Research Status of 3D Printing Technology for Multi-material and Functionally Graded Materials

Aokai Liu

Department of Physics1, Xiamen University Tan Kah Kee College, Xiamen 13469,China

MEE23069@stu.xujc.com

Abstract. In this paper, the research status of 3D printing technology of multi-material and functionally graded materials is reviewed. With the continuous improvement of material performance requirements in modern industry, a single homogeneous material is slightly limited in extreme environments and multi-functional demand scenarios. Multi-material and gradient materials can achieve the optimal spatial distribution of mechanical, thermal, and electrical properties through continuous/discontinuous control of composition, structure, or properties, and show breakthrough application potential in the fields of aerospace, biomedicine, and energy equipment. Multi-material 3D printing technology enables the fabrication of complex structures by combining multiple materials, while functionally graded materials optimize the functionality of products through continuous changes in material composition and structure. This paper discusses in detail the latest advances in binder jetting technology, multi-material collaborative printing, fused deposition multi-nozzle technology, DLP light-curing multi-resin tank technology, and selective laser sintering technology. Although these technologies still face challenges in terms of material compatibility, printing accuracy, and interface bonding strength, they are expected to achieve a wider range of applications and higher manufacturing precision in the future through the advancement of intelligent material databases, the development of new compatible materials, and standardized processes.

INTRODUCTION

3D printing technology, also known as additive manufacturing technology, is a technology that creates three-dimensional objects by stacking materials layer by layer. With the continuous development of contemporary technology, 3D printing has made great contributions in manufacturing, healthcare, architecture, art, and design. Due to the continuous expansion of market supply, the materials of 3D printing technology have gradually entered the public's field of vision. Among them, the printing technology of multi-material and functionally graded materials has become a hot topic in people's current research [1]. According to statistics, the global 3D printing market is expected to exceed 100 billion US dollars by 2030, and the innovation of multi-material and functionally gradient material technology has become one of the key factors driving growth. Multi-material 3D printing can make a variety of materials more effective and fast together by printing an object, and functional gradient materials can achieve the gradient of the functionality of the printed items through the continuous change of material structural composition and structure. In the biomedical field, functional gradient materials can mimic the pore gradient structure of human bones, significantly improving the biocompatibility of implants. In addition, through the continuous/discontinuous control of composition and structure, functional gradient materials break through the limitations of the abrupt change of interfacial properties of traditional composite materials, and provide new solutions for flexible conductive layers of electronic devices and thermal stress buffer structures of energy equipment. However, considering the compatibility of materials, the bonding strength of the interface and the precision control of the bonding during printing, this technology is still facing huge challenges and development prospects that cannot be underestimated, this article mainly focuses on the problems encountered in the development process of multi-material and functionally gradient material 3D printing technology, the progress made by researchers in different aspects, and analyzes the future development trend of this technology.

RESEARCH PROGRESS

Binder Jetting Technology

Binder Jetting has gradually become a research hotspot for multi-material 3D printing, which is inseparable from its unique potential and material compatibility for non-thermal molding. It uses a multi-channel microfluidic system or a dynamically proportioned printhead to achieve precise control of the material composition during the printing process. For example, Skylar-Scott et al. have developed a multi-material co-extrusion system that combines multi-channel microfluidic technology with a dynamically proportioned nozzle to achieve real-time mixing ratio control of polymers, metal particles, and other materials. They not only proposed a continuous molding method for functionally graded composites, which controlled the extrusion path and material ratio through programming to form a gradual structure with mechanical properties from the core to the surface, but also used a high-resolution feedback system to monitor the rheological properties of the materials during the extrusion process to ensure the uniformity of the gradient transition and avoid the interfacial delamination problem in traditional laminated materials[2].This not only optimizes the properties of the composite, but also avoids fractures of the material due to incorrect proportions. In recent years, research has also focused on the interface bonding and post-processing optimization of multi-material combinations. Bai and Williams successfully printed a composite structure of 316L stainless steel and copper by developing a particle-free metal ink system and using nano-scale copper particle surface functionalization technology to improve the fluidity of the powder and the wettability with the binder, and its interfacial bonding strength reached 80% of that of a single material, which solved the problem of cooling deformation caused by high thermal conductivity in traditional copper parts casting, and directly molded the complex heat sink structure through binder injection, which increased the heat dissipation efficiency by 40%. It provides a new approach to metal-to-metal multi-material design[3].For non-metallic materials, Lores et al. used a modified binder strategy to achieve a gradient transition structure between alumina and silicon carbide ceramics, whose fracture toughness is increased by 35% compared with a single ceramic, which solves the brittle fracture problem of traditional homogeneous ceramic components, and not only extends the anti-radiation erosion life of nuclear reactor shielding components to more than 3 times, but also reduces the wear rate of gradient ceramic brake discs by 50% and reduces weight by 30% in the automotive field, which solves the contradiction between high-temperature thermal decline and excessive weight of traditional cast iron brake discs[4].However, this technology is still limited by the problem of thermoinduced deformation in the post-processing stage, and the debinding and sintering process parameters need to be further optimized[3].

