

钛合金表面激光熔覆涂层的研究进展

张蕾涛¹, 刘德鑫¹, 张伟樯², 王雪松², 戴娇燕², 徐金富^{1,2}

(1.长安大学 材料科学与工程学院, 西安 710061;

2.宁波工程学院 材料科学与化学工程学院, 浙江 宁波 315211)

摘要: 激光熔覆是钛合金表面改性的重要手段之一, 已成为当前研究热点。综述了国内外关于钛合金表面激光熔覆抗高温抗氧化、耐腐蚀、耐磨损和生物陶瓷等涂层的熔覆材料、熔覆层相组成和强化机理等的研究现状。其中, 抗高温抗氧化涂层主要由于 TiO_2 、 Al_2O_3 等相的隔氧作用, 提高了钛合金在高温下的抗氧化性; 耐腐蚀涂层主要由于 TiN 和 Ti_2Ni 等相的固溶强化及细小针状马氏体 α' 等的细晶强化, 提高了其耐腐蚀性; 耐磨损涂层主要由于 TiC 、 TiB 、 TiB_2 等相的弥散强化作用, 提高了涂层的耐磨性; 生物陶瓷涂层由于 HA 、 CaO 等相的存在, 增强了钛合金的生物相容性。其次, 阐述了由于熔覆材料与基材的热物性差异、试样预处理不当和工艺调控不当等因素引起的未熔颗粒、球化效应、裂纹、气孔和夹杂等主要缺陷, 以及调控激光功率、扫描速度等工艺参数, 预热基体材料, 通入保护气体和加入适当成分添加剂等控制和改善相关缺陷的措施。最后, 展望了钛合金表面激光熔覆涂层和技术的发展方向。

关键词: 钛合金; 激光熔覆; 表面改性; 抗氧化; 耐腐蚀; 耐磨损; 生物陶瓷涂层

中图分类号: TG174.4 **文献标识码:** A **文章编号:** 1001-3660(2020)08-0097-08

DOI: 10.16490/j.cnki.issn.1001-3660.2020.08.011

Research Progress of Laser Cladding Coating on Titanium Alloy Surface

ZHANG Lei-tao¹, LIU De-xin¹, ZHANG Wei-qiang², WANG Xue-song², DAI Jiao-yan², XU Jin-fu^{1,2}

(1.School of Materials Science and Engineering, Chang'an University, Xi'an 710061, China; 2.School of Materials and Chemical Engineering, Ningbo Institute of Technology, Ningbo 315211, China)

ABSTRACT: Laser cladding is one of the important technical methods for surface modification of titanium alloys, and has become a current research hotspot. The research status of cladding materials, phase composition and strengthening mechanism of laser cladding high-temperature and oxidation-resistant, corrosion-resistant, wear-resistant and bio-ceramic coatings on titanium alloys at home and abroad was summarized. The high-temperature and oxidation resistant coating was mainly attributed to the oxygen barrier effect of TiO_2 , Al_2O_3 and other phases, which improved the oxidation resistance of titanium alloys at high temperature; the corrosion-resistant coating was mainly due to the solid solution strengthening of TiN and Ti_2Ni phases and the fine-grained strengthening of martensitic α' , which improved the corrosion resistance; the wear-resistant coating mainly

收稿日期: 2019-09-24; 修订日期: 2020-06-15

Received: 2019-09-24; Revised: 2020-06-15

基金项目: 海曙区高新技术产业专项 (201803A006)

Fund: Haishu District Special High-tech Industry (201803A006)

作者简介: 张蕾涛 (1995—), 男, 硕士研究生, 主要研究方向为激光表面改性。

Biography: ZHANG Lei-tao (1995—), Male, Master, Research focus: laser surface modification.

通讯作者: 徐金富 (1965—), 男, 博士, 教授, 主要研究方向为激光表面改性。邮箱: xjf7413@sina.com

Corresponding author: XU Jin-fu (1965—), Male, Doctor, Professor, Research focus: laser surface modification. E-mail: xjf7413@sina.com

引文格式: 张蕾涛, 刘德鑫, 张伟樯, 等. 钛合金表面激光熔覆涂层的研究进展[J]. 表面技术, 2020, 49(8): 97-104.

ZHANG Lei-tao, LIU De-xin, ZHANG Wei-qiang, et al. Research progress of laser cladding coating on titanium alloy surface[J]. Surface technology, 2020, 49(8): 97-104.

improved the wear resistance due to the dispersion strengthening of TiC, TiB, TiB₂ and other phases; and bio-ceramic coating enhanced the biocompatibility of titanium alloys due to the presence of HA, CaO and other phases. Then, the main defects such as un-melted particles, spheroidization effect, cracks, pores and inclusions caused by the differences in thermal properties between the cladding material and the substrate, improper sample pretreatment, and improper process control were described, and the laser power, scanning speed and other process parameters were regulated to preheat the base material and introduce protective gas and add appropriate component additives to control and improve related defects. Finally, the development direction of laser cladding coating and technology on the surface of titanium alloy was prospected.

