.83	[79]
SEBM	WTaRe (perpendicular to building direction)	1343±19	1762±40	19.45±1.05	[79]
LDED	TaMoNb	874	1140	5.8	[80]
LDED	$W_{0.16}TaMoNb$	800	840	2.5	[80]
LDED	$W_{0.33}TaMoNb$	810	895	3.2	[80]
LDED	$W_{0.53}TaMoNb$	808	890	3.4	[80]
LPBF	NbMoTaW	1196	1237	4.6	[81]
LPBF	$(NbMoTaW)_{99.5}C_{0.5}$	1725	1728	7	[81]
LDED	TiZrNbHfTa (Stock 1)	1460±30	~1900	22	[82]
LDED	TiZrNbHfTa (Stock 2)	1105±10	–	>40	[82]
LDED	TiZrNb	795±4	–	>40	[82]
LDED	$Ti_{27}Zr_{27}Nb_{27}Hf_{9.5}Ta_{9.5}$	910±50	–	>40	[82]
LDED	$Ti_{42}Zr_{22}Nb_{22}Hf_{7}Ta_{7}$	840±30	–	>40	[82]
LPBF	NbMoTa	1252.56	1282.94	15	[71]
LPBF	NbMoTaTi	1201.48	1380.27	23	[71]
LPBF	NbMoTaNi	1350.19	1356.19	11	[71]
LPBF	$NbMoTaTi_{0.5}Ni_{0.5}$	1750.46	2277.79	15	[71]
LPBF	WTaMoNbV	–	1391±166	–	[83]
LDED	$CNTs/CoCrMoNbTi_{0.4}$	–	2110.5	2.39	[84]
LPBF	RHEA01	1277.35	1597.62	9.5	[87]
LPBF	$Al_{10}Nb_{15}Ta_{5}Ti_{30}Zr_{40}$	1400	1700	>45	[85]
LDED	$AlMo_{0.5}NbTa_{0.5}TiZr$	2000	2368	–	[86]
LPBF	NbMoTaTiNi	1728	2753	21.75	[88]
LPBF	NbMoTaTiNi(HT1200)	1502	2596	33.55	[88]
LPBF	$Nb_{3}Ta_{3}(Ti_{2}Ni)_{4}$	395±36	–	>50	[89]
LPBF	$Nb_{3}Ta_{3}Mo(Ti_{2}Ni)_{3}$	915±47	–	>50	[89]
LPBF	$Nb_{3}Ta_{3}Mo_{2}(Ti_{2}Ni)_{2}$	1285±56	2447	27.1±2.6	[89]

Mo 元素含量设计了 $Nb_3Ta_3(Ti_2Ni)_4$、$Nb_3Ta_3Mo(Ti_2Ni)_3$ 和 $Nb_3Ta_3Mo_2(Ti_2Ni)_2$ 三种难熔高熵合金，并采用 LPBF 技术实现了三种合金的成形。高强 $Nb_3Ta_3Mo_2(Ti_2Ni)_2$ 合金的压缩屈服强度高达(1285±56) MPa，抗压强度为 2447 MPa，压缩应变为(27.1±2.6)%。高韧 $Nb_3Ta_3(Ti_2Ni)_4$ 合金展现出了抗压超塑性[89]。

由于难熔高熵合金本身的高脆性以及增材制造高温度梯度下的高热应力使得其成形过程中存在缺陷，因此关于其拉伸性能的研究相对较少(如表 2 所示[88-91])。Jeong 等[90]采用 LDED 成形了具有较低密度的难熔 TiNbCrVNi 合金，其拉伸屈服强度为 852 MPa，抗压强度为 1021 MPa，拉伸应变仅为 2.3%。Gou 等[91]采用 LDED 方法制备了拉伸延展性流变合金 $TiZrHfNb_x$(x=0.6，0.8，1.0)。该合金具有等轴晶组织，无须进行任何特殊的工艺控制或额外处理。增加 Nb 含量稳定了 BCC 相，抑制了 ω 相的形成。在水平方向加载时，TiZrHfNb 难熔高熵合金的拉伸屈服强度为 1034 MPa，断后延伸率为 18.5%，表现出了优异的拉伸性能。Li 团队[88]对 LPBF 成形 NbMoTaTiNi 难熔高熵合金的抗拉性能进行了测试，结果显示，其屈服强度为 1205 MPa，断后延伸率为 0.82%。该团队通过对 Mo 元素含量进行优化以及调整 Ti 和 Ni 元素的添加比例，成形了屈服强度为(1184±22) MPa、极限抗拉强度为(1403±35) MPa、断后延伸率为(4.4±0.7)%的 $Nb_3Ta_3Mo(Ti_2Ni)_3$[89]，其拉伸性能领先于其他所有增材制造的难熔高熵合金。

