Research progress on selective laser melting of hard composite materials

Xie Y X
Zhongshan Ploytechnic College, Guangdong Zhongshan 528404, China
yyxie52@zspt.edu.cn

Abstract. Composite materials are made of multiphase materials composed of two or more materials with different properties. Hard composite materials are often used as alloy materials for tool production due to their high hardness, high strength and good wear resistance. This paper briefly introduces the domestic and foreign research progress and technical status of hard composite materials by laser area melting, summarizes the influence of forming powder and process parameters on the forming performance characteristics of hard composite materials, as well as selective laser melting area of hard composite materials. The quality inspection and molding process simulation of the company, and prospects for the future development, provide a reference for the laser melting “3D printing” of hard composite materials.

1. Introduction
With the emergence of new technologies, the continuous development of processing technology, such as the emergence of additive manufacturing technology, which is highly praised as the "industrial revolution", provides people with a new processing idea. Because of its unique processing concept based on data production, "from scratch" and the characteristics of one-time molding without too many intermediate links, it not only makes it possible to process complex parts with special structures that are traditionally difficult or even impossible to process, it can also reduce production costs to a certain extent. Compared with the traditional mechanical manufacturing technology using subtractive methods, laser additive manufacturing technology has a series of advantages such as short cycle time, no molds, high flexibility, and freedom from material and part structure restrictions. Selective laser melting of metals (SLM) is one of the additive manufacturing technologies developed on the basis of selective laser sintering (SLS) in the past ten years. In recent years, with the continuous research progress of SLM metal printing technology, SLM technology in the manufacture of complex and special-structured metal products have made SLM very important, which has occupied a very important position in industrial-grade additive manufacturing, and it is widely used in aerospace, medical, automobile manufacturing, new material development, personalized art and other fields. Hard composite materials are often used as alloy materials for tool production due to their high hardness, high strength and good wear resistance. In the tool industry, hard composite materials have a pivotal position, especially under service conditions that require high tool strength, such as high-speed machining, mining, etc., the high wear resistance and high strength of hard composite materials can be fully reflected. Especially in the processing of complex parts with special structures, the method of additive manufacturing has advantages that traditional subtractive or equivalent material manufacturing can't match.

However, the material non-equilibrium physical metallurgy and thermophysical processes of laser additive manufacturing technology are very complex, and the interaction between the laser beam and
the powder, the molten pool and the powder bed, the ultra-high temperature gradient in the melting zone and the rapid rapid phenomena such as solidification, internal structure evolution of components, and thermal stress evolution under cycling conditions. Therefore, the biggest problem faced by the additive manufacturing of rigid composite materials lies in the various special internal defects, such as powder, generated in the local area between the powder layer and the powder layer of the component, and the inside of the single powder layer during the sample printing process. Agglomeration, powder volatilization and splashing, heal stress, local unfusion between layers, air gaps, fine ceramic inclusions, internal special cracks, abnormal nucleation and growth of crystal grains, etc., so as to affect the internal quality and mechanics of the final molded part performance and safety of components in service. These thermophysical interaction processes are often carried out on a microscopic scale, and the interaction between them is also very complicated, so it is difficult to observe and study them through traditional experimental methods. These processing characteristics severely restrict the essential understanding of the current metal additive manufacturing process microstructure control, internal defect formation, and deformation and cracking of printed parts.

In order to obtain high-performance controllable rigid composite components during the selective laser melting and forming of hard composite materials, this article summarizes and analyzes the current research status of SLM forming rigid composite materials, focusing on the laser selective melting and forming of rigid composite materials, the influence of material forming powder and process parameters on surface morphology and mechanical properties, forming quality monitoring and control research, and presenting still existing problems and future research directions.

2. SLM forming cemented carbide powder

The research on cemented carbide materials started as early as the middle of the last century. The earliest discovery of this material was the German Karl Schrotter, who used powder metallurgy in 1923 to add Co as a binder to WC, a cemented carbide with hardness second only to diamond[1,2]. Since then, people have realized the high strength, hardness, heat resistance and good wear resistance of this material. The material is often used to make wear-resistant and high-hard tools and molds. However, traditional cemented carbide materials also have insufficient fine powder, and there are problems such as insufficient toughness and short service life of the tools and molds after sintering. Therefore, in material research and development, in order to take into account the hardness and toughness of the final tools and mold products, in continuous research and development, people have developed new types of ultra-fine and nano-grained cemented carbide, coarse-grained cemented carbide, functionally graded cemented carbide and other alloy materials that meet people's higher performance requirements for cutting tools. Among these newly developed powders, the fine particle size and sphericity of ultra-fine and nano-grained cemented carbide powders provide good technical support for SLM molding.