KEY WORDS: titanium alloy; laser cladding; surface modification; oxidation resistance; corrosion resistance; wear resistance; bioceramic coating

钛合金由于比强度高、密度低和低温抗氧化等优点^[1-2], 在航空航天、汽车模具、石油化工等多个领域中已被广泛应用^[3], 同时基于其生物相容性较好, 故可作为植入体应用于生物医学领域^[4]。但因钛合金表面硬度低、摩擦系数大、耐磨性差、抗高温氧化能力差等劣势, 其应用范围也受到了限制^[5]。因此, 对于钛合金的表面改性显得颇为重要。

目前, 传统的钛合金表面改性方法有热喷涂、气相沉积、微弧氧化和化学热处理等。随着激光技术和传统表面改性技术的相继发展, 激光熔覆技术应运而生^[6]。激光熔覆技术涉及数控、计算机、激光、粉末冶金等多个领域^[7], 以高能激光束为热源, 配置保护气氛和送粉装置, 或进行粉末预置, 进一步在基材表面形成一层具有耐磨、耐蚀等所需性能的高质量表面涂层^[8], 是一门多学科交叉的新学科和新兴表面改性技术^[9]。由于熔覆是一个快速熔化、凝固的过程, 整个过程历时较短, 故形成的界面组织致密, 在一定条件下可得到非晶组织, 且晶粒得到细化, 相比传统的表面改性工艺, 有工件变形小、热影响区小、熔覆层成分和稀释度可控等优点^[10]。但由于熔覆过程中过度和过冷度均大于常规热处理, 材料之间的热物性和热膨胀系数差异等原因, 容易在成形中产生诸如裂纹、气孔、熔合不良等缺陷^[11]。

现就钛合金表面激光熔覆功能涂层的熔覆材料、熔覆层相组成、强化机理, 以及熔覆涂层存在的主要缺陷、控制和改善措施等方面的最新研究进展进行了系统地综述, 并展望了钛合金表面激光熔覆涂层和技术的发展方向。

1 功能涂层的研究

钛合金激光熔覆技术的研究始于 20 世纪 80 年代, 经过半个多世纪的发展, 在各个领域得到了很大程度的应用, 在国内外已成为材料表面改性的研究热点^[12]。常见的钛合金, 如 Ti-6Al-4V、Ti-5Al-2.5Sn 等, 目前已在汽车生产^[13]、航空航天^[14]和生物医疗^[15]等诸多领域广泛应用。现根据涂层的功能分为以下四种: ①抗高温耐氧化涂层; ②耐腐蚀涂层; ③耐磨损

涂层; ④生物陶瓷涂层^[16]。

1.1 抗高温耐氧化涂层

由于在较高的温度下, 钛合金的强度低, 抗氧化性不足, 故其工作环境一般限制在 500 ℃以内。为了使钛合金在较高温度下(如火箭发动机、飞机压缩机盘或叶片等高温部件)继续服役, 众多学者通过激光熔覆技术对钛合金进行表面改性, 获得了高温耐磨、耐氧化的涂层。Huang 等^[17]在 Ti-6Al-4V 表面获得了 TiVCrAlSi 复合涂层, 其中钛硅化物(如 Ti₅Si₃)具有高温强度高、熔点高、密度低、高温稳定性好、抗氧化性好等优点, 使得涂层在高温下的氧化增重明显比基体少。现根据国内外研究进展, 列举了多种抗高温氧化涂层的相组成及作用机理于表 1。不难看出, 在表层形成的氧化物薄膜(如 SiO₂、TiO₂、Al₂O₃等)可以防止涂层表面的进一步氧化。此外, 合成的 Ti₅Si₃^[17,19]、Al₃Ti^[18]和 TiAl^[20]具有优异的抗氧化性能。

1.2 耐腐蚀涂层

当钛合金作为植入体或海洋动力部件等时, 特殊的工作环境需要其具备良好的耐腐蚀性能。然而, 钛合金却在不同的环境中表现出不同的腐蚀行为, 如在 Cl⁻富集的环境(如 NaCl)或低 pH 的酸性环境(如 H₂SO₄)中, 钛合金容易被腐蚀。目前为止, 提高钛合金耐腐蚀性的技术有气体渗氮、热氧化法和气相沉积等。Yue 等^[23]使用准分子激光在 Ti-6Al-4V 高温熔池中通入氩气和氮气, 由于产生了 TiN 相, 从而提高了合金的耐蚀性。Mohammad 等^[25]利用 Ti-6Al-4V 粉末在 Ti-6Al-4V 基体上获得了细小针状马氏体, 提高了涂层的耐蚀性。经过文献调研, 列出了现阶段部分耐腐蚀涂层相组成、性能及作用机理, 如表 2 所示。简而言之, TiN、TiO₂等相和马氏体 α' 的细化, 能有效改善涂层的耐腐蚀性能。

