Research status of laser additive manufacturing for metal: a review

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Abstract

Additive manufacturing (AM) especially laser additive manufacturing (LAM), a novel manufacturing technique of layer-by-layer forming according to geometric model, provides a decent option for materials processing. It owns advantages of rapid prototyping, customization, high material utilization, and the ability to form complicated structures. This paper reviews popular LAM techniques of selective laser sintering/melting, laser metal deposition and laser direct writing. The development status of metallic materials including pure metal, steel, superalloy, titanium and aluminum alloy is presented. The challenges and application limitations of LAM are involved and the development trend in the future is forecasted. In summary, this paper gives an overview of metal LAM expecting to make helpful suggestions on future research and development.

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1. Introduction

As the pillars, energy, information and materials take the significant role in modern social development. In these three pillars, materials are the basis of energy and information. Development of materials and its manufacturing technology is closely related to progress of human society. Recently, additive manufacturing (AM) technology as a unique manufacturing technology is widely attractive for its forming process. AM technology, is also called material increase manufacturing, rapid prototyping, layered manufacturing, solid free-form fabrication and 3D printing, which has been...
accurately defined as a process of joining materials to make objects from 3D model data by American Society for Testing and Materials (ASTM) [1–7]. The process is usually layer upon layer from bottom to top, which is opposed to subtractive manufacturing methodologies (e.g. cutting). More recent advances in metal components manufacturing using 3D solid models embedded in computer aided design (CAD) software pose the prospect for layer by layer fabrication of complex, custom metal or alloy products which is almost impossible to achieve by a conventional processing (e.g. forging, casting) [8–10]. AM technology reduces large process time by reason of no need of traditional process tools and procedures. It is attractive that production with complex structure and geometry can be achieved by AM technology, which is hard to achieve by subtractive manufacture or cast. Meanwhile, AM technology has already been applied in much fields, such as automotive, aerospace, architecture, biomedical, electronics industries and provides new ideas for the development of manufacturing.

Almost all AM technologies origin from the rapid prototyping technology, which was pioneered in the 1980s to produce models and prototype parts. And it has been expanded rapidly to the present. AM technology owns the characteristics of short cycle time, extensive choices of materials, excellent ability to fabricate complex parts and digital intelligent manufacturing compared with traditional processing [11,12]. A variety of materials including metals, ceramics, polymers and composite materials can be utilized in AM process. Nowadays, polymers are widely applied in AM technology, such as thermoplastics resins, thermosetting resins and photosensitive resins [13–18]. Chacon et al. [19] studied the effect of process parameters on mechanical properties in additive manufacturing of polyactic acid structures by using fused deposition modelling. Zhang et al. [20] developed a 3D printing reprocessable thermosets material system by a two-step polymerization strategy, which is reshapability, repairability and recyclability. Moreover, polymers have been widely used and maturely studied in AM technology. At present, metals as applied materials in industry have been more focused in the AM field [21–31]. However, research on metal AM is the scientific frontier filled with challenges in the AM field, because it faces numerous difficulties, such as low manufacturing efficiency and low forming accuracy [2,32,33]. According to the difference of heat sources, AM technology for metal can be roughly classified into three types: wire and arc additive manufacturing (WAAM) [34,35], electron beam additive manufacturing (EBAM) [36,37] and laser additive manufacturing (LAM) [36,38]. WAAM is mainly suitable for rapid prototyping of large size components, while EBAM and LAM are both applicable for small parts. LAM is the most promising AM technology for metal currently. Majorly LAM contains two classed: synchronous powder feeding (or wire feeding) forming method represented by laser metal deposition (LMD) [39] and powder bed forming method represented by selective laser melting (SLM) [40]. The forming of high performance parts can be realized by LMD technology whose mechanical properties are equivalent to forgings. Besides LMD method. And SLM method can be used for manufacturing precision parts of complex shape.

Many authors have been dedicated to studying LAM for metals to obtain a better AM method with high manufacturing efficiency and forming accuracy [41–46]. Researches are mainly focused on the optimization of process parameters, the design of LAM materials, and the achieved properties, which will make it possible for AM to meet the metallic components demands from aerospace, automotive, rapid tooling and biomedical industries. In this paper, recent researches on LAM for metals are reviewed and the unsolved problems in AM field are discussed.

2. Laser additive manufacturing techniques

In LAM process, parts are built by means of melting metal powders or rarely wires layer by layer [38,47]. The molten pool is generally produced by the energy input of an Nd: YAG, diode or CO₂ laser, supplying argon or helium to prevent oxidation. Meanwhile, the metallic powder is fed by a coaxial (or side multi-jet) nozzle or spread by laying powder device [48–53]. Nowadays, the established laser additive manufacturing techniques contain selective laser sintering, selective laser melting, laser metal deposition, etc.

2.1. Selective laser sintering (SLS)

SLS as a kind of powder bed forming AM method, is a typical AM process based on pre-spreading of powder, subsequent computer control and laser sintering, which generates complex parts by consolidating successive layers of powder on top of each other and consolidating the selected areas [47,54]. The SLS system generally includes a laser, a feed container and gas protection system as shown in Fig. 1 [47]. Besides, a significant part not shown is computer controlling system, which controls and selects the sintering area. Different types of lasers are employed, including CO₂ [55,56], Nd: YAG [57], which has a significant effect on the consolidation of powders. The laser absorptivity of materials and operative binding mechanism of

![Fig. 1 – Schematic of a typical SLS apparatus [47].](image)
powder densification are determined by the laser wavelength and input laser energy density respectively.

The procedure of SLS mainly contains 5 steps [21]. Primarily, a substrate for components fabrication is fixed on the workbench. After that, the protective gas is passed into the forming room to reduce the oxygen content below a required standard. Then a thin layer of the loose powder with a usual thickness of 20–150 μm is spread on the substrate by laying powder device. Subsequently, the laser beam scans the powder bed surface to form layer wise profiles according to CAD data compiled. The last step is repeating above 4 steps until completion.

The binding mechanisms during metallic SLS mainly can be classified into four categories: solid state sintering (SSS), liquid phase sintering (LPS), chemically induced binding and full melting, which depends on properties of materials and input laser energy density [47,58]. SSS is a thermal process that occurs at temperature between 0.5T_{Melt} (melting temperature of the material) and T_{Melt}. There are various physical and chemical reactions with diffusion in SSS process. It involves neck formation between adjacent powder particles as shown in Fig. 2 [59]. The free energy reduces with particles growing, which provides the dominant driving force for sintering.

SSS can processes nearly all kinds of materials, so long as the necessary kinetic energy is enough to transport of vacancies across the grain boundaries and consolidate powder via volume diffusion. However, the SSS powder generally need be preheated to increase the diffusion velocity of atoms. Gusarov et al. [58] studied SSS of titanium powder using "soft" laser radiation by the method of experimental combined with numerical simulation. It shows that the degree of sintering (D/2R, cf. Fig. 2) above the α/β-transition temperature was higher than that below the temperature owing to the forming of β-Ti phase.

The structural material remains solid throughout and the binder material is liquefied in most LPS which is a partial melting process. LPS contains two categories such as: different binder mixing with structural materials and no distinct binder mixing with structural materials. So far mechanisms of multicomponent metal powder and prealloyed powder processed by SLS belong to LPS [60]. Fig. 3 shows the mechanism of LPS [47]. As displayed in Fig. 3, the first part of the dashed line is the LPS mechanism since only the rearrangement phase takes place. The multicomponent powder mixture is generally composed of the high melting point metallic component acting as the structural metal, the low melting point metallic component taking as the binder, and a small amount of additives such as fluxing agent or deoxidizer. The operative liquid phase temperature is carefully determined between these two different melting temperatures by adjusting laser processing parameters. The binder, thus, melts completely to form liquid phase, while the structural metal remains its solid cores in the liquid. Solid particles rearrange under the influence of capillary forces exerted on them by the wetting liquid that results in the densification of the solid/liquid system. The liquid/solid wetting characteristics and the capillary force exerted on particles determine the particle rearrangement rate and resultant success of SLS.

The prealloyed powder exhibits semisolid state called mushy zone at the temperature between solidus and liquidus. Thus supersolidus liquid phase sintering (SLPS, a type of LPS) act as metallurgical mechanism for SLS of prealloyed powders [61]. As is shown in Fig. 4, the liquid phase appears along grain boundaries wets solid particles and grain boundaries. Rearrangement of solid particles and solution reprecipitation occur makes the semisolid powder rapid dense. Niu et al. [62] demonstrated that SLPS mechanism is operative during SLS of high-speed steel powder. The thick ring microstructure formed at the austenitic grain boundaries, which is accord with the SLPS mechanism in Fig. 4. In order to realise the incongruent melting of particles in the mushy zone, it requires a strict control of laser processing parameters in SLS process of prealloyed powders through SLPS mechanism. However, chemically induced binding and full melting are seldom used in SLS process [63].