表2 增材制造难熔高熵合金的拉伸性能

Table 2 Tensile properties of AMed RHEAs

Process	Composition	Tensile yield strength R_e /MPa	Tensile strength R_m /MPa	Elongation after fracture A /%	Ref.
LPBF	NbMoTaTiNi	1205	–	0.82	[88]
LPBF	NbMoTaTiNi(HT1100)	1105	–	1.1	[88]
LPBF	$Nb_3Ta_3(Ti_2Ni)_4$	671±31	1036±17	9.2±0.6	[89]
LPBF	$Nb_3Ta_3Mo(Ti_2Ni)_3$	1184±22	1403±35	4.4±0.7	[89]
LPBF	$Nb_3Ta_3Mo_2(Ti_2Ni)_2$	1212±16	–	0.82±0.06	[89]
LDED	TiNbCrVNi	852	1021	2.3	[90]
LDED	$TiZrHfNb_{0.8}$	782	–	13.1	[91]
LDED	TiZrHfNb	1048	–	10	[91]
LDED	TiZrHfNb (in horizontal direction)	1034	–	18.5	[91]

4.2 激光增材制造难熔高熵合金的高温力学性能

难熔高熵合金的研究重点还是在其高温强度上。高熵合金由于组成元素本身具有较高的熔点，而且具有较好的热稳定性，因而被认为是新一代高温高强结构的替代材料。在难熔高熵合金激光增材制造过程中，制约其高温性能的是缺陷的控制以及低熔点元素含量的调控。Li等[80]采用LDED制备了NbMoTa合金，其在1000 ℃时的压缩屈服强度和压缩应变（ε_{tc}）分别为530 MPa和8.5%，如表3所示。该团队通过添加少量Ti和Ni元素，解决NbMoTaX系合金成形过程中的裂纹缺陷。$NbMoTaTi_{0.5}Ni_{0.5}$合金在600 ℃下具有1279.34 MPa的压缩屈服强度[71]。进一步优化Ti和Ni元素的含量后，RHEA01合金1000 ℃下的压缩屈服强度提升至724.45 MPa[87]。此系列难熔高熵合金与航空航天中常用的T-111、C103、Nb-1Zr高温合金相比具有更加优异的性能。Jeong等[90]测试了LDED制备的TiNbCrVNi合金的高温抗压性能，如图6所示，可见，其在1000 ℃和800 ℃时的拉伸屈服强度均不足100 MPa。

表3 增材制造难熔高熵合金的高温压缩性能

Table 3 Compression properties of AMed RHEAs at high temperature

Process	Composition	R_{ec} /MPa	R_{mc} /MPa	ε_{tc} /%	Ref.
LDED	TaMoNb (1000 ℃)	530	684	8.5	[80]
LPBF	$NbMoTaTi_{0.5}Ni_{0.5}$ (600 ℃)	1279.34	1669.75	28.42	[71]
LPBF	$NbMoTaTi_{0.5}Ni_{0.5}$ (800 ℃)	756.92	1033.63	28	[71]
LPBF	$NbMoTaTi_{0.5}Ni_{0.5}$ (1000 ℃)	554.61	651.36	11	[71]
LPBF	RHEA01 (600 ℃)	1131.42	1207.21	8	[87]
LPBF	RHEA01 (800 ℃)	693.34	1150.53	10	[87]
LPBF	RHEA01 (1000 ℃)	724.45	993.84	10	[87]

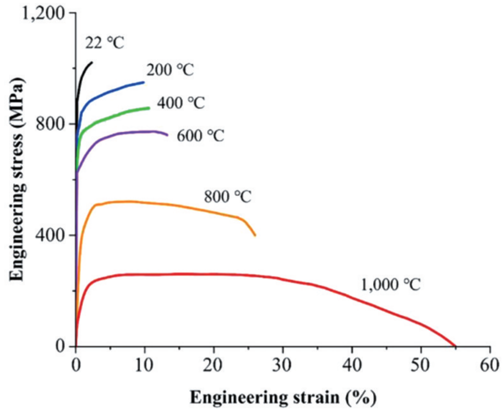

图6 TiNbCrVNi合金的拉伸性能曲线[90]

Fig. 6 Tensile property curves of TiNbCrVNi alloy[90]