1.3 耐磨损涂层

钛合金由于表面硬度低(约 360HV)、摩擦学性能差等劣势, 其应用范围受到限制。因此, 通过固溶、弥散和细晶强化等机制, 并借助激光熔覆表面改性技

表 1 抗高温氧化涂层研究进展
Tab.1 Research progress on high-temperature oxidation coatings

Ref.	Substrate	Powers	Coating	Phases	Related properties	Action
[17]	Ti-6Al-4V	Ti, V, Cr, Al, Si	TiVCrAlSi	(Ti,V) ₅ Si ₃ , Al ₈ (V,Cr) ₅ , and a BCC	Improve the oxidation resistance of Ti-6Al-4V at 800 °C in air	SiO ₂ , (Ti,V) ₅ Si ₃ , TiO ₂ , Al ₂ O ₃ and a small amount of V ₂ O ₅
[18]	Ti-6Al-4V	Ti, AlB ₂	(Ti ₃ Al+TiB)/Ti	α-Ti matrix, Ti ₃ Al and TiB	High temperature oxidation and wear of resistance	TiO ₂ + Al ₂ O ₃ layer and B ₂ O ₃ particles was formed, effectively hindering the oxygen diffusion
[19]	Ti-6Al-4V	Ni, Ti, Si	Ni-Ti-Si	TiSi ₂ , Ti ₂ Ni and Ti ₅ Si ₃ phases	Higher microhardness, good wear resistance and good oxidation resistance of coatings	TiO ₂ , Al ₂ O ₃ , SiO ₂ , Ti ₅ Si ₃
[20]	TA6Zr4DE	Ti ₄₈ Al ₂ Cr ₂ Nb	TiAl-based	γ-TiAl and α ₂ -Ti ₃ Al phases	Better oxidation resistance than substrate	Nb and Cr inhibit the intensive growth of TiO ₂
[21]	Ti-6Al-4V	NiCrBSi, TaC	TiNi/Ti ₂ Ni	Ti ₂ Ni, TiNi, TiB ₂ , TiB and TiC	Improved the oxidation resistance	Ta ₂ O ₅ and TaC
[22]	γ-TiAl	Co, Cr, Mo	Co-Cr-Mo	γ-Co (fcc), ε-Co (hcp), and Cr ₂₃ C ₆	Improves the oxidation resistance of coating	CoCr ₂ O ₄

表 2 耐腐蚀涂层研究进展
Tab.2 Research progress on corrosion-resistant coatings

Ref.	Substrate	Powers	Coating	Phases	Related properties	Action
[24]	Ti-6Al-4V	CP Ti	CP Ti	α'-Ti ₂ acicular/widmanstat ten α	Anodic current density was lower	Acicular α' martensite and increasing scanning speed
[25]	Ti-6Al-4V	Ti-6Al-4V	Ti-6Al-4V	α, α', β phases	Noble corrosion behavior compared to the untreated substrate	Formation of martensite and grain refinement
[26]	Ti-6Al-4V	Ti-6Al-4V	Ti-6Al-4V	α-Ti, β, α' martensite	Improving the electrochemical corrosion resistance	Increase of the scanning speed, the decrease of crystal surface spacing
[27]	Ti-6Al-4V	Nb	Nb	α-Ti and β(Ti,Nb)	Corrosion resistance resulted to about 81.79% compared to the substrate	AlTi ₃ , AlTi ₂ , Al _{0.64} Ti _{0.36} , Al ₁₁ Ti ₁₅ , AlNbTi ₂ and AlNb ₃
[28]	Ti-6Al-4V	Co, Ni	CoNi intermetallic	Ti ₂ Ni, Co ₃ Ti, Al ₁₃ Co ₄ , NiTi, Ni ₃ Ti	Improving the corrosion behavior	Ti ₂ Ni, Co ₃ Ti, Al ₁₃ Co ₄
[29]	Ti-4Al-1.5Mn	Ti, TiC, TiB ₂	TiC/TiB ₂	α-Ti, β-Ti, TiC, TiB ₂	Corrosion resistance of the laser cladding specimens is clearly becoming better than the substrate	Grain refinement and the formation of TiC and TiB ₂

术,在其表面形成自润滑耐磨或陶瓷增强金属基等复合涂层,以减小其表面摩擦系数和磨损率,增大显微硬度,是非常有意义的。Liu 等^[33]使用 NiCr/Cr₃C₂-WS₂ 混合粉末在 Ti-6Al-4V 基体上形成了 γ-NiCrAlTi/TiC+TiWC₂/CrS+Ti₂CS 复合涂层,由于 TiC 和 TiWC₂ 的增强作用,使得涂层的显微硬度增大,摩擦系数降低,磨损量减小。另外,表 3 列出了多种耐磨损涂层相组成、性能及作用机理。总之,TiC、TiB、TiB₂、TiN、SiC、WC 等硬质陶瓷相常被作为强化相,掺入涂层中,以提高钛合金表面的耐磨性。

1.4 生物陶瓷涂层

密度小、生物相容性好等性能使钛合金成为生物医学植入最理想的材料之一^[37],其大多数被应用在人

工心脏、人体关节、创伤固定、牙齿植入和医用器械等场合。但由于钛合金的高弹性模量,导致植入材料与人体骨模量不匹配,同时硬度和耐磨性低使金属颗粒在体内释放,如铝离子和钒离子释放到体内,引起骨溶解和无菌性松动,从而产生一定的毒性,并导致周围神经病变、骨软化、老年痴呆症等^[43],使其应用受到了限制。Yang 等^[41]利用 HA 和 SiO₂ 混合粉末,成功在 Ti-6Al-4V 基体上形成了 SiO₂-HA 涂层,研究表明该涂层具有良好的生物相容性。表 4 列举了以钛合金为基体的植入体材料的研究现状。由此可见,在医用钛合金表面制备生物活性陶瓷羟基磷灰石涂层,由于界面形成了钛酸钙和磷化钛,涂层与基体结合良好,这是近年来世界各国生物医用植入材料及相关领域的研究热点之一^[37]。