Fig. 2 – Neck formation in SSS (a), neck formation between two stainless steel powder particles (b) [59].

Fig. 3 – Schematic of LPS mechanism [47].
2.2. Selective laser melting (SLM)

SLM as a derivative for SLS, which belongs to powder bed forming AM method. The properties of some productions cannot be satisfied by SLS although SLS is a common technology to produce parts for a long term and able to process almost any type of material. Thus, SLM was developed on base of SLS in the late 1980s [64–66]. The major advantages of SLM are not only the capacity for preparing parts of nearly arbitrary geometry but also the ability to process a variety of materials to almost full density yielding bulk material properties [60]. The apparatus and procedures of SLM are similar to SLS as shown in Fig. 2. However, in contrast to SLS, the binding mechanism is full melting, which needs more energy supported by high-power laser beam. The variation leads high microstructural and mechanical properties of production. SLM shows better suitability to produce full dense parts approaching 99.9% density in a direct way, without post-infiltration, sintering or hot isostatic pressing (HIP) [67]. Another advantages of SLM is the ability to process nonferrous pure metals with high density, which is hardly processed by SLS. Common metals in industry including Ti, Al, Cu and so on can be well processed by SLM, which is widely generalized in additive manufacturing. In addition, microhardness of production of SLM is much higher than SLS because of less defects.

Nevertheless, there are some problems encountered in SLM process [68–73]. The major problems are high surface roughness and low part accuracy affected by stair-effect. Moreover, the high thermal gradients reinforce layered residual stresses due to full melting and solidification in a very short time. Because a large degree of shrinkage tends to occur during liquid–solid transformation, accumulating considerable stresses in SLM process [74,75]. The residual stresses arising during cooling are regarded as key factors responsible for the distortion and even delamination of the final products. Besides that, the instabilities of molten pool may result in spheroidisation of the liquid molten pool and attendant interior porosity. Therefore, the conformation for a suitable process window is considered as the key via optimization of laser processing and powder depositing parameters to yield a moderate temperature field to avoid the overheating of SLM system.

The mechanical performance of parts printed by SLM is determined by the evolution of the grain structure in terms of grain size, morphology, orientation. Similar to welding process, the grain growth in SLM is a localized solidification process, which is a competitive growth toward the center of the molten pool. The melt pool appears by reason of the interaction between traveling laser beam and material. The solidification of the partially melted grains takes place via epitaxial growth on the substrate or previous layer after laser beam leaves. The shape of the liquid—solid interface can be planar, cellular, columnar dendritic, or equiaxed dendritic is governed by $G$ (temperature gradient), $R$ (solidification rate), $\Delta T$ (undercooling) and $D_s$ (solute diffusion coefficient), cf. Fig. 3a [72,76–78].

Except the grain morphology, the grain growth directions are aligned in the thermal gradient direction during solidification proceeds. As shown in Fig. 5b, the epitaxial grains have multiple orientations in the initial solidification stage. However, the grain favors to grow along particular crystallographic orientations [78]. Therefore, the grains with the same or close orientations as the temperature gradient grow faster while the grains with other orientations gradually stop growing due to the competitive growth of different grains. The unidirectional columnar grain structure during solidification caused by competitive growth is typical in parts made by SLM process.

Recently, the numerous researches are carried out to investigate the SLM processing of metallic and composite powders. Meier and Haberland studied the effect of process parameters on properties of 316L stainless steel (X2CrNiMo17-13-2) produced by SLM method [69]. It demonstrated that a narrow process window arranged accurately can achieve an optimized combination of properties but cannot be applicable to other geometries, dimensions or orientations. Thjis et al. [79] found that elongated grains emerged during the SLM processing for Ti–6Al–4V, whose direction depends on the local heat transfer condition determined by the scanning strategy, cf. Fig. 6. Vranken et al. [80] further investigated the effect of heat treatment on microstructure and mechanical properties of Ti–6Al–4V produced by SLM, which is based on previous researches their group did [79]. It showed that microstructure and mechanical properties (e.g. ductility) of Ti–6Al–4V parts processed by SLM optimized via appropriate heat treatment. Aboulkhair et al. [81] concluded that the type of pores formed in the SLM process for AISi10Mg depends on the scanning speed applied. With increasing scanning speed, keyhole pores formed and metallurgical pores decreased. SLM also provides an amazing approach for function materials for its wonderful manufacturing ability. Wu et al. [82] successfully produced permanent magnetic Nd-Fe-B materials with high density of 91%, remanence of 0.65 T and maximum energy product of 62 kJ/m³ by SLM, which was comparable to the state-of-the-art in the field. Nonetheless, the relative density and integrity was constrained by the intrinsic brittle nature of the intermetallic Nd$_2$Fe$_{14}$B phase (principal phase).

2.3. Laser metal deposition (LMD)

LMD is a representative synchronous powder feeding forming AM method. LMD is also called laser engineering net shaping (LENS), direct metal deposition (DMD), laser rapid forming (LRF), direct laser fabrication (DLF) in different regions and research institutes, in that those LMD technologies were developed and named independently by a variety of institutes and universities. LENS is created at Sandia National Laboratory [28,83,84], DMD is developed by University of Michigan.
while LRF is invented by Huang Weidong team in Northwestern Polytechnical University of China \[86-89\] and DLF is developed at University of Birmingham \[90\]. All these LMD methods were defined as part of directed energy deposition (DED) by ASTM. LMD can be utilized to fabricate metal components from CAD solid models as well, similar as SLS/SLM. But its material addition method is synchronous powder feeding, which is different from SLS/SLM. In addition, spot diameter of LMD is in millimeter level while SLS/SLM is in micron level. Therefore, manufacturing accuracy of SLS/SLM is higher compared with LMD.

In LMD processing, movement track of laser spot along with 3D models sliced into several layers and scan path, the focused laser beam melts the metal powder fed and creates a molten pool on the substrate, the molten metal powder solidifies to form a finally object. As shown in Fig. 7, the synchronous powder feeding system of LMD is coaxial or side usually \[91\]. Powder and laser beam have the same central axis, which results in the higher flexibility and accuracy due to the focused powder displayed in Fig. 7a. Fig. 7b shows that powder beam fed by side powder nozzle is rectangular generally, which is suitable for fitting a large amount of powder fed. The side powder feeding cannot ensure aim of delivering feed and laser focus, which makes accuracy and surface roughness worse than coaxial powder feeding. LMD with side powder feeding system is used to produce coatings of tubular parts normally. Compared to SLS/SLM technology, LMD is more suitable for repairing parts due to its high flexibility.

LMD technology developed from laser cladding has a higher deposition rate usually, compared with SLS/SLM based on powder bed forming method. It is no doubt that LMD can shorten production cycle available. What's more, LMD can be utilized to make parts with complex surfaces instead of some conventional machining technology, which can solve a series of problems machining hard, material wasting, tool wear etc. The ability to realize the preparation of parts with hollow structures and material gradients is undoubtedly one of significant advantages of LMD. The components fabricated by LMD generally have compact texture and excellent material properties without heat-treatment. LMD also get its bottlenecks at present. Material utilization of LMD is low (about 1/4 to 1/3) while use ratio of SLM is nearly 100%. Meanwhile, thermal stress is high in LMD processing resulting to interlaminar cracking workpiece. The average particle size, spot diameter and layer thickness of LMD are all higher than SLM, resulting in the size accuracy and surface roughness of LMD components worse. Hence, LMD combined with subsequent machining can improve manufacturing accuracy of parts, which makes parts meet work condition needs.

Fig. 5 – Schematic of the effects of G and R on grain morphology (a), grain growth in SLM including initial epitaxial growth and subsequent competitive growth (b) \[72,76-78\].

Fig. 6 – Influence of the scanning strategy. Micrographs of sample scanned with a unidirectional scan vector: top view (a); side view (b); front view (c); and the scanning strategy and parameters applied (d). Micrographs of sample scanned with the use of alternating hatch directions: top view (e); side view (f); front view (g); and the scanning strategy and parameters applied (h). \[79\].
At present, LMD technology is widely application in automotive, aerospace, medicine, and other industries to replace some conventional forming methods [92–97]. The heat-affected-zone with LMD is smaller and easier to control than welding techniques so that it can repair damaged blades on aero engines or gas turbines without damaging the underlying part [98]. Li [99] utilized LMD process to repair directionally solidified superalloy GTD-111 (a kind of γ’ strengthened Ni-based superalloy) and investigated the effect of LMD process parameters on the formation of René 80 (also called PARXAIR Ni138, a kind commercial alloy powder with almost the same composition of GTD-111) deposition on a GTD-111 substrate. The results showed that René 80 had a multi-layered, directionally solidified microstructure were successfully deposited on GTD-111 substrate by LMD with optimized parameters. The metallurgical bonding between deposit formation and substrate revealed the potential of LMD for parts repair.