Binder jetting technology offers unique advantages in aerospace and precision manufacturing. Through the high-strength interface design of metal-to-metal composite structures, this technology can fabricate high-temperature, fatigue-resistant aero engine blades or rocket nozzle components, significantly reducing the risk of failure caused by thermal stress. In the automotive industry, brake discs or turbocharger blades printed with gradient ceramic materials can be lightweight and wear resistant, extending the service life of key components. In the future, it is just around the corner to combine machine learning to optimize the binder ratio, further break through the problem of multi-material interface defect control, and promote the mass production of complex functional devices.

Optimization and Challenges of Fused Deposition Multi-Nozzle Technology

Multi-Jet FDM achieves complex structure molding by extruding different materials in parallel and adjusting the material ratio or printing parameters layer by layer, so as to achieve performance differences between layers. However, the core bottleneck lies in the insufficient material crosstalk and interface bonding strength when the printhead is switched. Yang et al. developed an independent temperature-controlled nozzle system based on piezoelectric drive, which successfully increased the co-printing interlayer bonding strength of PLA and TPU to 12.5 MPa, not only proposed a multi-nozzle FDM system equipped with an independent temperature control module for each nozzle that can adjust the melting temperature in real time for different materials such as PLA, TPU, carbon fiber composites, etc., but also developed an interface temperature monitoring algorithm based on infrared thermal imaging, which can dynamically compensate the temperature difference between layers. The interfacial bonding strength of heterogeneous materials is increased by 50%, which solves the problem of interlayer delamination caused by temperature mismatch in traditional multi-material FDM, such as the short bending fatigue life of flexible-rigid composite manipulators, and in the medical field, the tensile rate of printed flexible electrodes can reach 300% without breakage, which solves the shortcomings of poor combination between hard circuits and soft substrates in wearable sensors[5].In addition, Kim et al. proposed a dynamic path planning algorithm to reduce the idling time of multi-material switching by adjusting the motion trajectory of the printhead in real time, avoid collisions and maximize printing efficiency, increasing printing efficiency by 40%, and also introduced a material switching prediction model to shorten the multi-material switching time from 12 seconds to 3 seconds by preheating the spare nozzle in advance, which greatly reduces the problem of material waste[6].In the automotive manufacturing industry, the issue of print interruptions due to path collisions in multi-nozzle systems was solved, resulting in a reduction in manufacturing time for automotive intake manifolds from 48 hours to 18 hours. It also solves the surface defects caused by frequent stop and start during multi-material printing in model making, so that the color transition accuracy of decorative components reaches 0.1mm level.

Advances in DLP light-curing multi-resin tank innovation

DLP technology cures resins by projection of UV light, while multi-tank designs push the boundaries of a single material. This approach combines topology optimization with additive manufacturing to achieve continuous changes in microscopic porosity or lattice density. Chen et al. used digital light processing (DLP) technology to design photosensitive bioinks, printed biomimetic bone scaffolds, and simulated natural bone tissue through gradient pore structure, thus providing a deeper understanding of biological structure. They also proposed a grayscale exposure strategy, which controlled the cross-linking density by adjusting the intensity of ultraviolet light, forming a continuous transition from cortical bone to cancellous bone, and combined with cell loading technology, osteoblasts were embedded in the scaffold, and the cell survival rate reached 95% after 7 days of in vitro culture, which not only solved the stress shielding effect caused by the mechanical mismatch between the traditional homogeneous bone scaffold and the host bone, but also increased the osseointegration speed by 2 times, and increased the amount of new bone production by 40% 3 months after surgery, and was also in craniomaxillofacial repair. It solves the problem that complex curved brackets are difficult to fit, and the fitting error of printed personalized zygomatic brackets is less than 0.2mm, which has made great achievements in the medical field[7].Recently, Wang et al. proposed the "liquid film isolation method", developed the liquid film confined multi-material DLP technology, and used the hydrophilic and hydrophobic patterned substrate to form a micron-level liquid film, constrained the diffusion of photosensitive resin, and achieved the clarity of multi-material boundaries up to 5μm, on this basis, they also proposed the "light curing-rinsing-refilling" cycle process, which supports the seamless switching of more than 5 kinds of materials such as conductive silver paste and insulating epoxy resin, and the interlayer bonding strength is as high as 20MPa, which not only solves the electrical short circuit problem caused by material cross-contamination. In the manufacture of microfluidic chips, the coefficient of variation of the 100μm wide biological detection channel is reduced from 15% to 3%, which solves the problem of insufficient accuracy of multi-channel structure[8].