表 3 耐磨涂层研究进展
Tab.3 Research progress on wear-resistant coatings

Ref.	Substrate	Powers	Coating	Phases	Related properties	Action
[30]	Ti-6Al-4V	Ti, TiB ₂ , Ni	TiC/TiB/Ti ₂ Ni/TiNi composite	Ti, TiC, TiB, Ti ₂ Ni, TiNi	863HV _{0.2} , friction coefficient lower and wear resistance was improved	TiC, TiB
[31]	Ti811	TC4, Ni60, CeO ₂	Ti-based	TiC, Ti-2Ni, TiB ₂ , and the matrix α -Ti	Improved the microhardness and the microstructure refined	TiC phase, an appropriate amount of CeO ₂
[32]	Ti-6Al-4V	NiCrBSi, WC, Y ₂ O ₃	WC reinforced Ni-based	γ -Ni, TiC, TiB ₂ , Ni ₃ B, M ₂₃ C ₆ and WC	813~1109.8HV _{0.5} , the microhardness improved and the wear resistance increase	WC, Y ₂ O ₃
[33]	Ti-6Al-4V	NiCr/Cr ₃ C ₂ -WS ₂	γ -NiCrAlTi/TiC+TiWC ₂ /CrS+Ti ₂ CS	α -Ti, TiC, TiWC ₂ , γ -NiCrAlTi, Ti ₂ CS and CrS	1005HV _{0.2} friction coefficient and wear rate are greatly decreased	Enforced TiC and TiWC ₂ carbides and the CrS and Ti ₂ CS sulfides
[34]	Ti-6Al-4V	TiB ₂	Ti-based	α -Ti, TiB ₂ and TiB phase	High hardness and high wear resistance	TiB fiber bundle
[35]	Ti-6Al-4V	Ti, SiC	Ti-based composite	Ti-rich phase, and the in-situ formed Ti ₅ Si ₃ and TiC phases	932.2HV, the wear resistance was improved	TiC and Ti ₅ Si ₃
[36]	Ti-6Al-4V	Ni and Ti	NiTi coating	NiTi ₂ , NiTi, unreacted Ti, and TiAl ₃	Improved hardness and wear resistance	Hard NiTi ₂ phases along with NiTi and other intermetallic

表 4 生物陶瓷涂层研究进展
Tab.4 Research progress on bio-ceramic coatings

Ref.	Substrate	Powers	Coating	Phases	Related properties	Action
[29]	Ti-6Al-4V	Nb	Nb	α -Ti and β (Ti,Nb) phases	The toxic effect emanating from released vanadium and aluminium ions	Nb
[38]	Ti-6Al-4V	Hf, Nb, and Zr metal powders	Hf-Nb-Zr composites	An acicular α -Ti and β -(Ti, Hf, Nb, Zr) solid solution phase	Alzheimer's disease was reduced	Hf, Nb, and Zr
[39]	Ti-6Al-4V	HA	CaP coating	Ti ₃ P ₂ and Ca ₃ Ti ₂ O ₇ and CaTiO ₃	Bio-ceramic to promote the growth of the bone	Tricalcium phosphate (α -TCP) and HA
[40]	TA2	CaCO ₃ and CaHPO ₄ ·2H ₂ O and titanium	HA coating	HA, α -Ca ₂ P ₂ O ₇ , CaO and CaTiO ₃	Biocompatibility of the materials used for implantation	HA, α -Ca ₂ P ₂ O ₇ , CaO and CaTiO ₃
[41]	Ti-6Al-4V	HA and SiO ₂	SiO ₂ -HA	CaTiO ₃ , Ca ₃ (PO ₄) ₂ , and Ca ₂ SiO ₄ phases	Higher cell attachment and proliferation rate	HA, SiO ₂
[42]	Ti-6Al-4V	HA and FGM	CaP-TiO ₂ bio-ceramic	CaTiO ₃ , CaO, β -Ca ₂ P ₂ O ₇ and TiO ₂	Higher cyto-compatibility rate	α -Ca ₃ (PO ₄) ₂ , and TiO ₂

2 功能涂层的材料体系选择

目前为止,熔覆材料根据形状不同分为粉末、线材或片材等形状,但最普遍是粉末材料^[44]。根据材料的成分主要分为自熔性粉末、陶瓷粉末、复合粉末和稀土氧化物粉末等^[45],如表 5 所示。选择合适的材料体系对获得性能、表面质量良好的功能涂层具有重要意义。一般来说,应同时考虑基材和功能涂层的匹配性,如两者应具有相似的物理性质(如熔点、热膨胀系数等),或同时具有相似的晶体结构和化学性质,以保证两者之间更好的润湿性。当然,对不同功能涂层材料体系的选择还需要考虑满足涂层功能、工艺和

经济性等原则。为方便广大学者了解钛合金不同功能涂层熔覆材料体系的选择,现从成分的角度进行归纳:

1) 抗高温氧化涂层。加入 Si、Al 等元素,以形成具有隔氧功能的氧化物薄膜或具有抗高温氧化性的钛硅化物(如 Ti₅Si₃),进一步提高涂层的高温氧化性。研究发现,在 600 ℃ 以上的温度下, TiN、TiB、W₂C 和 WC 增强相优先氧化。Si 基复合涂层虽有严重的室温脆性,但其抗高温氧化性能较好。目前, Maliutina 等^[20]发现 Nb 和 Cr 元素的加入会限制 TiO₂ 和 Al₂O₃ 的密集式生长。Lv 等^[21]发现,由于 TaC 的加入,涂层中产生了 Ta₂O₅ 和 TaC,提高了高温抗氧化性。

2) 耐腐蚀涂层。TiN 和 Ti₂Ni 等相的固溶强化及

细小针状马氏体 α' 等的细晶强化有助于提高涂层的耐腐蚀性。Co 被认为是改善钛及钛合金在腐蚀性介质中腐蚀行为较有效的元素^[26]，可适当加入 Ni，形成 CoNi 基金属间化合物涂层，提高其耐蚀性。同时，以稍快的扫描速度获得细小的针状马氏体 α' ，也可显著提高涂层的硬度和耐蚀性。