激光增材制造难熔高熵合金的力学性能直接决定了该材料的工程化应用，材料能否适应短期加速、结构承载、长期疲劳等应用场景，与其室温拉伸性能和塑性是否符合要求紧密相关，而难熔高熵合金的室温拉伸性能较差，直接限制了其在上述场景中的应用。因此，如何提高激光增材制造难熔高熵合金的室温拉伸强度和塑性是一个重要的研究课题。另外，在高温应用场景下，高温结构承载、热防护、动能打击等多种服役条件对材料的高温压缩强度和拉伸强度都有较高要求。目前，高熵合金的高温压缩强度可以达到500 MPa（1600 ℃）；在高温拉伸性能方面，由于材料组分和成形工艺的限制，部分牌号高熵合金的高温抗拉强度仅达到高温合金水平，“高熵”效应对高温抗拉强度的提升还需要进一步深入研究。

5　难熔高熵合金的激光增材制造工艺开发

单因素实验、熔池数值化搭接优化、数值模拟辅助等是难熔高熵合金激光增材制造工艺快速优化的常用策略。难熔高熵合金的激光增材制造成形工艺参数较多。LPBF成形工艺参数有激光功率、扫描速度、道间距以及层厚等，LDED成形工艺参数有激光功率、扫描速度、抬升量以及送粉速度等。宁波大学的Ye等[84]采用LDED技术制备了CNTs/CoCrMoNbTi$_{0.4}$合金，研究了不同工艺参数下成形零件的表面形貌、显微组织和力学性能。如图7所示，他们采用大光斑（3 mm）激光器，将扫描速度 V 设置为5 mm/s，在1400、1600、1800、2000、2200 W激光功率（对应的线能量密度分别为2.8、3.2、3.6、4.0、4.4 J/mm）下实现了薄壁件的成形。如图8所示，当线能量密度为3.6 J/mm时，成形的合金具有最好的表面质量、较少的缺陷（裂纹、孔隙和未熔合等缺陷较少）以及最高的显微硬度和抗压强度。由此通过单因素试验确定了CNTs/CoCrMoNbTi$_{0.4}$难熔高熵合金LDED成形的最佳线能量密度为3.6 J/mm。

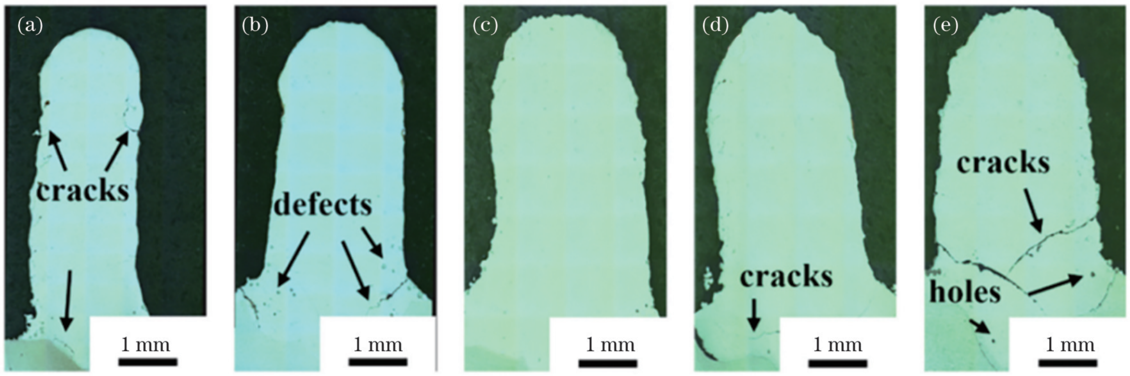

图7　不同工艺参数下薄壁件的截面形貌[84]。(a) 2.8 J/mm；(b) 3.2 J/mm；(c) 3.6 J/mm；(d) 4.0 J/mm；(e) 4.4 J/mm

Fig. 7　Cross-section morphology of thin-walled parts under different process parameters[84]. (a) 2.8 J/mm; (b) 3.2 J/mm; (c) 3.6 J/mm; (d) 4.0 J/mm; (e) 4.4 J/mm