Besides the repairing failure components, LMD process is also widely applied in fabricating fully dense solid or hollow light structural metal parts. Zhai et al. [100] studied the mechanical properties of LMD (called LENS in the research) Ti–6Al–4V intramedullary nail with regular crystal grain size and order structure made by LMD technology. Krishna et al. [101] developed titanium alloy hip stem prototypes whose relative density varied from 30% to 77% by combining the LMD technique. This technology is attractive for highly mechanically loaded electrical devices as well. Kini et al. [105] used LMD to in-situ synthesize a lean Cu–3.4Cr–0.6Nb conductive alloy hardened by Cr nano-scale precipitates and Laves phase micro-particles, which benefited from the cooling rate during LMD (10⁵–10⁶ K/s).

2.4. Laser direct writing (LDW)

LDW method is a kind of indirect LAM technology for metal, which is different from direct LAM technology like SLM and LMD. LDW apparatus was originally developed as a substitute for micro-stereolithography (micron level resolution), whose resolution can reach submicron level and even nano level. LDW method was used to fabricate polymer materials parts but it is now widely used for manufacturing of optical elements. Nowadays, LDW apparatus has been developed from building 2D structure to 3D structure. Fig. 9 shows the LDW apparatus toward 3D structure fabrication [106]. In LDW processing, a special ink comprising metallic particle and organic solution is pre-coated on a substrate, a laser beam is focused on the metallic particle film and scans following the planned path. Finally, the components are sintered and the indirect body is removed, so this technology is a kind of indirect LAM technology. The whole process is like writing on a paper, so that it is named laser direct writing.

The surface oxidation of metallic particles is one of the challenging issues during the sintering process after inkjet printing of the micropattern. Ink with small size particles and laser sintering with high speed have solved the problem to some extent [107–109]. Watanabe et al. [110] wrote a horseshoe-shaped bridge by LDW using Cu nanoparticle ink, shown in Fig. 10. The fabrication accuracy was close to sub-micron level and the thickness of line was ca 0.5 μm. It suggested the possibility of a 3D interconnection at micro scale.

A novel category of AM technique called direct metal writing (DMW), which was developed by Lawrence Livermore National Laboratory [31]. Although DMW is also called direct writing, but it has lots of difference from ordinary LDW. Most metal AM processes relying on powder-based melting techniques (e.g. SLM and LMD) that have some limitations. The complicated histories in powder melting processing may cause residual stresses, micro-cracks within metal objects [72]. In order to ameliorate these problems, DMW utilizes the
method that noble extrudes semi-solid alloy slurries to make metal parts owning full density and needed shape without complex fusion and solidification histories in forming processing. As shown in Fig. 11, the DWM system uses resistance heater that provides lower energy rather than laser heat source to make alloy ingots into semi-solid state, so that this method is more suitable for metallic alloys with low melting point. Semi-solid alloy slurries refer to metal melts of solid–liquid mixtures in the region between solidus and liquidus lines in the equilibrium phase diagram. Rheological behavior of semi-solid alloy, i.e. unique viscosity and shear thinning characteristic, which easier to build geometries during printing.

Chen et al. [31] fabricated prototypes of Bi$_{75}$Sn$_{25}$ (at. %, a low temperature Bi–Sn binary semi-solid alloy) by employing well-setting rheological parameters DMW system. It illustrated that DMW approach can control the microstructural features during solidification facilely and allow steady state printing of 3D-structure metallic parts. Although DMW does not belong to LAM techniques, its working principle with using semi-solid alloy to formation suggests an exquisite and flexible idea for LAM. The fundamental principle of DMW can be extended to other universally used metallic materials such as steel, Al alloy, Ti alloy etc., which will be a key to development of metal AM.

Currently, researchers and institutes have developed a vast array of novel AM approaches including many non-LAM techniques. Nanoparticle jetting (NPJ) exploited by XJET Ltd. Israel, for instance, is a typical and mentionable AM technology based on nanoparticle suspension ink [111]. NPJ techniques can produce metallic or ceramic customized components at large scale with low cost and high efficiency. During the processing, nanoparticle suspension ink within the required viscosity limitations is deposited onto a heated build plate where carrier-liquid is evaporated. The next layer is printed after liquid fully evaporated. Finally, the part is obtained since removing support material and sintering. NPJ equipment mainly involves two types: XJET 700 Carmel and XJET 1400 Carmel, and difference between the two are ink used and forming size. It was reported that University of Delaware collaborating with XJET Ltd. intended to develop cutting-edge antenna technology for 5G network called "Passive Beam Steering" using XJET 1400 Carmel 3D Printer. Yongduk et al. [112] characterized composition and microwave dielectric properties of ZrO$_2$ samples fabricated by NJP (Fig. 12), and opened the potential for AM new microwave devices including antennae, lenses, and filters.

In summary, AM techniques involving LAM and non-LAM has made a great progress in recent years. In especial some typical LAM technologies e.g. SLM and LMD get considerable development and have better commercial application in a lot of project fields. AM technology appeals to industry because of its unique charm. Whereas almost conventional LAM also has some shortcomings that properties of metal parts damaged by complex histories in powder melting processing. What’s more, low deposition rate of SLM and low forming accuracy of LMD limit their further application range. DMW which controls semi-solid alloy to formation and current emerging indirect AM avoid complex thermal process and the thought will give some inspiration to LAM. Particularly it is saving for working procedure and material that indirect body (support material) of indirect AM processing can be removed easily. In contrast
support material of direct AM (LAM, etc.) is usually removed by wire electrical discharge machining due to metallurgical bonding between support material and metal parts. Development of AM techniques and facility relates to parts manufacturing industries. It is convinced that LAM techniques will be developed further with higher forming accuracy and manufacturing efficiency in the future days.

3. Metallic materials for laser additive manufacturing

In general, LAM techniques utilize metallic materials, i.e. pure metal or alloy, whose form is usually powder or rarely wires. And common alloys used in LAM are steel, titanium alloy, superalloy etc. With the development of LAM industry, the requirement for LAM metallic powder becomes rigorous so that the powder used in powder metallurgy and spray cannot satisfy the process normally. Due to laser parameter and binding mechanism, the characteristics of powder including sphericity, size distribution, fluidity, apparent density, impurities and wettability should be considerate and optimized. Sphericity and fluidity of powder are the key to AM forming. To obtain better properties of parts, sphericity of powder should usually be no less than 80%. The particle size of powder used in LMD is not too small and ca 50–150 \( \mu \text{m} \) in that adsorption force between nozzle and small size powder is high which results in nozzle plugging. In comparison the particle size of SLM powder can be smaller, and powder utilization can attain about 100% because powder reuse does not compromise part quality \([113]\). And most of spherical powder for LAM is generally produced by atomization.

3.1. Pure metal for laser additive manufacturing

As concerns AM technology, pure metal is not a major candidate material, by the reason that characteristics of pure metal, e.g. mechanical properties, anti-oxidization, anti-corrosion, are relatively weak compared to alloy. Besides SLS technique had an unsuccessful early attempts to build pure metal bulks. So far pure metal for LAM were studied more in some specific field. Pure Ti and Zn are most used in biomaterials due to the desirable biocompatibility. And pure Ag and Cu attract attention by electronic element industry with the chief cause of wonderful electrical conductivity. Study on pure Ti is more focused on than other pure metal in LAM field. Grains of LMD coarsen than SLM because of the difference between the two during melting and solidification process, which renders that SLM is more suitable for investigation on pure metal LAM.

Recently attention to Ti and its alloy has become increasing in biomedical domain owing to their biocompatibility, corrosion resistance, mechanical properties, making them more...

![Fig. 10](image1.png)

**Fig. 10** – Optical micrograph of 3D structure before prepared (a) and prepared by laser direct writing using Cu nanoparticle ink (b) \([110]\).

![Fig. 11](image2.png)

**Fig. 11** – Schematic (a) and real photo (b) of the DMW system \([31]\).
absorbing than conventional metallic biomaterials (e.g. 316L stainless steel and cobalt-chromium alloys) [114]. At early stage, commercially pure titanium (CP-Ti) and Ti–6Al–4V were introduced as biomaterials. CP-Ti has no negative health impacts without Al and V element alloying additions, and it owns lower elastic modulus and higher corrosion resistance as well which avoids stress shielding and fits for human implantation. Thus CP-Ti medical implant made by LAM has significant potential and has been researched widely, despite relatively lower mechanical properties in comparison to its alloy.