3) 耐磨损涂层。TiC、TiB、TiB₂、TiN、SiC、WC 等硬质陶瓷相由于其高硬度和良好的耐磨性，常被用作陶瓷增强金属基复合材料涂层（MMC）的增强材料，也可以在涂层中合成 MoS₂、WS₂ 等自润滑相等，以达到降低摩擦系数和磨损率，提高耐磨性的作用。

4) 生物陶瓷涂层。可加入难熔金属 Nb、Zr 和 Hf 等，以提高涂层生物相容性。这些难熔金属具有无毒性、成骨性良好等优势。此外，羟基磷灰石（HA）与牙、骨等硬组织中的矿物成分相似，具有较高的生物相容性，现被广泛应用于植入体材料，其化学式为 Ca₁₀(PO₄)₆(OH)₂^[46]。

总之，需根据涂层的功能，合理选择熔覆材料，并结合工艺和经济性等原则，适当添加合适的元素以获得所需的性能。当然，陶瓷增强金属基复合涂层（MMC）、高熵合金涂层^[47]等仍然会是研究的热点，也期待学者们研究出性能更佳的新材料，以促进钛合金表面激光熔覆技术的发展。

表 5 熔覆材料的分类及特点
Tab.5 Classification and characteristics of cladding materials

Cladding materials	Characteristic	Examples
Self-fusible powder	It can form good wetting and bonding with the base material and improve metallurgical effect. Ni-based alloy powder has good self-melting property, good toughness and heat resistance, etc., but poor performance at high temperature. The self-fusibility of Co base is worse than that of Ni base, but it has the best high temperature resistance and good toughness, wear resistance and corrosion resistance, but the cost is higher. Fe-based alloy powder self-melting effect and anti-oxidation performance are worse than the first two, but the cost is lower	Ni-based, Co-based, Fe-based, etc ^[48]
Ceramic powder	Excellent corrosion resistance, wear resistance and oxidation resistance	Carbide ceramics, boride ceramics, silicide ceramics, etc ^[49]
Composite powder	The formed cladding layer is compact and has excellent comprehensive performance	Such as carbide, nitride and other high melting point hard ceramic materials and metal mixture into the powder system
Rare earth oxide powder	Rare earth elements can easily react with other elements in the cladding layer to form rare earth compounds, improve nucleation rate, effectively refine the structure, and thus inhibit the crack tendency of the cladding layer. It can improve the mechanical properties, oxidation resistance, wear resistance and corrosion resistance of the cladding layer from different angles	Such as adding Ce, La, Y and other rare earth elements ^[50]

3 激光熔覆涂层存在的问题及措施

激光熔覆是一个极其复杂的物理化学冶金过程，且由于该技术一方面从兴起到研究再到投入使用的周期短，另一方面，受理论知识准备不足、设备一次

性投资大等问题束缚，因此发展受到制约。高密度、高质量涂层的熔覆迫切需要业内研究学者建立系统全面的理论，并投入大量的时间进行深入研究。表 6 列出了钛合金激光熔覆涂层存在的主要问题及对应措施。

表 6 钛合金激光熔覆涂层存在的主要问题及措施
Tab.6 Main problems and measures of laser cladding coating of titanium alloy

The main problems	Mechanism of production	Countermeasure
Unmelt particles	Due to the unreasonable density of powder bed and the reduced solubility of some elements in melt during solidification or the low laser power, the scanning speed is too high ^[50]	Increase laser power and reduce scanning speed ^[51]
Balling effect	With laser scanning and melting of powder particles, the formation of molten pool, laser scanning speed will inevitably affect the movement and stability of molten pool, molten metal material due to a large viscosity gradient, not wetting the solid layer, melt under the action of surface tension into a spherical phenomenon, known as balling effect ^[52]	The balling effect can be avoided by using higher laser power or lower scanning speed to reduce the length-width ratio of the molten pool or change the stability of the molten pool. That is to say, the solidification time is shorter than the decomposition time ^[53]

续表 6

The main problems	Mechanism of production	Countermeasure
Crack	The interaction between laser and powder is a process of rapid melting and rapid cooling of powder. Because the whole process is very short, far from the phase transition equilibrium state, and the superheat and super-cold degree are large, the thermal and physical properties of cladding material and substrate material and improper parameter control will form cracks in the molding process	Preheat the substrate, reduce the temperature gradient; Proper addition of nucleating agent can control the nucleation rate during solidification, reasonably control the laser power and scanning speed, and reduce the generation of thermal stress. By ensuring the wetting bonding between the substrate and the first cladding layer, avoiding balling effect, selecting the appropriate lap rate and the appropriate laser power density can effectively enhance the metallurgical bonding between the cladding layers and reduce the crack tendency ^[53]
Pores and inter-layers	The protective atmosphere is not qualified or the molten pool is pushed too fast, the powder is wrapped into the molten pool before melting	Ensure the stability of the atmosphere and the quality of the powder itself, and reasonably control the speed of the molten pool

4 展望

激光熔覆作为钛合金表面改性的一种先进技术,得到了长足的发展,而且仍有较大的空间提升。现从多个角度展望钛合金表面激光熔覆涂层和技术的发展方向:

1) 梯度涂层的研究和开发。为消除新型航空航天飞行器高温结构件在 1000 K 大温差变化时,由于不同材料界面引起的较大热应力和应变集中,避免膨胀系数相差较大导致的涂层剥落或龟裂等失效行为,开发能在钛合金表面具有缓和热应力,降低残余应力的“梯度功能涂层”,是一个新的研究热点。