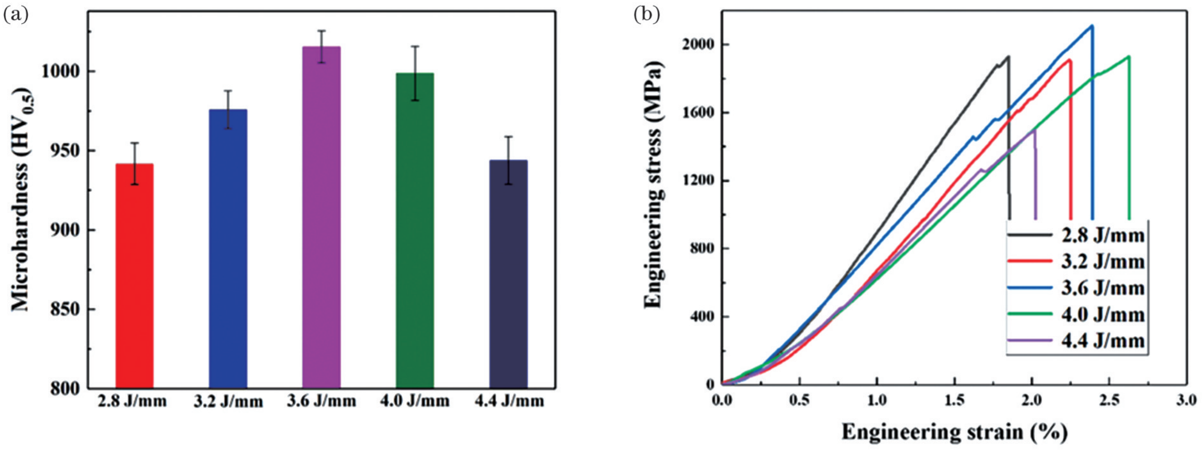

图8　试样在不同加工参数下的性能测试结果[84]。(a)合金截面的平均显微硬度；(b)合金在室温压缩下的工程应力-应变曲线

Fig. 8　Performance test results of the samples under different processing parameters[84]. (a) Average microhardness of alloy cross-section; (b) engineering stress-strain curves of the alloy under compression at room temperature

西安交通大学的Li教授团队[72]采用LPBF成形了Nb$_{30}$Mo$_{10}$Ta$_{30}$Ti$_{20}$Ni$_{10}$合金，并发现通过熔池搭接可以显著改进成形质量，图9为溶池搭接优化示意图。他们采用数值分析方法以功率、扫描速度、道间距、层厚等参数为变量进行工艺优化。实验结果表明：采用优化工艺成形的Nb$_{30}$Mo$_{10}$Ta$_{30}$Ti$_{20}$Ni$_{10}$合金的致密度为99.99%，室温抗拉强度为1.46 GPa，室温抗拉强度较优化前提高了48.9%。

如图10所示，西安交通大学的Li团队[92]采用热力学和力学模型与FD-FE相结合的方法，成功地模拟并改进了LPBF成形WTaMoNb难熔高熵合金的整个过程，并成形出了无翘曲的复杂结构——涡轮叶片样件。他们基于LPBF基本传热理论，采用有限差分/有限元耦合算法，结合移动嵌套网格技术，大幅降低了计算量，获得了激光加工过程中成形件的实时温度分布和应力应变分布。该研究有助于深入分析激光增材加工工艺特征，从而有助于LPBF一体化成形WTaMoNb复杂结构样件的工艺优化。

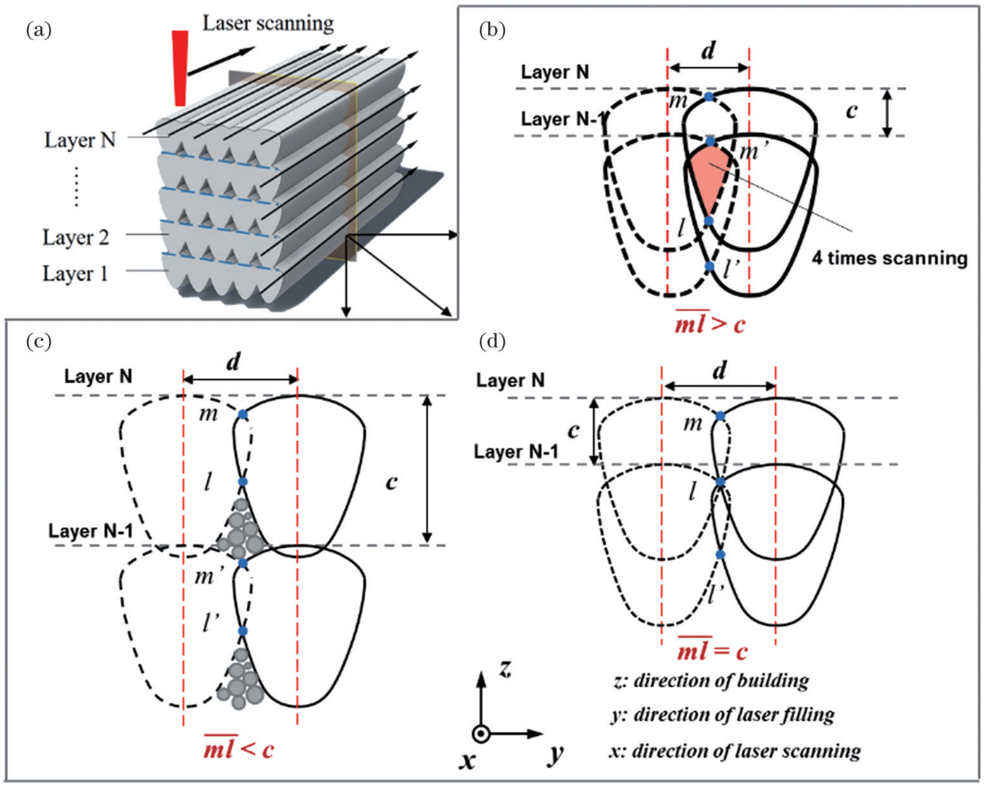

图 9　LPBF 成形过程以及参数之间的几何关系[72]。(a)简化的 LPBF 成形过程。不同情形下，层厚 c 与通道间距 d 之间的几何关系：(b) $\overline{ml} < c$，(c) $\overline{ml} > c$，(d) $\overline{ml} = c$