Ferreri et al. [115] studied the high-quality electron backscatter diffraction (EBSD) characterization of CP-Ti made by SLM. And Na et al. [116] investigated effect of laser power on performance of CP-Ti fabricated by SLM. Results showed microhardness of samples increased with increasing laser power at a constant scan speed, caused by the increase in the concentration of oxygen and nitrogen. Huang et al. [117] designed and manufactured lattice structures of CP-Ti, Ti–6Al–4V, Ti50Ta by SLM and proved their superior cell biocompatibility. In addition, comparative consequence of various LAM techniques employed for CP-Ti has been inspected [118]. Fig. 13 shows the microstructures and mechanical performance of cast, SLM, LMD (called LENS in this article) sample. The laser processed CP-Ti, i.e. SLM and LMD, presented microstructures distinct to those of cast sample, and grains were slightly larger in LMD than SLM specimen due to formerly processed layer re-heated much more and removal of heat hard during LMD process. The SLM sample showed a best strength of 427 MPa which was higher than those of the LMD (395 MPa) and cast sample (408 MPa) by reason of martensitic phase structure presented in SLM CP-Ti. A high yield strength is desirable for implants as it improves the capacity of the material to resist against permanent deformation [73]. What’s more, Montufar et al. [119] provided a benchmark research report for robocasting (a novel AM technique) and SLM for the custom fabrication of CP-Ti scaffolds for bone tissue engineering that involved the processing-microstructure-property relationship.

In addition to LAM of pure Ti, many other LAM pure metals have a certain amount of researches as well. Zn based metals have exhibited promising applications for biodegradable medical implants and researches on LAM of Zn are relatively rare. Chen et al. [120,121] established pure Zn metal parts with relative density above 99.90% by SLM method and discussed the effect of processing parameters like argon gas flow and laser energy input on evaporation and formation quality. It was instructive for other active metals with high evaporation tendency e.g. Mg and Al alloys. Besides Han et al. [122] and Higashi et al. [123] investigated pure Al and pure Mo of SLM respectively. Huang et al. [124] did a comparative study on pure Cu made by SLM and cold spray (CS), as shown in Fig. 14. Brittle fracture and ductile fracture occurred in SLM Cu parts (Fig. 14a and b) but only brittle fracture existed in that of CS.
SLM parts had higher tensile strength compromising with that of CS due to the metallic bonding, which revealed properties close to wrought C11000 Cu component.

3.2. Steel for laser additive manufacturing

To date, prealloyed powder has been applied for various LAM processes. A majority of research efforts have been focused on Fe based, Ti based, and Ni based alloys powder, among which some material and process combinations have entered a mature phase of practical applications. Steel, material acquainted fairly early by humans, is indispensable to our life and most used widely in such diverse applications as tools and structural components during construction industry, manufacturing industry and daily life, owing to its advantages of popular price and reliable performance (decent yield strength, ultimate tensile strength, etc.). It is no exaggeration to say that steel is the material basis of modern society. And it is a longstanding challenge to obtain lighter, stronger, and more ductile materials [125-127]. As the workhorse material, steel is of course a focus of materials scientists and engineers in AM field. Certainly AM techniques used for steel fit manufacturing industry of components, tools and models with the capability to form complex geometry compared to conventional synthesis/manufacturing technique as rolling, forging, etc. Currently there are relatively few mature commercial steel powders for AM techniques, thus powders for thermal spraying, laser cladding or alloying are still in AM use.

Stainless steel (SS), a variety of steel with excellent corrosion and oxidation resistance, gets the most attention in AM domain. Researchers did a large number study on them exploring the potential to replace conventional techniques. Generally, SS contains 12.5 at. % Cr element at least changing electrode potential to improve corrosion resistance, and sometimes contains Ni, Mo, Ti, etc. SS can be divided into martensitic SS, ferrite SS, austenitic SS, austenitic-ferrite SS and precipitation hardened SS according to the phase composition. Thereinto austenitic SS, in particular, has good comprehensive performances and is more attractive to AM. 304 SS and 316 SS are two type of common commercial austenitic SS, and 316 SS owns better corrosion resistance and high-temperature strength with adding Mo. Chen et al. [128] combined experimental and numerical simulation of the microscale residual stresses in SLM 316L SS (close to composition of 316 SS, with lower carbon content), and established the relationship between microscale residual stresses and mechanical behavior of AM SS. Furthermore, a coupled cellular automata microstructure simulations for 316L SS considering local non-equilibrium models for rapid solidification were presented and simulations were validated with experiments, which reported the experimental results were not only qualitatively in good agreement with simulations but also quantitatively [129]. Higher scanning speed led an obvious inhomogeneity of carbon concentration in as-SLMed 316L SS. Some other properties of 316L SS manufactured by SLM like tribology performance [130] and fatigue strength [131] were investigated as well, and they showed similar or even better performances compared with conventional 316L SS.

Wang et al. [132] demonstrated 316L SS printed via SLM (in the article called laser powder bed fusion, LPBD), which exhibited an exceptional combination of strength and ductility well surpassing that of the conventional. Microstructure of SLM 316L SS showed an awfully unusual grain shape, distribution, and orientation gradient via EBSD measurements. Further microstructure characterization revealed a broad range of internal boundaries, subgrain structures, and chemical segregations. Therewith deformation behavior of as-built 316L SS at different strain levels was investigated detailedly and revealed concurrent deformation mechanisms involving dislocation slips, cellular wall evolution, and deformation twinning, shown in Fig. 15. At a relatively low strain (~3%), dislocation slip was the main deformation mechanism,
but twinning became an important mechanism dominant with strain increasing to ~12%. Hierarchically heterogeneous microstructures, including solidification cellular structure, low-angle grain boundaries, and dislocations, made the superior properties of SLM 316L SS arise.

In addition, 304 SS, another typical austenitic SS, has a wide application in daily life due to its good mechanical properties, corrosion resistance, processability, and lower prices. There have been some research achievements of LAM 304L SS. Shi et al. [133] discovered that high laser power, low scanning speed, narrow scan spacing and small thickness of powder layer make 304L parts densification in SLM. Abolhassani et al. [134] numerically analyzed and experimentally validated the melt-pool behaviors during SLM of Al2O3-reinforced and a eutectic mixture of Al2O3-ZrO2-reinforced AISI 304 SS composites and showed that the geometry of the melt pool is significantly dependent on reinforcing particles, owing to the variations in the melting point and the thermal conductivity of the powder mixture. And Huang et al. [135] found that the grain shapes of LMD 304 SS were similar to those of SLM specimens, and static tensile properties of LMD specimens were all higher than those of the wrought specimens.

Except for austenitic SS, other SS such as martensitic SS have been investigated a lot in AM field as well. Ferguson et al. [136] built a semi-empirical model of deposit size and porosity in 420 SS and 4140 steel during LMD processing. The fully dense steel specimens can be obtained when the ratio of powder feed rate to laser traverse velocity was not above a certain level (Fig. 16). Krishna et al. [137] utilized LMD technology to carry out surface modification of AISI 410 SS, and the surface hardness increased considerably by reducing the retained austenite whose amount depended on LMD parameters. 17-4 PH SS is a martensitic precipitation hardened SS

Fig. 15 – Deformation structures of SLM 316L SS at different levels of strain: at ~3% tensile strain, deformation microstructures (a,b,c), EBSD inverse-pole figure (IPF) map, image quality (IQ) map and kernel average misorientation (KAM) map acquired from a solidification cell region (d), plots of the misorientation angle variation (e); at ~12% tensile strain, deformation microstructures (f,g) [132].
containing Cu and Nb. 17-4 PH SS can be employed in some atrocious conditions due to its better strength and excellent corrosion resistance in contrast to general martensitic SS. Hu et al. [138] used SLM method to fabricate 17-4 PH SS samples and did the following heat treatment for as-built samples: solution treatment followed by aging. Results showed that the processing parameters impacted on density of samples by changing the behavior of the molten pool. Both microhardness of SLM and heat treated samples were isotropic, and average microhardness of heat treated samples was much higher than that of SLM samples.

Besides some tool steel are also attractive to scholars in AM domain. H13 steel is a C–Cr–Mo–Si–V hot work die steel, which is widely used in industry [139,140]. H13 steel is usually used to make injection molds because of its high toughness, high stability in heat treatment, and high resistance to thermal fatigue cracking. With development of industry, requirements for molds become high so that the original method cannot meet it. Hence AM technology is considered as a new available method. Some numerical simulations of LAM H13 steel were carried out, and temperature field, stress field and so on during LMD or SLM process can be predicted to guide the practical production and make improved products [141,142]. Wang et al. [143] carried out a comparative study on thermal fatigue properties of H13 steels processed by SLM, SLM following thermal treatment and forging. After thermal fatigue tests (650 °C/30 °C), SLM and thermally treated SLM H13 showed secondary hardening properties, whereas forged H13 exhibited some softening behavior. It was the reasons for increased thermal fatigue resistance of H13 steels that amount of retained austenite, typical cell-like substructures increased and grain size refined in SLM specimen via microstructural observed.