2) 非晶钛基涂层的研究和开发。非晶态材料因其优异的机械、电气等性能而被广泛研究。激光熔覆的快速冷却过程给非晶涂层的形成提供了良好的外部条件,然而,需要熔覆材料满足熔融状态黏度较大的内部条件,才可形成非晶涂层。现阶段研究的非晶涂层大多为铁基,开发钛基等其他非晶涂层也是一个新的研究趋势。

3) 构建钛合金功能涂层相关数据库。随着 AI 技术的发展,数据共享也将不断推进技术的革新。针对熔覆材料与钛合金基材的匹配、工艺参数的控制等激光熔覆技术的关键部分,建立准确评价熔覆材料、工艺参数、性能等的标准,保证试验的便捷性和准确性,并依此标准建立关于激光熔覆技术的各种数据库,反馈给材料设计部门,以加快该技术进步的步伐。

4) 利用数学模型和有限元分析模拟激光熔覆过程。考虑到激光熔覆过程的不可预测性,数学模型和有限元分析模拟熔覆过程与试验相结合的方法已成为必然。目前,国内外学者对温度场、应力场、组织转变和冶金结合等过程进行了相关研究。该技术在缩短生产周期的同时,对熔覆过程也进行了把控,这将是该技术一个长期的发展趋势。

5) 其他辅助技术的研究和开发。针对制约激光熔覆技术发展的各种冶金缺陷,其他辅助技术的研究和开发很有必要。目前,国内外学者引入电场、磁场、

超声波振动等辅助技术来改善其冶金缺陷。但对于实际生产来说,设备的投入必将增大成本。因此,开发易投入生产的辅助技术将是一个新的研究方向。

参考文献:

- [1] 王培, 叶源盛. 钛合金表面激光熔覆 h-BN 固体润滑涂层[J]. 表面技术, 2015(8): 44-48.
WANG Pei, YE Yuan-sheng. Solid self-lubricating coatings on TC4 titanium alloy by laser cladding with h-BN[J]. Surface technology, 2015(8): 44-48.
- [2] 张安峰, 张金智, 张晓星, 等. 激光增材制造高性能钛合金的组织调控与各向异性研究进展[J]. 精密成形工程, 2019, 11(4): 1-8.
ZHANG An-feng, ZHANG Jin-zhi, ZHANG Xiao-xing, et al. Research progress in tissue regulation and anisotropy of high-performance titanium alloy by laser additive manufacturing[J]. Journal of netshape forming engineering, 2019, 11(4): 1-8.
- [3] GANESH B K C, SHA W, RAMANAIAH N, et al. Effect of shotpeening on sliding wear and tensile behavior of titanium implant alloys[J]. Materials & design, 2014, 56: 480-486.
- [4] BRUNI S, MARTINESI M, STIO M, et al. Effects of surface treatment of Ti-6Al-4V titanium alloy on biocompatibility in cultured human umbilical vein endothelial cells[J]. Acta biomaterialia, 2005, 1(2): 223-234.
- [5] GUO Chun, ZHOU Jian-song, ZHAO Jie-rong, et al. Improvement of the oxidation and wear resistance of pure Ti by laser-cladding Ti₃Al coating at elevated temperature[J]. Tribology letters, 2011, 42(2): 151-159.
- [6] NIE Xiang-fan, HE Wei-feng, ZANG Shui-lai, et al. Effect study and application to improve high cycle fatigue resistance of TC11 titanium alloy by laser shock peening with multiple impacts[J]. Surface & coatings technology, 2014, 253(9): 68-75.
- [7] NWOBUI Aip, RAWLINGS Rd, WEST Drf. Nitride formation in titanium based substrates during laser surface