Fig. 9　LPBF forming process and geometric relationship between parameters[72]. (a) Simplified LPBF forming process. Geometric relationship between the layer thickness c and the channel spacing d for the following cases: (b) $\overline{ml} < c$, (c) $\overline{ml} > c$, and (d) $\overline{ml} = c$

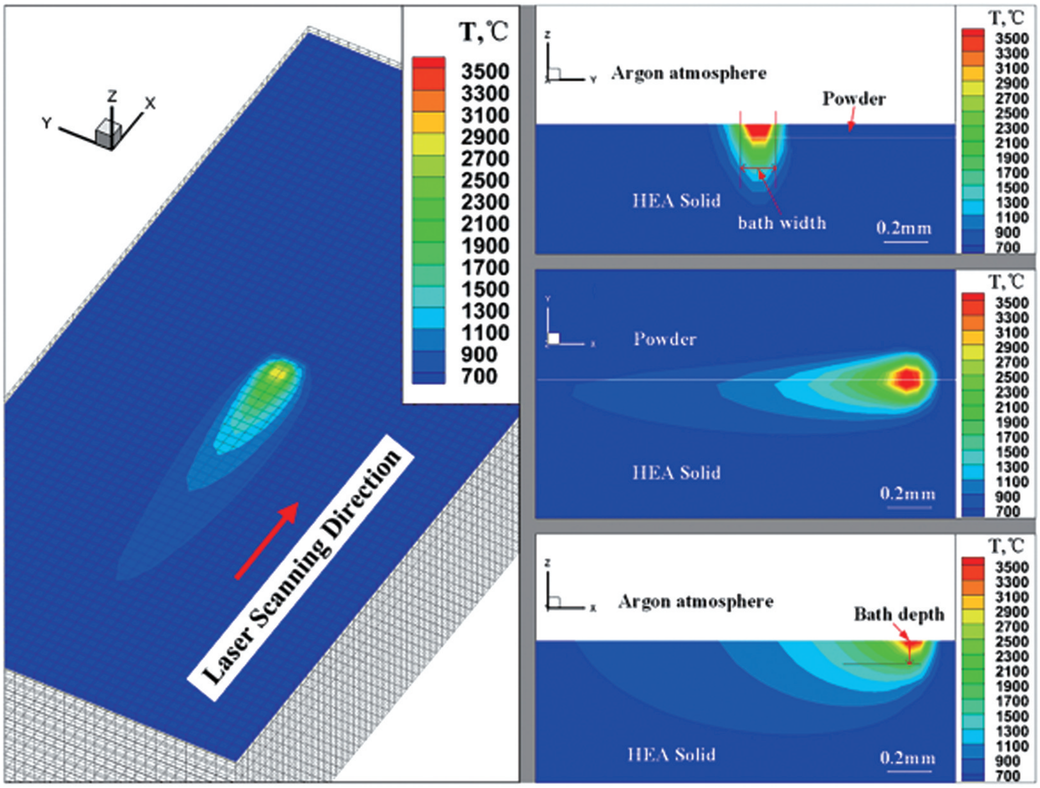

图 10　LPBF 工艺 200 s 激光光斑周围微区(4 mm×2 mm×1 mm)的温度分布[92]

Fig. 10　Temperature distribution in the micro-region (4 mm×2 mm×1 mm) around the 200 s laser spot of LPBF process[92]