Furtherly Yan et al. [144] investigated the effect of tempering treatments on mechanical properties and microstructure of SLM H13 steel. They found that tensile properties of as-printed H13 steel specimen was unsatisfactory, especially whose elongation at fracture was only ~2.42%, most likely affected by high residual stresses and defects formed during SLM processing. However, tempering could improve properties of H13 specimens. Specimen after tempering at 600 °C exhibited high ultimate strength (1938 ± 62 MPa) and moderate fracture strain (5.8 ± 0.61%) owing to decreased residual stress and secondary-precipitated phase (VC), which exceeded those fabricated by conventional methods. Specimen possessed a high ductility (~10.95%) and decent strength after tempering at 700 °C, and its microstructure was close to the conventional one and consists of the tempered martensite, Cr-rich carbides (M23C6 and M7C3) with large size and V-rich VC/VC precipitates, cf. Fig. 17. The strength was mainly contributed to grain boundary strengthening, precipitation strengthening and dislocation strengthening at the moment.

3.3. Titanium alloys for laser additive manufacturing

Titanium and its alloys own amounts of exceptionally properties such as low density, high specific strength, excellent corrosion and oxidation resistance, and good biocompatibility, letting to an increasing utilization in aerospace, marine, chemical industries and biomedical devices [145,146]. Based on so many outstanding features of titanium alloys, they can be used in specific high-end equipment manufacturing industry instead of steels and other metallic materials. Pure titanium at room temperature has a hexagonal close packed (hcp) structure, called α-Ti. And it can transform to the body centered cubic (bcc) structure at elevated temperature (888 °C) which is called β-Ti. According to the phase of titanium, commercial titanium alloys fall into five categories: α, near-α, α-β, near-β and β alloys, indicated in Fig. 18a [147]. The final structure of titanium alloy depends on the cooling speed from β transus temperature, shown in Fig. 18b [148]. In LAM processing, it tends to form a fully α′ microstructure due to the high cooling rate (usually 10³−10⁵ °C/s).

Ti–6Al–4V, a kind of α-β titanium alloy, is one of most widely used titanium alloy in industry. It has an excellent combination of mechanical performances particularly its specific strength which is superior to steels and aluminum alloys. Motivated by demands for market and fabrication costs, the fabrication of Ti–6Al–4V in AM has been investigated. In contrast to conventional methods, metal parts built by LAM suffer rapid melting and solidification, letting to the disparate microstructures and performances possibly. Layer-by-layer sintering leads to microstructural columnar grain formation due to the directionality of heat extraction, resulting in an anisotropic feature that degrades the mechanical behavior of the molten pool.
strength of the component in certain directions. This leads to unpredictable mechanical behavior incompatible with stringent property requirements [148].

Effect of AM parameters of microstructures and properties of SLM or LMD Ti–6Al–4V alloy has been investigated a lot. Influence of laser energy density (LED) on microstructures and mechanical properties of SLM Ti–6Al–4V alloy was studied by Wei et al. [149]. LED is a comprehensive characterization of laser parameters, and it can be described as follows [149]:

\[
LED = \frac{P}{vhd}
\]  

(1)

where \(P\), \(v\), \(h\), and \(d\) are laser power, scanning speed, hatch spacing and layer thickness, respectively. The results indicated that the laser energy density had a crucial effect on structures and properties of as-print parts. And all the relative density, microhardness and tensile properties of SLM Ti–6Al–4V initially increased and then decreased with increasing laser energy density. In addition, other people did some similar research on SLM Ti–6Al–4V alloy as well, and gave the analogous conclusions [150,151].

Artzt et al. [152] investigated the effect of contour parameters on roughness and subsurface residual stresses in SLM Ti–6Al–4V. Samples were fabricated by an SLM 280\(^{\text{HL}}\) with an integrated melt pool monitoring system using fixed laser parameters (power, scanning speed and hatch spacing) and different contour parameters (volume, \(V\) and contour lines, \(C_L\), in Fig. 19a). There were two kinds of \(C_L\) scanning contour, i.e. from the outside to the inside (\(O\rightarrow I\)) and starting from the inside to the outside (\(I\rightarrow O\)). Two different roughness properties, the arithmetic mean height (\(S_a\)) and the maximum height (\(S_H\)), were for roughness characterization. Residual stresses of

![Fig. 17](image1.png) TEM results of the specimen after tempering at 700 °C: bright-field micrograph of lath-type martensite with dislocations and carbides (a), bright-field micrograph showing the M\(_{23}\)C\(_6\) carbide and corresponding SAED (selected area electron diffraction) pattern (b), bright-field micrograph showing the M\(_{23}\)C\(_6\) carbide and corresponding SAED pattern (c), and dark-field micrograph showing the fine V\(_6\)C\(_7\) precipitates distributed in the matrix (d) [144].

![Fig. 18](image2.png) Schematic quasi-vertical section for ternary titanium alloys containing both \(\alpha\) and \(\beta\) and stabilizing solute (a) and schematic of continuous cooling transformation curve (b) [147].
samples were investigated by the method shown in Fig. 19b and c. Only $\sigma_{zz}$ was considered for analysis and discussion in the paper. As shown in Fig. 19d and e, contour parameters made obvious effect on roughness and residual stresses of SLM Ti–6Al–4V samples. However, the roughness could not be reduced without negatively affecting the residual stress, and authors thought this was like to Pandora’s Box. Probably when using appropriate contour strategy, best roughness results were given but with highest residual stresses. As-built components might substantial crack when the residual stresses in build direction exceeding tolerable limits. Therefore, any parameter optimization has to be carried out carefully.

Zhang et al. [148] did a comparative study between the features of metallic fused filament fabrication (mFFF) Ti–6Al–4V sample and SLM one. mFFF, a variant of FFF, turns into a promising alternative to powder bed technique (e.g. SLM). As is shown in Fig. 20, there were more pores in mFFF samples at different sintering temperature (Fig. 20a–e) in contrast to SLM sample (Fig. 20f). And SLM sample showed smaller grains, smaller porosity and a larger amount of $\beta$-Ti beside Young’s modulus and hardness compared to mFFF samples. In addition, it is valid to improve performances of titanium alloys via heat treatment after LAM, e.g. annealing and HIP. Mower and Long [153] utilized direct metal laser sintering (DMLS) to produce Ti–6Al–4V alloy specimens, which is technically a special instantiation of SLS. Specimens after DMLS were treated with HIP 900 °C/2 h at 102 MPa and microstructures of specimens were shown in Fig. 21. The wrought specimen presented isolated lamellar $\alpha$–$\beta$ colonies interspersed between nearly equiaxed connected $\alpha$ grains (Fig. 21a). DMLS ones revealed long, slender needle-like martensitic $\alpha'$-phase in Fig. 21b and c. Structure of HIP one was similar to those without HIP, but the alpha lath thickness after HIP is much greater. In practical production, only virgin powder is recommended used and the rest of unfused powder should be discarded, because the unfused powder might have a negative effect on properties of parts. Researchers [113,154] concluded that there were no critical changes in the mechanical properties of SLM Ti–6Al–4V after several powder reuse cycles, which proved SLM with high material utilization.

Besides Ti–6Al–4V, there were also some LAM studies on other titanium alloys. Liu et al. [155] utilized an LMD technique to fabricate Ti–5Al–5Mo–5V–1Cr–1Fe alloy specimens, which is one of $\alpha$–$\beta$ titanium alloys. The microstructures revealed bamboo-like $\beta$ grain morphology at macro level with fine basket-weave structure and $\alpha$ grain boundary. And specimens realized high tensile strength of 1178 MPa approximately and lower elongation of about 5% only, owing to rapid cooling and the inter-granular continuous $\alpha$ phase, respectively. The similar microstructures were observed in some LMD Ti–6Al–2Zr–1Mo–1V alloy which is a type near $\alpha$ titanium alloy and a common structural titanium alloy [156,157]. Moreover, Ti–5Al–5Mo–5V–3Cr [158], Ti–5.54Al–3.38Sn–3.34Zr–0.37Mo–0.46Si [159], Ti–6Al–2Zr–2Sn–3Mo–1.5Cr–2Nb [160], and other Ti-alloy of LAM processing were investigated as well.