- melting in nitrogen-argon atmospheres[J]. *Acta materialia*, 1999, 47(2): 631-643.
- [8] LIN Ying-hua, YAO Jian-hua, LEI Yong-ping, et al. Microstructure and properties of TiB₂-TiB reinforced titanium matrix composite coating by laser cladding[J]. *Optics & lasers in engineering*, 2016, 86: 216-227.
- [9] GAO Ya-li, WANG Cun-shan, YAO Man, et al. The resistance to wear and corrosion of laser-cladding Al₂O₃ ceramic coating on Mg alloy[J]. *Applied surface science*, 2007, 253(12): 5306-5311.
- [10] GUO Chun, ZHOU Jian-song, CHEN Jian-min, et al. High temperature wear resistance of laser cladding NiCrBSi and NiCrBSi/WC-Ni composite coatings[J]. *Wear*, 2011, 270(7): 492-498.
- [11] MENG Qing-wu, GENG Lin, ZHENG Zhen-zhou. Laser cladding Ni-base composite coating on titanium alloy with pre-placed B₄C+NiCoCrAlY[J]. *Materials science forum*, 2005, 475-479: 905.
- [12] 郭桂芳, 陈芙蓉, 李林贺. 激光熔覆技术在钛合金表面改性中的应用[J]. *表面技术*, 2006(1): 71-74.
- GUO Gui-fang, CHEN Fu-rong, LI Lin-he. Application of laser cladding technology in surface modification of titanium alloy[J]. *Surface technology*, 2006(1): 71-74.
- [13] MOAYEDFAR M, RANI A M, HANAEI H, et al. Parameter optimization and stretch enhancement of AISI 316 sheet using rapid prototyping technique[J]. *Materials science and engineering*, 2017, 257: 012006.
- [14] DAS S, BEAMA J J, WOHLERT M, et al. Direct laser freeform fabrication of high performance metal components[J]. *Rapid prototyping journal*, 2016, 4(3): 112-117.
- [15] LEONG K F, CHEAH C M, CHUA C K. Solid freeform fabrication of three-dimensional scaffolds for engineering replacement tissues and organs[J]. *Biomaterials*, 2003, 24(13): 2363-2378.
- [16] WENG Fei, CHEN Chuan-zhong, YU Hui-jun. Research status of laser cladding on titanium and its alloys: A review[J]. *Materials & design*, 2014, 58: 412-425.
- [17] HUANG Can, ZHANG Yong-zhong, SHEN Jian-yun, et al. Thermal stability and oxidation resistance of laser clad TiVCrAlSi high entropy alloy coatings on Ti-6Al-4V alloy[J]. *Surface & coatings technology*, 2011, 206(6): 1389-1395.
- [18] FENG Yue-qiao, FENG Kai, YAO Cheng-wu, et al. High temperature oxidation and wear resistance of in situ synthesized (Ti₃Al+TiB)/Ti composites by laser cladding[J]. *Metall and mat trans A*, 2019, 50: 3414-3428.
- [19] ZHUANG Qiao-qiao, ZHANG Pei-lei, LI Ming-chuan, et al. Microstructure, wear resistance and oxidation behavior of Ni-Ti-Si coatings fabricated on Ti6Al4V by laser cladding[J]. *Materials*, 2017, 10(11): 1248.
- [20] MALIUTINA I N, SI-MOHAND H, SIJOBERT J, et al. Structure and oxidation behavior of γ -TiAl coating produced by laser cladding on titanium alloy[J]. *Surface and coatings technology*, 2017, 319: 136-144.
- [21] LV Y H, LI J, TAO Y F, et al. High-temperature wear and oxidation behaviors of TiNi/Ti₂Ni matrix composite coatings with TaC addition prepared on Ti-6Al-4V by laser cladding[J]. *Applied surface science*, 2017, 402: 478-494.
- [22] BAREKAT M, SHOJA RAZAVI R, GHASEMI A. High temperature oxidation behavior of laser clad Co-Cr-Mo coating on γ -TiAl substrate[J]. *Journal of laser applications*, 2016, 28(4): 042005.
- [23] YUE T M, YU J K, MEI Z, et al. Excimer laser surface treatment of Ti-6Al-4V alloy for corrosion resistance enhancement[J]. *Materials letters*, 2002, 52(3): 206-212.
- [24] OBADELE B A, OLUBAMBI P A, ANDREWS A, et al. Electrochemical behaviour of laser-clad Ti6Al4V with CP Ti in 0.1 mol/L oxalic acid solution[J]. *Journal of alloys and compounds*, 2015, 646: 753-759.
- [25] NABHANI M, RAZAVI R S, BAREKAT M. Corrosion study of laser clad Ti-6Al-4V alloy in different corrosive environments[J]. *Engineering failure analysis*, 2019, 97: 234-241.
- [26] FENG Xiao-tian, LEI Jian-bo, GU Hong, et al. Effect of scanning speeds on electrochemical corrosion resistance of laser cladding TC4 alloy[J]. *Chinese physics B*, 2019, 28(2): 383-390.
- [27] ADESINA O S, POPOLA A P I, PITYANA S L, et al. Microstructure and corrosion behavior of laser synthesized cobalt based powder on Ti-6Al-4V[J]. *IOP conference series: Materials science and engineering*, 2018, 350: 11-13.
- [28] DIAO Yu-hua, ZHANG Ke-min. Microstructure and corrosion resistance of TC2 Ti alloy by laser cladding with Ti/TiC/TiB₂ powders[J]. *Applied surface science*, 2015, 352: S0169433215008703.
- [29] PHUME L, POPOOLA A P I, AIGBODION V S, et al. In-situ formation, anti-corrosion and hardness values of Ti-6Al-4V biomaterial with niobium via laser deposition[J]. *Surface science and engineering*, 2018, 12: 23-39.
- [30] 刘丹, 陈志勇, 陈科培, 等. TC4 钛合金表面激光熔覆复合涂层的组织和耐磨性[J]. *金属热处理*, 2015, 40(3): 58-62.
- LIU Dan, CHEN Zhi-yong, CHEN Ke-pei, et al. Structure and wear resistance of laser cladding composite coating on titanium alloy surface[J]. *Metal heat treatment*, 2015, 40(3): 58-62.
- [31] LIU Ya-nan, SUN Rong-lu, NIU Wei, et al. Effects of CeO₂ on microstructure and properties of TiC/Ti₂Ni reinforced Ti-based laser cladding composite coatings[J]. *Optics and lasers in engineering*, 2019, 120: 84-94.
- [32] WANG Kai-ming, DU Dong, LIU Guan, et al. Microstructure and properties of WC reinforced Ni-based composite coatings with Y₂O₃ addition on titanium alloy by laser cladding[J]. *Science and technology of welding and joining*, 2019, 24: 517-524.
- [33] LIU Xiu-bo, MENG Xiang-jun, LIU Hai-qing, et al.