6　难熔高熵合金复杂构件的形性一体化制造

尽管激光增材制造具有成形复杂结构的技术优势，但因工艺技术问题，成形难熔高熵合金复杂结构件的报道较少。研究人员实现了难熔高熵合金简单试样的激光增材制造，如图11～13所示。以预制混合粉为原材料，采用LPBF成形的方块试样如图11所示，试样表面粘粉较多，尺寸精度和表面质量较差。如图12所示，LPBF也能成形拉伸样件，但该样件需要进行打磨和抛光后才能用于拉伸性能测试。难熔高熵合金本身具有极高的脆性，再加上激光增材制造高能激光束作用下的高温度梯度产生的高热应力，难熔高熵合金在成形过程中极易产生裂纹[71]和翘曲[92]缺陷，如图14所示。西安交通大学的Li教授团队致力于难熔高熵合金激光增材制造大尺寸样件的工艺研究，他们采用嵌套网格技术建立有限差分/有限元模型，对LPBF成形WTaMoNb合金的过程进行了数值模拟优化，得到了成形过程中的温度场以及应力和应变场。为了使温度分布尽可能均匀，同时也为了尽可能减小应力和应变，他们对工艺参数进行了修正。他们采用优化后的参数成形了无翘曲的方块形试样和缩比的涡轮叶片样件(如图15所示)，首次实现了复杂结构难熔高熵合金试样的精确整体成形[92]。

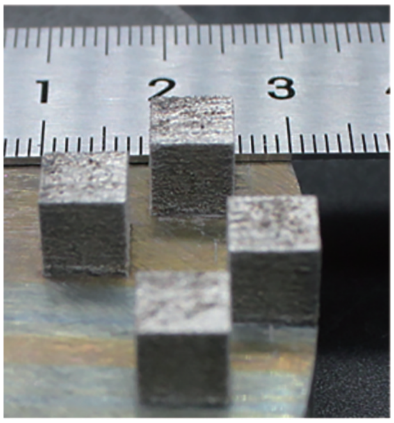

图11　LPBF成形样件[89]

Fig. 11　LPBF formed samples[89]

图12　LPBF成形的拉伸样件(抛光后)[89]

Fig. 12　Tensile samples formed by LPBF(after polishing)[89]

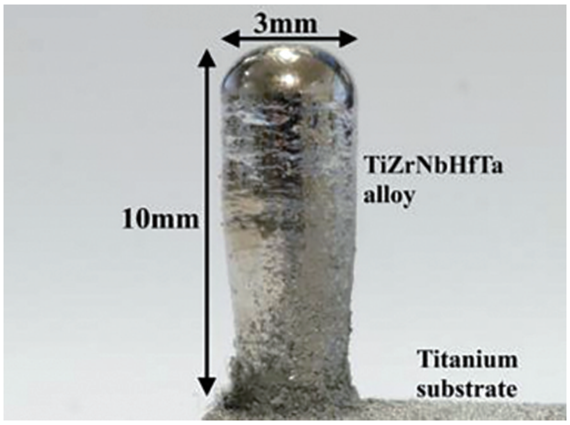

图13　LDED成形的初始样件[76]

Fig. 13　Original sample formed by LDED[76]

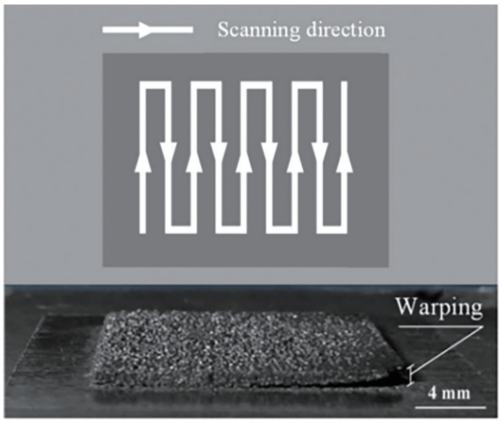

图14　未改进LPBF工艺成形的高熵合金出现翘曲变形[92]

Fig. 14　Warping deformation of HEA formed by LPBF without improvement[92]

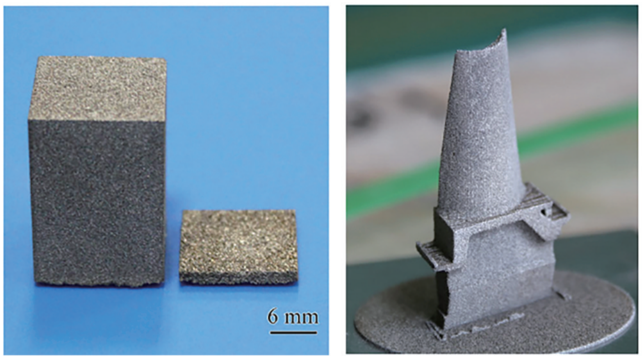

图15　改进LPBF工艺成形的样件[92]

Fig. 15　Samples formed by improved LPBF forming[92]

西安交通大学的耿佳乐[93]采用LPBF工艺分别以Z字形扫描策略和条带扫描策略(如图16所示)成形了缩比叶轮实物图。如图16所示，采用Z字形扫描策略时，A点的温度梯度是最大的。在带状扫描策略中，激光回到同一点所走过的最远路程是带状区域最宽处的两倍，重复受热的间隔时间仅为Z字形扫描方式的