With the acceleration of population aging and the increase of accidents in contemporary society, there is a huge market demand for medical implants [146]. Compared with SS, cobalt-base alloys and other common used alloy materials, titanium alloys have got a lot of attention for so long in medical implants industry because of their low density, high specific strength, excellent corrosion resistance, and particularly good biocompatibility and the low elasticity modulus close to...
natural bone. The shapes of medical implants like artificial joint and interbody fusion cage are usually complex so that AM technology has a huge advantage in this manufacturing industry. After development, there are three generations of biomedical titanium alloy. In contrast to the first-generation (Ti–6Al–4V) and the second-generation (α-β Ti-alloys represented by Ti–5Al-2.5Fe and Ti–6Al–7Nb), elasticity modulus of the third-generation, β titanium alloy without Al and V elements, is lower and more close to human cortical bone, which can avoid stress shielding and promote healing. Currently Ti–Nb, Ti–Mo, Ti–Zr, Ti–Nb–Hf and Ti–Nb–Zr alloys as third-generation were developed with better biocompatibility [161,162]. Zhang et al. [163] manufactured SLM Ti–24Nb–4Zr–8Sn alloy which obtained decent mechanical properties and studied the effect of process parameters. It is reported that Joimax Ltd. Germany, Renovis Surgical Technologies Ltd. US have produced titanium alloy medical implants using LAM technology.
3.4. Superalloy for laser additive manufacturing

Superalloy is a kind of alloy materials mainly used in extreme duty conditions at high temperatures. The work temperature is generally above 600 °C and can reach ~0.7 of absolute melting temperature [164–166]. They can retain their mechanical performances for a long period at elevated temperature. Besides high-temperature strength, superalloys possess a super combination properties including oxidation resistance, fatigue resistance and breaking tenacity. Thus superalloy is more utilized in aerospace and energy industries. According to the matrix element, superalloys are iron-based, cobalt-based and nickel-based alloys. Fe-based superalloy can be also called heat resistant steel, and the operation temperature can reach 750–780 °C only, which limits its further applications in heat-resistant parts. The part of heat resistant steel was discussed specifically in Section 3.2. Co-based superalloy maintain decent properties serving at 730–1100 °C and are usually produced as vanes, combustor sections and aircraft turbines [167]. Furthermore, most of the advanced engineering applications uses Ni-based superalloys as they offer an excellent combination of corrosion resistance, strength, and toughness along with good metallurgical stability, fabricability, and weldability [166]. They are used for components that require chemical resistance and strength at elevated temperature like turbines, rockets, heat exchangers, etc.

Most superalloys own face-centered cubic (fcc) structure resulting in lower creep rate and restricted phase transformations. But the crystal of cobalt is hcp structure below 417 °C and becomes fcc structure at higher temperature. To avoid the transformation from fcc to hcp structure at serving period of components, tissues of Co-based alloys are the stable austenite from room temperature to the melting point by Ni alloying. The strength of Co-based superalloy is slightly lower at moderate temperature by lacking coherent reinforcements, which is only 0.5–0.7 of that of Ni-based alloy. But strength of it is superior when temperature is above 1000 °C. By a significant reason that there are deficient cobalt reserves in most countries all over the world, Co-based alloys have a limited development. Thus there are relatively few researches on Co-based alloy at materials and even AM field in contrast to Ni-based alloy. Common commercial Co-based superalloy include DZ40M, Hayness series alloy, etc. Ni-based superalloy is the most widely used in industry among superalloys. It has a lot outstanding properties: considerable solubility of alloying elements into the matrix, controlled solidification removes the grain boundaries inhibiting failures at high temperatures and its usage in single-crystal form, and the formation of precipitation phases enhancing high-

Fig. 22 – Electron back scattered diffraction images of DZ40M alloy specimens: as-LMD (a,b), after solution treatment at 1280 °C/4 h (c,d) and after aging treatment at 950 °C/12 h (e,f,g) [169].
temperature properties. Common commercial Ni-based superalloys involve Hastelloy X, Nimonic series and Inconel series alloys.

Generally, there are two strengthening mechanism of solution strengthening and precipitation strengthening used in superalloy. It is the theory of solution strengthening that other metal elements like Cr, Mo, and W solubilize in matrix forming solid solution, which results in lattice distortion and improved strength. The secondary phases such as $\gamma'$, $\gamma''$, carbide are precipitated from supersaturated solid solution to strengthen alloys by aging treatment, i.e. precipitation strengthening. The $\gamma'$ phase is fcc crystal structure same to matrix phase and its lattice constant is similar to matrix as well. The fine coherent $\gamma'$ phase is the dispersive precipitation in matrix phase and blocks dislocation motion, providing strength at elevated temperature and creep resistance. And the amount of $\gamma'$ phase is governed by temperature and chemical composition. The $\gamma'$ phase is an intermetallic compound of A$_3$B type. A can be Ni, Co element, B can be Al, Ti, Nb, Ta, etc., and Cr, Mo, Fe can act as A as well as B. Ni$_3$(Al,Ti) is a typical $\gamma'$ phase in Ni-based alloy. Powder metallurgy process are more used to produce precipitation strengthening superalloy and make superalloy which is hard to get plastic obtain plasticity even superplasticity. Casting respected by directional solidification is the conventional manufacturing process of superalloy. However, superalloys processed via directional solidification have coarsen dendritic crystals and their strength and plasticity have more room to improve. What's more, alloys fabricated by directional solidification are used as cast condition generally in that the plasticity are damaged after heat treatment [168]. Therefore, AM method is a nice attempt to fabricate superalloys.

To explore the possibility of AM instead of directional solidification for Co-based alloys, Meng et al. [169] investigated properties and microstructures of LMD DZ40M alloy, Co-based superalloy developed from X40 alloy, and the effect of heat treatment. The dendritic crystals of LMD DZ40M alloy was refined and there were eutectic of $\gamma'$ and primary M$_7$C$_3$ as well as block-like MC (Fig. 22a and b). As is shown in Fig. 22c and d, Cr$_7$C$_3$ and M$_6$C were precipitated after 1280 °C/4 h. The tensile strength at room and elevated temperature of LMD specimen as well as ones after heat treatment were higher than that of directional solidification one but the plasticity was slightly lower.

Compared to LAM Co-based superalloys, researches about LAM Ni-based alloys are relative more due to their wide applications and outstanding strength at moderate and elevated temperature. Inconel 718, a heat resistant precipitation hardenable nickel-chromium iron alloy with a certain amount of Nb, Mo elements added, is most widely used Ni-based superalloy. It is more employed in high-end equipment and advanced manufacturing industries because of its high performances from room to elevated temperature. It can be used as the state after solution or precipitation strengthening. Inconel 718 is hard to machining due to its fast deformation hardening. On the other hand, the material cost of Inconel 718 is rather expensive and a large amount of materials is wasted during machining processing, which causes the manufacturing processing costs increased. The both made people explore a new manufacturing method for Inconel 718. And AM technique is an available choice. Researches on Inconel 718 of AM is the most among Ni-based superalloys. The effect of LED on LAM Inconel 718, i.e.

![Fig. 23](image-url)
comprehensive influence constituted of parameters like laser power, scanning speed, etc., was investigated [170–172]. The LAM Inconel 718 samples presented decent properties and applicable LAM parameter windows were set up. Parimi et al. [173] investigated the influence of the variations in the deposition path and the laser power on the microtexture, grain structures and intermetallic particle morphology development. Inconel 718 samples were fabricated using deposition path of unidirectional or bidirectional deposition by LMD technique. It can be seen in Fig. 23a–c, significant microstructural differences, especially with respect to the dendrite growth morphology, were observed. The dendrites were oriented at 50–60°, 45–50° and 75–85° to the substrate during low power unidirectional, low power bidirectional and high power bidirectional scanning strategy respectively. And the dendrites were oriented in a zigzag fashion in low power bidirectional deposition path. The differences of grain orientation between three samples were mainly attributed to the variation in the contribution of vertical and horizontal heat fluxes ($q_v$ and $q_h$ in Fig. 23d, respectively). The layered pattern was not observed at high laser power which was not similar to that at low power, while a strongly $<100>$ textured columnar structure was formed, mainly due to the fact that the higher values of heat input results in the epitaxial growth of the grains, other than re-nucleating from the previous layers.

Furthermore, heat treatment also plays a significant role in improving performances of LAM Inconel 718 alloy. Lambarri et al. [174] utilized LMD technique to deposited Inconel 718 alloy on the substrate of wrought plates and heat treated the alloys after deposition. The microstructure of wrought Inconel 718 revealed $\gamma$-Ni solid solution matrix along with precipitates mainly needle-like Ni$_3$Nb ($\delta$ phase). Fig. 24d showed that the microstructure of LMD sample was mainly dendritic with the presence of niobium carbides, alumina and Laves phase. The same kind of precipitates as in the untreated sample were found in both wrought and LMD samples after solution treatment refer to Fig. 24b and e. The solution treated wrought sample showed similar microstructure with very fine $\delta$-particles and small amount of niobium carbides dissolved in the matrix led to increased Nb content in the matrix. The solution treated LMD sample also showed the dendritic growth with the presence of needle-like $\delta$ precipitates as well as alumina and carbides. The dendritic structure was still evident in solutionized LMD sample, but it was not as clear as before. The tiny intragranular $\delta$ phase was again found after full solution-aging treatment without other visible changes in comparison with the solutionized samples, as noticed in Fig. 24c and f. However, $\gamma'$ and $\gamma''$ precipitates were not detected during the SEM analysis. As is shown in Fig. 24g, the full solution-aging treatment made microhardness of both samples increase dramatically perhaps due to undetected $\gamma'$ and $\gamma''$ precipitate. The stress–strain curve in Fig. 24h revealed the tensile characterization of LMD Inconel 718 undergone full treatment. All four tensile samples were prepared.