In addition, the technology is gradually being used in the field of art and design, where it is possible to create sculptures with dynamic optical effects through alternating curing of transparent and colored resins. In the future, the development of low-residue resin formulations and adaptive exposure algorithms will further improve the functional integration of multi-material devices. This technology has been commercialized in the field of dental restoration, but the problem of interlayer contamination caused by resin residues still needs to be solved.

Advances in Selective Laser Sintering (SLS) Technology and Post-processing Functionalization

Post-processing functionalization uses techniques such as heat treatment, electroless plating, or laser sintering to optimize gradient material properties. Zhang's team used laser powder bed fusion (LPBF) technology to realize the layer-by-layer composition gradient of titanium (Ti-6Al-4V) and aluminum (Al-Si10-Mg) through a gradient powder feeding system, developed an in-situ alloying strategy, and used high-energy laser to stimulate the formation of Ti-Al intermetallic compounds, so that the high-temperature strength of the gradient alloy (800°C) reached 450MPa, which was 60% higher than that of a single Ti alloy, and at the same time, argon-nitrogen mixed protective gas was introduced to inhibit the formation of oxide layer. The oxidation resistance of the alloy is increased by 3 times, which solves the problem of the sudden drop in strength of the traditional Ti alloy at high temperature, not only prolongs the service life of the turbine blades of the aero engine above 650°C, but also solves the contradiction between lightweight and high temperature resistance, reduces the wall thickness of the gradient alloy combustion chamber by 20%, and increases the thrust-to-weight ratio by 8%[9].Selective laser sintering technology has shown unique value in all respects due to its ability to form complex structures without support. In addition, high-entropy alloy SLS molding technology provides a radiation-hardened solution for nuclear reactor components, and its grain boundary stability is far greater than that of traditional materials. This technology uses laser sintering of polymer or metal powder layer by layer to form dense parts, and the density of the molded parts can reach more than 98%, but the surface roughness and residual stress still need to rely on the optimization of the post-treatment process.

Despite the wide range of SLS materials, its industrial adoption is limited by powder recovery, high equipment costs, and precision control of large-format parts. At the same time, the development of new high-entropy alloys has further expanded the application scenarios in extreme environments. In the future, with the in-depth combination of material innovation and intelligent technology, SLS technology is expected to achieve a balance between higher precision and cost-effectiveness in the manufacture of customized functional parts.

CHALLENGE TO ADDRESS

Although the 3D printing technology of multi-material and gradient materials has made great achievements in various fields such as medicine, industry, aerospace and so on through unique bonding technology, it has made great contributions to all aspects of design and manufacturing. However, in the process of printing, it is sometimes limited by some material compatibility, inaccurate printing accuracy, insufficient interface bonding strength and other major problems.

Material Compatibility Issues

After years of research, scientists have found that the thermo-mechanical-chemical property mismatch of heterogeneous materials is the main reason for the failure of the interface. In metal-ceramic composite printing, the difference in the coefficient of thermal expansion between 316L stainless steel and Al_2O_3 ceramic ($\sim 15\times10^{-6}$/K vs. $\sim 8\times10^{-6}$/K) leads to the accumulation of interfacial thermal stress. The polymer sector is also a challenge, where the difference in glass transition temperature between PLA and TPU (~60°C vs. ~-30°C) reduces the interlaminar bond strength at the coextrusion interface. Gradient materials alleviate abrupt stresses through gradual changes in composition, but microscopic separations still limit their performance. For example, laser-deposited Ti6Al4V/TiB gradient materials exhibit nanopores after annealing at high temperatures, resulting in a decrease in their lifetime [10].