25%，温度梯度也仅为 Z 字形扫描方式的 25%。如图 17 所示，叶轮并没有发生开裂、翘曲等缺陷，但其粗糙度较大，通过测量可知叶型壁厚为(1.8±0.5) mm，与设计值相差 0.5 mm，尚未达到工程精度控制要求。

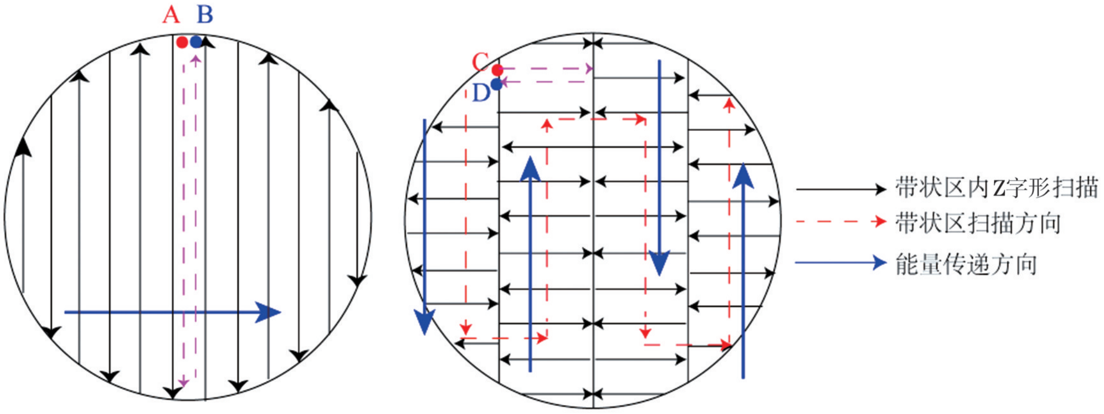

图 16　Z 字形(左)和带状扫描策略[93]

Fig. 16　Z-shape (left) and strip (right) scanning strategies[93]

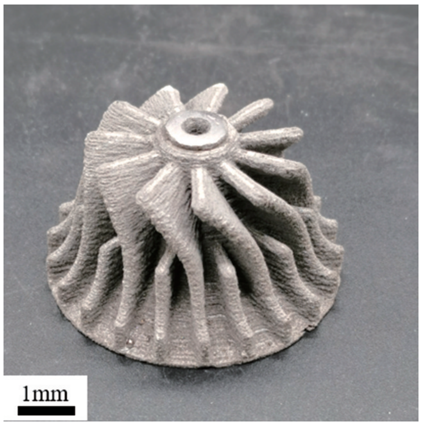

图 17　LPBF 成形的 $Nb_3Ta_3Mo(Ti_2Ni)_3$高熵合金叶轮实体[93]

Fig. 17　$Nb_3Ta_3Mo(Ti_2Ni)_3$ high entropy alloy impeller entity formed by LPBF[93]

总体而言，难熔高熵合金复杂构件一体化控形控性制造的研究报道较少，而工程应用级零件的制备不仅需要难熔高熵合金材料和激光增材制造工艺的迭代进步，还需要更多理论探索和研究投入，以解决材料的原理性脆性，突破拉压不平衡的困境，改善成形过程中的缺陷，最终实现难熔高熵合金复杂构件的整体成形，切实推动难熔高熵合金这种新材料在航空航天、核工程、武器装备等多领域广泛应用。

7　结　　论

采用真空电弧熔炼技术制备难熔高熵合金面临尺寸受限、复杂结构难以成形、成分偏析严重、研发周期长等问题。发展难熔高熵合金的激光增材制造技术，有利于推进难熔高熵合金的快速研发迭代。采用激光直接熔炼可以避免成分偏析以及对高温熔炼设备的需求。发展材料制备与成形一体化技术，可为大承载、耐高温、耐腐蚀的航空航天、核工程、国防装备部件的制造提供新途径。

1）难熔高熵合金激光增材成形的首要任务是缺陷控制。激光增材制造难熔高熵合金的显微组织缺陷主要包括裂纹和孔隙：裂纹缺陷主要分为热裂纹和冷裂纹，少量纳米颗粒的加入、工艺优化以及后处理可以消除裂纹缺陷；孔隙缺陷可以分为未熔合孔隙、冶金孔隙、微孔隙、收缩孔隙 4 种类型，孔隙缺陷的主要控制方法为工艺优化。通过对缺陷进行控制，可以初步实现难熔高熵合金的成形及其性能的大幅提升。

2）难熔高熵合金增材制造是快速开发新合金的有效方法。激光增材制造可以实现难熔高熵合金的快速开发迭代。通过机械混粉或预制合金粉，激光增材制造技术可以实现多种金属粉末的变组分比例成形，进而实现合金组成的快速筛选以及合金性能评测。