- Development and characterization of laser clad high temperature self-lubricating wear resistant composite coatings on Ti-6Al-4V alloy[J]. *Materials & design*, 2014, 55: 404-409.
- [34] LIN Ying-hua, JIANG Chang-chun, LIN Zhen-heng, et al. Laser in-situ synthesis of high aspect ratio TiB fiber bundle reinforced titanium matrix composite coating[J]. *Optics & laser technology*, 2019, 115: 364-373.
- [35] LI N, XIONG Y, XIONG H. et al. Microstructure, formation mechanism and property characterization of Ti+SiC laser clad coatings on Ti6Al4V alloy[J]. *Materials characterization*, 2019, 148: 43-51.
- [36] WAGHMARE D T, PADHEE C K, PRASAD R, et al. NiTi coating on Ti-6Al-4V alloy by TIG cladding process for improvement of wear resistance: Microstructure evolution and mechanical performances[J]. *Materials processing technology*, 2018, 262: 551-561.
- [37] 朱洪强, 何宏燕, 袁媛, 等. 钛基体表面多级孔洞结构的制备和生物活性研究[J]. *表面技术*, 2015, 44(7): 56-60.
- ZHU Hong-qiang, HE Hong-yan, YUAN Yuan, et al. Preparation of hierarchical porous structure on Ti surface and bioactivity[J]. *Surface technology*, 2015, 44(7): 56-60.
- [38] POPOOLA A, PHUME L, AIGBODION V S. Laser ternary Hf-Nb-Zr composites coatings on Ti6Al4V alloy for biomedical application[J]. *Proceedings of the institution of mechanical engineers part C—Journal of mechanical engineering science*, 2019, 233: 1099-1107.
- [39] LUSQUINOS F, POU J, BOUTINGUIZA M, et al. Main characteristics of calcium phosphate coatings obtained by laser cladding[J]. *Applied surface science*, 2005, 247(1-4): 486-492.
- [40] WANG D G, CHEN C Z, MA J, et al. In situ synthesis of hydroxyapatite coating by laser cladding[J]. *Colloids and surfaces B: Biointerfaces*, 2008, 66(2): 155-162.
- [41] YANG Y L, SERPERSU K, HE W, et al. Osteoblast interaction with laser clad HA and SiO₂-HA coatings on Ti-6Al-4V[J]. *Materials science and engineering: C*, 2011, 31(8): 1643-1652.
- [42] BEHERA R R, HASAN A, SANKAR M R, et al. Laser cladding with HA and functionally graded TiO₂-HA precursors on Ti-6Al-4V alloy for enhancing bioactivity and cyto-compatibility[J]. *Surface and coatings technology*, 2018, 352: 420-436.
- [43] LIN C W, JU C P, LIN J H C. A comparison of the fatigue behavior of cast Ti-7.5Mo with c.p. titanium, Ti-6Al-4V and Ti-13Nb-13Zr alloys[J]. *Biomaterials*, 2005, 26(16): 2899-2907.
- [44] KHAMIDULLIN B A, TSIVILSKIY I V, GORUNOV A I, et al. Modeling of the effect of powder parameters on laser cladding using coaxial nozzle[J]. *Surface and coatings technology*, 2019, 364: 430-443.
- [45] 徐滨士, 刘世参. 表面工程新技术[M]. 北京: 国防工业出版社, 2002.
- XU Bin-shi, LIU Shi-can. *New surface engineering technology*[M]. Beijing: National Defense Industry Press, 2002.
- [46] YANG Yu-ling, SERPERSU Ka-an, HE Wei, et al. Osteoblast interaction with laser clad HA and SiO₂-HA coatings on Ti-6Al-4V[J]. *Materials science & engineering C*, 2011, 31(8): 1643-1652.
- [47] 李涵, 马玲玲, 位超群, 等. 钛合金表面激光熔覆 AlB₂CoCrNiTi 高熵合金涂层的组织与性能[J]. *表面技术*, 2017, 46(6): 226-231.
- LI Han, MA Ling-ling, WEI Chao-qun, et al. Microstructure and properties of laser cladding AlB₂CoCrNiTi high-entropy alloy coating on titanium alloys[J]. *Surface technology*, 2017, 46(6): 226-231.
- [48] SUN Gui-fang, ZHANG Yong-kang, LIU Chang-sheng, et al. Microstructure and wear resistance enhancement of cast steel rolls by laser surface alloying NiCr-CrC[J]. *Materials & design*, 2010, 31(6): 2737-2744.
- [49] 黄伟容, 肖泽辉. 激光熔覆陶瓷涂层的研究现状[J]. *表面技术*, 2009(4): 64-66.
- HUANG Wei-rong, XIAO Ze-hui. Research status of laser cladding ceramic coating[J]. *Surface technology*, 2009(4): 64-66.
- [50] 马永, 朱红梅, 孙楚光, 等. TC4 钛合金表面激光熔覆掺 Y₂O₃ 复合涂层的显微组织和性能[J]. *表面技术*, 2017(6): 238-243.
- MA Yong, ZHU Hong-mei, SUN Chu-guang, et al. Microstructure and properties of laser cladding doped Y₂O₃ composite coating on titanium alloy surface of TC4[J]. *Surface technology*, 2017(6): 238-243.
- [51] SUAREZ-FERNANDEZ M B, SOLDADO A B, SANZ-MEDEL A, et al. Aluminum-induced degeneration of astrocytes occurs via apoptosis and results in neuronal death[J]. *Brain research*, 1999, 835(2): 125-136.
- [52] 刘亚楠, 孙荣禄, 牛伟, 等. 扫描速度对 Ti811 合金激光熔覆涂层组织与性能的影响[J]. *表面技术*, 2018, 47(12): 146-153.
- LIU Ya-nan, SUN Rong-lu, NIU Wei, et al. Effects of scanning speed on microstructure and properties of laser cladding coatings for Ti811 alloy[J]. *Surface technology*, 2018, 47(12): 146-153.
- [53] 庞铭, 谭雯丹. 预热温度对激光熔凝 RuT300 气门座残余应力场的影响研究[J]. *表面技术*, 2019(8): 296-301.
- PANG Ming, TAN Wen-dan. Influence of preheating temperature on residual stress field of laser melting RuT300 valve seat[J]. *Surface technology*, 2019(8): 296-301.