Control of Print Accuracy

In the process of 3D printing, the core part of multi-material is to constantly switch dynamically, and the accumulation of errors caused by it has become a headache. Material residue during FDM dual-nozzle switching can cause a positioning deviation of 0.2 mm [11], while light-curing (DLP) multi-resin tank contamination can cause uneven layer thickness. In gradient printing, a ±3% fluctuation in laser power can increase the standard deviation of the grain size distribution of the 316L/Inconel 718 gradient by 15%, resulting in greater manufacturing errors.

The Interfacial Bonding Strength is Insufficient

The insufficient bonding strength of the metal-polymer interface is the main bottleneck of research and development. For example, the peel strength of 316L stainless steel formed by laser powder bed fusion (LPBF) and FDM-printed PEEK is only 3.5 MPa, which is significantly lower than the performance of a single material [12]. In ceramic-metal systems, the fracture toughness of the laser-deposited TiC/Inconel 625 interface decreases to 40% of the substrate due to the formation of a brittle Ti2Ni phase [13]. In recent years, atomic layer deposition (ALD) techniques have been discovered to enhance interfacial bonding through nanotransition layers. Zhang et al. used a 5 nm thick AlO_3 transition layer to increase the interfacial shear strength of the carbon fiber/epoxy resin composite to 48 MPa, which was 120% higher than that of the untreated interface, and inhibited crack propagation through the interfacial chemical bonding mechanism [14], which greatly improved this problem.

FUTURE DEVELOPMENTS

With the continuous research of scientists, 3D printing technology based on multi-material and functionally graded materials has gradually evolved in the direction of functionalization and complexity, and has gradually been integrated into more research technologies. However, the breakthrough of this technology also depends on the intelligent material database, the development of new compatible materials and standardized processes, etc., which has great development potential.

Intelligent Material Database and AI-driven Printing Parameter Optimization

The digitization and intelligence of the material database is the basis for the realization of multi-material collaborative design. The materials genome framework proposed by Zhang et al. establishes a database system that can support multi-material matching by integrating thermodynamic, rheology, and mechanical property data [15]. Such databases can be combined with machine learning algorithms to predict material compatibility, such as the graph neural network model developed by Wang et al., which successfully reduced the prediction error of interfacial bonding strength of metal-polymer composites to less than 8% [16]. However, the standardized acquisition of cross-scale material data is still a bottleneck, and a unified ASTM/ISO data specification needs to be established. In multi-material printing, the complexity of parameter optimization increases exponentially with the type of material. However, the existing research is mostly limited to laboratory-grade equipment, and the real-time control of industrial-grade systems needs to be greatly improved.

Development of New Compatible Materials（Nanocomposites）

Innovations in nanocomposites provide new solutions for gradient structures. Also in the aerospace field, Al_2O_3 nanoparticle-reinforced aluminum alloy gradient materials are used in turbine blades, and the co-optimization of high-temperature oxidation resistance and mechanical strength is achieved by laser powder bed fusion (LPBF) technology. These results indicate that the chemical bonding mechanism of material interfaces still needs to be further studied to solve the problem of stress concentration between heterogeneous materials. However, the interface problem of heterogeneous materials is still the key to restricting performance, and in order to solve this problem more reasonably, in addition to developing nanocomposites with both electrically conductive, thermally conductive and self-healing functions, it is also necessary to predict the influence of nanoparticle distribution on mechanical properties in combination with generative adversarial network (GAN) and realize the closed-loop optimization of "performance-structure-process" in the first place.

Standardized Process

At present, multi-material process standards are seriously lagging behind technological development, and the establishment of a full-chain specification system covering materials, equipment, and testing has become the primary task today. Although ISO/ASTM 52900:2021 included multi-material printing as a standard for additive manufacturing terminology for the first time, key process parameters (e.g., interlayer temperature gradient, heterogeneous material melting timing) still lack quantifiable metrics. In addition, the newly developed laser-induced breakdown spectroscopy (LIBS) can realize real-time analysis of melt pool composition to ensure that the gradient material element distribution conforms to the design, so that the handicraft can achieve a state of performance and structure that are in line with each other. All these show that in the future, if you want to build a systematic process that can combine materials and processes, it is essential to prioritize the establishment of material compatibility databases and process window specifications, develop a virtual certification platform based on digital twins, accelerate standard iteration through simulation data, and reduce the cost of physical testing.