3）激光增材制造难熔高熵合金的合金化对其力学性能影响显著。NbMoTaW 系合金具有极高的强度，但塑性较差，通过适当添加低熔点塑性元素和减少基体脆性元素可以实现此类合金的强韧化。HfNbTaZr 系合金的塑性较好，但屈服强度普遍较低，可以通过添加强化元素进行强化。由于成形裂纹缺陷难以控制，激光增材制造难熔高熵合金的抗拉性能研究较少，还需要开展更多研究工作，尤其是材料机理和成形工艺方面的研究。

4）难熔高熵合金必须走材料结构一体化的道路，激光增材制造是向构件制造发展的重要途径。材料和工艺的进步是难熔高熵合金激光增材制造复杂构件整体成形的前提，目前已具备成形简单试样的能力，但仍需要进行深入研究来加快激光增材制造难熔高熵合金形性一体化制造工业化应用的进程。

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Development of Refractory High Entropy Alloys by Laser Additive Manufacturing: Regulating Material Properties and Manufacturing Processes (Invited)

Li Dichen[1,2*], Zhang Hang[1,2**], Cai Jianglong[1,2]

[1]*State Key Laboratory of Mechanical Manufacturing Systems Engineering, Xi'an Jiaotong University, Xi'an* 710049, *Shaanxi, China*;

[2]*School of Mechanical Engineering, Xi'an Jiaotong University, Xi'an* 710049, *Shaanxi, China*

Abstract

Significance Refractory high entropy alloy (RHEA) has superior properties such as high strength, high hardness, high temperature resistance and high corrosion resistance, which is expected to become a new material of high-temperature structure. RHEA has huge application prospects in aerospace, nuclear engineering, weapons and other fields. At present, the RHEA prepared by vacuum arc melting technology has some problems, such as large size limitation, difficult formation of complex structure, serious component segregation and long development cycle. RHEA formed by laser additive manufacturing has obvious advantages such as uniform composition, excellent microstructure and properties, integral forming of complex shape, *etc*. It has application potential in raw material development and high-performance parts preparation, so it has received hot attention in the research field.

Progress The primary task of RHEA formed by laser additive manufacturing is defect control. The microstructure defects of RHEA produced by laser additive manufacturing can be divided into cracks and pores. The crack defects can be divided into hot crack and cold crack. The addition of a small number of nanoparticles, process optimization and post-treatment can eliminate the crack defects. Pore defects can be divided into four types: unfused pore, metallurgical pore, micro pore and shrinkage pore. The main control method of pore defects is process optimization. By controlling the defects, the forming of RHEA and its properties are improved greatly. Additive manufacturing of RHEAs is an effective method to develop new alloys quickly. The process parameters of laser additive technology are numerous, strongly coupled and nonlinear. Single-factor experiment, numerical overlap optimization of molten pool and numerical simulation are the rapid optimization strategies for laser additive manufacturing of RHEA. Laser additive manufacturing enables rapid development iterations of RHEA. By mechanical mixing powder or preforming alloy powder, laser additive manufacturing technology can realize the formation of various metal powders by varying component ratios, and realize the rapid screening and performance evaluation of alloy composition. NbMoTaW alloys have very high strength but poor ductility, which can be strengthened and toughened by appropriately adding low melting point ductility elements and reducing brittle elements in the matrix. HfNbTaZr alloy has good plasticity, but the yield strength is generally low, which can be strengthened by adding strengthening elements. Due to the difficulty of controlling the forming crack defects, there are few studies on the tensile properties of RHEA formed by laser additive manufacturing. And more research work is needed, especially major breakthroughs in material mechanism and forming process. Finally, the complex structural parts formed by laser additive manufacturing for RHEA is still in the initial attempt stage.

Conclusions and Prospects In this paper, the research on RHEAs formed by laser additive manufacturing is reviewed, and the development approaches, forming process and defect control, and the main research and challenges on mechanical properties of refractory high entropy alloys at multiple temperature stages are summarized. The research progress of complex parts of refractory high entropy alloy is introduced. Finally, the future application and development trend of RHEA formed by additive manufacturing are discussed. The integrated manufacturing of materials and shape is essential for RHEA, and laser additive manufacturing is the development direction of component manufacturing. The progress of materials and processes is the prerequisite for the integral forming of complex components in RHEA formed by laser additive manufacturing. At present, it has the ability to form simple samples, so more in-depth research is needed to accelerate the industrial application process of integrated manufacturing of shape and properties for RHEA in laser additive manufacturing.

Key words laser technique; laser additive manufacturing; refractory high entropy alloy; alloy development; integrated manufacturing