Fig. 24 – SEM images of the wrought (a,b,c) and LMD Inconel 718 (d,e,f) at the as-built condition and after heat treatment, microhardness distribution (g), and stress–strain curves of fully aged LMD specimen (h) [174].
perpendicular to the substrate from the same LMD alloy, which declared the homogeneity of LMD sample. The tensile strength of LMD alloy was close to that of wrought but the plastic behavior was significantly lower associated probably to the difference in the number of twin boundaries. While, other post-treatments may also play an important role. For instance, shot peening, laser shock peening and other surface enhancement technologies could improve fatigue properties of products. But for the LAM parts with high residual stresses caused by rapid heating and cooling, the effect of these treatments may be detrimental [175].

Except for Inconel 718 alloy, the second-generation single-crystal Ni-base superalloy CMSX-4 also exhibits excellent performances and applied potential. Lopez-Galilea et al. [176] reduced the defects of CMSX-4 alloy produced by SLM and post HIP like pores, cracks, segregation, and topologically close-packed phases in contrast to conventionally cast alloy. Besides, GH3536 alloy is a kind of Ni-based superalloy with brilliant properties, whose elemental composition is very close to Hastelloy X. Different form Inconel 718, GH3536 has higher theoretical operating temperature (reaches 1200 °C above) with more content of Mo and no Nb. Our team fabricated GH3536 alloys using LMD technique. The LMD samples were close to full density (relative density of 99.17–99.88%). The average microhardness was about 250 HV0.2. And the ultimate tensile strength reached 679 MPa which was slightly higher than ASTM standard (minimum 655 MPa) [177], but it was lower compared with the SLM ones (668–910 MPa) [178–181]. The ductility was not better than wrought alloys. The hardened structure for the LAM GH3536 alloy was mainly ascribed to the high-density dislocation [180]. In addition, heat treatment plays an important role in improving the micro-structures of LAM GH3536 alloy. Solution and HIP processing both make the strength slightly decrease properly but ductility increase obviously for LAM GH3536 alloy.

### 3.5. Aluminum alloys for laser additive manufacturing

Aluminum alloys are characterized by low density (2.63–2.85 g/cm³), decent strength (UTS of 110–650 MPa), adequate hardenability, good corrosion resistance and excellent weldability, which are suitable for use in a range of applications, such as automotive, defense and aerospace equipment manufacturing, and machinery and tools production [182]. Aluminum alloys are generally divided into two kinds of cast and wrought alloys according to processing technic. Conventionally the alloying elements content of cast Al alloys is more than that of wrought alloys. The micro-structures of cast Al alloys are basically eutectics with low melting point, making them suit for casting due to the good...
fluidity avoiding heat crack. The common cast Al alloys include Al–Si, Al–Zn and Al–Mg series. While Mn and Mg elements are often added in wrought Al alloys to improve the corrosion resistance. The possibility of manufacturing advanced lightweight Al parts using LAM opens up additional application opportunities and promotes the use of difficult-to-machine alloys.

Whereas, Al alloys face numerous challenges in LAM domain. Firstly, Al alloy powder is dangerous when produced, processed, transported and deposited by the character of combustibility, oxidizability, moisture absorption. Secondly Al alloy powder is hard to spread in SLM processing due to its high viscosity and poor fluidity. Al alloy powder is highly susceptible to oxidation and oxide film formed is compact, which results in hindering the combination of cladding layer and substrate or the upper layer. Laser reflectivity of Al is high (about 91%), suggesting the need for high laser power to overcome. In addition, some other objective causes also limit the development of Al alloys in AM domain. There may not be much of an advantage to produce Al alloy components by LAM methods in that the cost of conventional manufactured alloys is low. The available commercial Al powders for LAM are mainly AlSi10Mg and AlSi7Mg, and other high strength Al alloy for LAM still needs to be developed.

The major challenges include minimizing porosity and cracking due to laser absorption of Al. In order to solve this problems, processing parameters optimization is an inescapable topic. The most examined parameters are nothing else than laser power, scanning speed, hatch spacing, powder feeding rate and scanning strategy [183]. LAM fabricating Al

Fig. 26 – Optical micrographs showing the evolution of hot cracking sensitivity in YOZ and XOY plane (a) and EBSD images with grey levels and bold lines for grain boundaries exhibiting microstructures (b) with various volume fraction YSZ addition [188].
alloy part is frequently conducted in an inert atmosphere typically argon. And the requirements for Al alloy powders in LAM are indeed necessary including spherical morphology, good flowability and packing density, minimal gas pores, and Gaussian particle-size distribution. Wu et al. [184] observed that melting mode determined by laser power and scanning speed affected the microstructures of AlSi10Mg alloy fabricated by SLM. The increase of laser energy density modified the distribution of Si via materials vaporisation and melt reflow, forming Si network. This caused a better wear resistance of SLM specimens than cast and the wear mechanisms were dominated by abrasive wear not adhesive wear. Hane mann et al. [185] inquired in-situ alloying of AlSi10Mg with 25 wt. % and 50 wt. % Si addition using SLM. High relative densities were achieved by adjusting power and scanning speed but the optimized parameters window was dependent on Si content that can alter melting temperature and latent heat of fusion. They considered that application of higher laser power and lower scanning speed could decrease crack formation. Compared with the cast AlSi10Mg, the SLM alloy exhibited higher strength but lower uniform elongation and lower temperature of the best thermal treatment [186].

For a long period, crack-free LAM parts can be achieved using just some Al–Si based cast Al alloys. The weldability of wrought Al alloy is worse and the thermal gradient promotes growth of columnar crystal during LAM process, resulting in formation of heat cracks. And this limits the applications of wrought Al alloys in AM. The common methods for decreasing crack tendency are optimization of process parameters and preheating substrate. Tan et al. [187] employed SLM technique to manufacture 2024 Al alloy and investigated the effect of laser power and scanning speed on densification. The processing parameters were set up as power of 200, 225, 250, 275, 300, 325, 350, 375 W and scanning speed of 600, 870, 1200, 1650 mm/s. The components were built on an Al platform preheated at 200 °C to ensure the formability and reduce hot-cracking. Pores and cracks were observed in all SLM samples and the cracks were nearly straight and parallel to the building direction (Fig. 25a). The porosity was high but crack length was significant reduction at the condition of low power and high scanning speed or high power and low scanning speed, i.e. LED was too low or high calculation method referring to Eq. (1). Furthermore, the pores formed in the SLM samples were classified into three categories (irregular voids, spherical pores and large cavities) in terms of their distinctive morphology and size as indicated in Fig. 25b and c. In their work, heat cracks were not completely avoided due to the impossibility to completely eliminate the columnar grains by optimizing process parameters, which presented a low SLM processability of 2024 Al alloy.

It is nearly impossible to obtain a compact and crack-free LAM Al alloy component via optimization of process parameters to control the heat stress. Because parameters control has no ability to significant reduce temperature gradient in order to decrease heat stress sharply. And it may be a fruitful method that alteration in powder content or addition of nucleating agent induces heterogeneous nucleation and grain refinement [187]. The development of large columnar structures is suppressed improving possibility to achieve crack-free parts. Opprecht et al. [188] attempted to add various volume fraction (0.05, 0.2, 1 and 2 vol.%) yttrium stabilized zirconia (YSZ) into Al6061 base powder as SLM materials. Fig. 26a indicated that heat cracks significantly decreased with addition of YSZ increasing and crack-free manufacturing realized when 2 vol.% YSZ added. The fine equiaxed columnar bimodal grain microstructures were observed with no less than 1 vol.% addition of YSZ, which illustrated the effect of YSZ quantity on grain refinement. The reason of crack-free parts could owe