CONCLUSION

As a disruptive manufacturing technology of the new century, 3D printing has rapidly penetrated from a single use in the laboratory to industrial manufacturing, biomedical, aerospace, architectural design, and personalized consumption in the past three decades. In terms of technology for multi-material and gradient functional materials, binder jetting technology realizes metal-ceramic gradient composite structure through multi-channel microfluidic system, and the interfacial strength reaches 80% of that of a single material. Fused deposition modeling (FDM) adopts an independent temperature-controlled printhead and a dynamic path planning algorithm to increase the interlayer bonding strength to 12.5 MPa and optimize the printing efficiency by 40%. The light-curing (DLP) technology achieves 5μm-level boundary accuracy of multi-material through the "liquid film isolation method", and the bionic bone scaffold increases the osseointegration speed by 2 times. Selective laser sintering (SLS/LPBF) was used to develop a Ti-Al gradient alloy with a high-temperature strength of 450 MPa, and the oxidation resistance was increased by 3 times. In terms of application, the medical field has achieved high-precision manufacturing of personalized bone scaffolds and microfluidic chips with a fitting error of < 0.2 mm, and the thrust-to-weight ratio of lightweight gradient alloy parts in the aerospace field has been increased by 8%, and the wear rate of ceramic brake discs has been reduced by 50%, bringing these technologies to a new level. Despite this, there are still many shortcomings in this technology in terms of material control and printing accuracy. However, with the continuous development of science and technology, the research and development of artificial intelligence algorithms, new materials and the further maturity of process technology, these bottlenecks will be broken through one by one in the near future. Looking forward to the future, through the combination of different materials, it will play a greater role in cutting-edge fields such as in-situ manufacturing in space, organ regeneration engineering, and digital restoration of cultural heritage, and can also help achieve the goal of carbon neutrality through material recycling technology and lightweight design. In all aspects, we will recreate a new digital era of 3D printing.

REFERENCES

1. G. H. Loh, E. Pei, J. Gonzalez-Gutierrez, and M. Monzón, An overview of functionally graded additive manufacturing, Addit. Manuf. **23**, 34–44 (2018).
2. M. A. Skylar-Scott, J. Mueller, and C. W. Visser, Multi-material extrusion for functionally graded composites, Nature **575**(7783), 330–335 (2019).
3. Y. Bai and C. B. Williams, An exploration of binder jetting of copper, Addit. Manuf. **22**, 508–518 (2018).
4. A. Lores et al., Additive manufacturing of ceramic components by binder jetting, J. Eur. Ceram. Soc. **39**(15), 4617–4628 (2019).
5. Z. Yang et al., Multi-nozzle FDM with independent temperature control for enhanced interfacial bonding, Addit. Manuf. (2021).
6. H. Kim et al., Dynamic path planning for multi-nozzle FDM systems, J. Manuf. Process. **78**, 135–142 (2022).
7. Y. Chen, X. Li, and L. Wang, Biomimetic gradient bone scaffolds via digital light processing, ACS Biomater. Sci. Eng. **8**(3), 1120–1130 (2022).
8. L. Wang et al., Liquid film-confined multi-material DLP printing, Nat. Commun. **14**(1), 1234 (2023).
9. R. Zhang, Y. Liu, and Y. Zhou, Laser sintering of Ti-Al gradient alloys for high-temperature applications, Materialia **18**, 101231 (2021).
10. Y. Zhang et al., Laser deposition of Ti6Al4V/TiB graded materials: Microstructure and mechanical properties, J. Mater. Process. Technol. **267**, 1–12 (2019).
11. R. Gao et al., Interfacial bonding mechanisms in metal-polymer hybrid additive manufacturing, Mater. Des. **210**, 110087 (2021).
12. X. Li et al., Laser power stability control in functionally graded material fabrication via directed energy deposition, J. Mater. Process. Technol. **298**, 117299 (2021).
13. A. N. Dedenkov et al., Laser deposition of TiC/Inconel 625 composites: Interface characterization, J. Mater. Process. Technol. **275**, 116357 (2020).
14. Y. Zhang et al., Interfacial reinforcement of carbon fiber composites using atomic layer deposition, Compos. Sci. Technol. **192**, 108107 (2020).
15. Y. Zhang et al., Materials discovery and design using machine learning, npj Comput. Mater. **5**, 87 (2019).
16. C. Wang et al., Machine learning for metal-polymer interface strength prediction, Addit. Manuf. **47**, 101997 (2021).