Fig. 27 – SEM image showing laser molten pool boundary and submicro cellular grains (a), TEM bright field showing the high density of dislocation piled up and dislocation network (b), SAED pattern showing the primary fcc phase and tetragonal α precipitate phase (c), HRTEM showing dislocations (d) nanotwin coupled with stacking fault (e,f) and calculated equilibrium phase fractions for equiatomic CoCrFeMnNi HEA (g) [201].
High-entropy alloys (HEA), which is defined as near-equimolar alloys of five or more elements, is attracting ever increasing attention because of the unique properties in a variety of applications [189]. The concentration of each element is 5–35 at. %. The early common thought is that alloy with more metal elements tend to embrittlement but it is absolutely not suitable for HEAs. The HEA was developed since 1990s. Its definition is the high entropy and the high entropy means that the alloy system is more confused. According to Boltzmann relation, the mixed configuration entropy (S) of HEA can be depicted by the following [189]:

$$\Delta S_{conf} = - R \sum_{i=1}^{n} (c_i \ln c_i)$$

(2)

where $R$ is the molar gas constant and its value is 8.314 J/K mol, $c_i$ is the mole fraction of the element in alloy. If the metallic elements are equimolar, the $S$ is maximized and Eq. (2) can be simplified as following [189]:

$$\Delta S_{conf} = R n$$

(3)

where $n$ represents the number of elements in alloy. When $n = 5$, $S = 1.61 R$. Generally, alloy with $S \geq 1.5 R$ is identified as HEA. In its system, high entropy avoids the formation of intermetallic compounds resulting to form simple solid solution. HEA is characterized of high entropy, lattice distortion, sluggish diffusion and “cocktail” effect [190–193]. Particularly the amazing “cocktail” effect, i.e. the synergistic response among the various element in HEA will give rise to various unexpected properties, suggests improving structures to obtain excellent overall performances through decent material constituent design or addition of some specific elements. Currently there are defects such as pores and inclusions accompanying with component segregation in HEAs manufactured by conventional manufacturing methods of vacuum arc melting and casting due to the low cooling speed. The booming AM technologies are attractive naturally. LMD technique is the first for high entropy for HEAs fabrication. FeCoCrNiAlB$_5$ [194], Al$_6$Co$_3$FeCu$_{10}$NiCoCr [195], 6FeNiCoSiCrAlTI [196], FeNiCoAlCu [197] and AlCoCrFeNi [198] HEAs were fabricated via LMD and presented properties exceeding casts. Furthermore, Dobbelstein et al. [199] had a nice try at producing compositionally graded TiZrNbTa refractory HEA by in-situ alloying of elemental powder blends during LMD. This technique might be an effective tool for small scale specimen production and fast material screening.

And SLM has been introduced to build HEA using the developed HEA powders [200], Li et al. [201] fabricated equiatomic CoCrFeMnNi HEA by SLM and discovered the sub-micro cellular grains due to large degrees of undercooling within melt pools (Fig. 27a). It revealed high-density dislocation pile-up and dislocation entanglement arranged inside cellular grain (Fig. 27b). A primary fcc phase and tetragonal $\sigma$ precipitate phase with an orientation relationship [011]fcc/ [167]$\sigma$, see Fig. 27c. The nanotwins with stacking faults nearby were observed in SLM HEA (Fig. 27e and f), which was identified in other investigations of LAM CoCrFeMnNi HEA as well [202–204]. The $\sigma$ precipitate phase was not previously found in conventional casting, which illustrates that SLM had different solidification and subsequent solid-state phase transformation mechanisms compared with slowly solidified one. And this made the enhancement of mechanical property for SLM HEAs. The control of phases in LAM HEAs is the key to improve performances. Generally, HEAs are individuality customized suiting for AM techniques. Thus HEAs perhaps would become a focused issue in LAM field. Properties of HEAs hinge on the material design. Machine learning can provide a great deal to this [205].

4. Conclusions

The research status of laser additive manufacturing for metal has been reviewed in this paper and conclusions have been drawn as follows:

Additive manufacturing (AM) technique is a novel manufacturing method which forms components layer upon layer form bottom to top via CAD date input of geometric model. It has numerous benefits of rapid prototyping, customization, high material utilization, and the ability to form complex structures which is hardly realized by conventional manufacturing processes such as casting/wrought plus machining. Hence AM technology owns enormous potential in industrial circle. And with long period development, AM has a wide and successful application in automotive, aerospace, architecture, biomedical, electronics industries and etc. For metallic parts fabrication, AM can be divided into three typical categories: laser additive manufacturing (LAM), wire and arc additive manufacturing (WAAM) and electron beam additive manufacturing (EBAM) depending on the heat sources. All of them possess own advantages and application scopes. WAAM is mainly suitable for rapid prototyping of large size components, while EBAM and LAM are usually applicable for small parts. Among the most popular LAM, there are synchronous powder feeding (e.g. laser metal deposition, LMD) and powder bed forming method (e.g. selective laser sintering/melting, SLS/SLM). They possess different characteristics. SLS is considered as the earliest powder bed forming AM method and it is just appropriate for alloy but no pure metals. But SLM which was developed based on SLS can be applicable for almost metallic materials. The binding mechanism of full melting make the parts fabricated using SLM approach nearly full dense. LMD can be utilized to produce gradient materials components and repair damaged components thanks to the characters of synchronous materials feeding. Generally, components produced by SLM has higher manufacturing accuracy and materials utilization rate but lower production efficiency than LMD.

Microstructures and physicochemical properties of LAM metallic parts is the major concern. The optimization of processing parameters is meaningful. The optimization means
decent laser energy density and best combination of laser power, scanning speed, hatch spacing, layer thickness, scanning strategy, spot diameter and etc. Generally the LAM process window of commercial alloy powders is wide. The as-built parts can achieve decent performance within that window. While it is so significant to optimize the LAM processing parameters for novel alloy. And the numerical simulation has great guiding significance for optimization of parameters. The temperature field and stress field during LAM processing can be forecast simulation. The reactions and products after solidification can be calculated and speculated. Numerical simulation associated with experiment will make effort to investigate the activities and mechanism of rapid melting and solidification in LAM process. For some metallic materials whose LAM products accompany with defects like cracks, the quality can be improved via adding additives with specific function during LAM processing. Zirconia and some rare earth oxide might be good options as additives, and they make grain refinement. The additives and some in-situ produced phases make a critical difference to eliminate defects. Additionally, appropriate heat treatments can enhance performance of LAM metallic parts as well. And usually the optimum heat treatments of AM parts are basically same as conventional process.

The forming qualities rely on the improvement of LAM equipment. There are shortages in current LAM processing, so a large room for developing equipment exists. Smaller spot diameter means better accuracy of manufacturing. The development of powder feeder and powder atomization technology may play a role in AM equipment. All of these make sure of higher forming precision. Though deposition rate of LMD is high, forming precision and materials utilization rate (about 1/4 to 1/3) are relative low, more used in fabrication of billet. It does not much conform to the principle of AM. The size of SLM build chamber is usually limited which restricts formation of large-scale metallic parts. Complicated thermal history and residual stress caused by rapid melting and solidification may bring negative effect on microstructures and properties of LAM parts especially micro-cracks and pores. It requires the optimization of process parameters and materials design. And the cost reduction of alloy powders for LAM is significant to the development of LAM. Recently some indirect AM techniques like nanoparticle jetting (NPJ) has been established. The indirect AM uses mixed materials of alloy powder and organic binder (acts as support material). The metal components are obtained since removing support material and sintering. These technologies have advantages of low cost, desktop work, no complicated thermal history, which LAM does not have. Particularly it is saving for working procedure and support material of indirect AM can be removed easily. Direct metal writing (DMW) which controls semi-solid alloy slurries to formation avoids complex thermal process as well. They all give suggestions to development of LAM.

Most LAM researches so far have focused on the common commercial alloy such as 316L stainless steel, Ti–6Al–4V titanium alloy and Inconel 718 nickel base superalloy. These alloys possess remarkable properties indeed, but an excess of repetitive studies on them make no more sense. The other metallic materials should be paid more attention to. H13, 17-4 PH and 15-5 PH high-strength steel as well as Hayness, Hastelloy, Nimonic and Inconel series superalloys all have outstanding performances and wide use range, which should receive attention. The LAM process of alloys with high laser reflectivity particularly aluminum alloys is also a difficulty. High-entropy alloy is a research hotspot in AM field because of the characterization of high entropy, lattice distortion, sluggish diffusion and “cocktail” effect. Expect for these alloys, AM specific alloys might hold unprecedented potential for the future. The development of advanced material will be a major direction of LAM investigations in the future. With development of artificial intelligence, machine learning will take an important role in LAM materials design.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Nomenclature

AM Additive manufacturing
ASTM American Society for Testing and Materials
CAD Computer aided design
WAAM Wire and arc additive manufacturing
EBAM Electron beam additive manufacturing
LAM Laser additive manufacturing
LMD Laser metal deposition
SLM Selective laser melting
SLS Selective laser sintering
SSS Solid state sintering
LPS Liquid phase sintering
SLPS Supersolidus liquid phase sintering
HIP Hot isostatic pressing
LENS Laser engineering net shaping
DMD Direct metal deposition
LRF Laser rapid forming
DLF Direct laser fabrication
LDW Laser direct writing
DMW Direct metal writing
NPJ Nanoparticle jetting
CP-Ti Commercially pure titanium
CS Cold spray
SS Stainless steel
LFBD Laser powder bed fusion
LED Laser energy density
mFFF Metallic fused filament fabrication
DMLS Direct metal laser sintering
YSZ Yttrium stabilized zirconia
HEA High-entropy alloy
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