In terms of powder preparation, for powder-processed molded parts, the composition ratio of the powder has a greater impact on the molded parts. Studies have found that with the increase of Co content, the strength, fracture toughness and bending strength of WC-Co cemented carbide powder sintered cemented carbide increase, but the hardness gradually decreases[3]. Therefore, in order to obtain good comprehensive mechanical properties during powder preparation, strict proportional composition control is generally required. For the powder SLM molding, the characteristics of the powder itself are also particularly important. Generally speaking, the powder is required to have good fluidity, high bulk density, sphericity and concentrated particle size distribution. Ni P et al.[4] formed WC-16%Co cemented carbide powder SLM and found that the particle size of the powder has a key influence on the powder spreading effect during the SLM process, and the appropriate particle size ratio can increase the looseness of the powder, as shown in figure 1. Packing density is beneficial to increase the density of hard alloy printed samples.
The common preparation methods of cemented carbide are spray conversion method, chemical vapor reaction synthesis method and high-energy ball milling method[5]. Under the environmental effect of balancing the quality of preparation and the process of preparation, the spray conversion method has obvious advantages in the preparation of powder materials[6]. Some countries started early and invested heavily in powder production. Well-known companies such as Nanodnye, Sandivik, Tokyo Tungsten Co., Ltd. have developed from micron-level WC grains to nano-level grain-size powders. Although China started relatively late, it has also made some progress. Zhuzhou Cemented Carbide Group successfully prepared WC-0.5MC-6Co cemented carbide with an average grain size of 400-600 nm, hardness greater than 93 HRA, and strength greater than 3800 MPa. However, in general, there is a big gap between the cost of manufacturing equipment and manufacturing technology and that of developed countries. The key manufacturing equipment and technology have to rely on imports. The output is mainly low- and mid-range products with high performance, high precision, and high additional cost. The quality of valuable tools, molds, engineering machinery accessories and other products needs to be improved.

3. Research on SLM printing of rigid composite materials

In recent years, with the emergence of metal additive manufacturing technology, especially the rise of SLM technology, its layer-by-layer processing methods, excellent manufacturing capabilities of complex shapes and far higher performance than traditional manufacturing products have caused widespread follow[7-10]. The printing of hard composite materials is different from that of metal-based alloys. Because carbide is the alloy base, during the printing process, the melting point of the carbide and the metal of the binder phase differ greatly. It is easy to evaporate during the melting process; and during the melting process, carbon element is prone to redox reaction with oxygen and hydrogen in the atmosphere, which seriously affects the final tissue composition and material structure of the molded part, and can't achieve the required performance. At present, the research of laser melting forming hard composite materials is mainly focused on printing materials and processing technology. In the research of tungsten-based hard alloy materials, due to the high melting point of W, it is difficult to melt and during the melting and sintering process of W alloy. The instability of carbon has limited the progress of material research, but some W alloy and some WC cemented carbide research progress has also been made.

In terms of macro performance, Campanelli S. L. et al.[11] used SLM to form WC/Co/Cr powder, at an energy density of 12.5 J/cm$^2$, corresponding to a laser power of 100 W, and a scanning speed of 40 mm/s. The relative density was 97.53%. The metallographic photo of the transverse cross-section is shown in figure 2. When the team of Professor Gu D al.[12] studied TiC/Inconel 718 composite powders, they found that a volume energy density of 300 J/m can significantly increase the internal density of the printed parts, with the highest density reaching 96.74%.
At low energy density, molded parts tend to have high porosity. Increasing the laser power will help to enhance the continuity of the molten pool, promote the connection between the melt channels and between the layers, and reduce the porosity of the WC-Co alloy, but it is easy to increase the brittleness of the parts and cause crack expansion; at the same time, through data analysis, it is found that the selection of scanning power, scanning distance, and scanning speed has an interactive effect on the relative density of the molded part and the Co content of the internal binder phase of the molded part. Uhlmann E et al. used a single factor method to study the effects of laser power, scanning speed, and scanning distance on 17% Co content WC-Co alloy prints, and found the law of scanning parameters and density, as shown in figure 3.

In terms of the microscopic forming mechanism, since SLM printed hard composite gold has undergone the process of melting and recrystallization, it is very necessary to analyze the phase change and characterize the structure of the hard composite. Some studies have shown that the WC hard composite material has a complicated phase transition process during the printing process. Meiners W and others selected three different scanning speed parameters of 0.8, 1.0, 1.2 ms\(^{-1}\) for SLM printing of WC-Ni alloy, and found that the internal structure of cemented carbide has an important relationship with the processing parameters, as shown in figure 4.

Khmyrov R S et al. studied the SLM printing of WC-Co alloys with different Co content of 75%, 72.4%, 50%, and 6%. The printed samples were analyzed by XRD and found that WC alloy materials with different Co contents were printed inside. With different phases, different degrees of
decarburization phases appear during the molding process. Domashenkov A et al. [17] found that the decarburization of WC resulted in the complete conversion of the pure Co matrix to the ternary Co4W2C compound. Despite the difference in the initial WC particle size, the synthesized bulk samples have almost the same microstructure. Kang N et al. [18] found that the addition of WC significantly improved the surface quality of SLM processed samples. Elemental analysis showed that due to diffusion, metallurgical bonding occurred in the interface area.

In terms of material printing characteristics research, most of the WC alloy printing materials currently studied are mainly those with high Co content, or only the role of WC as a strengthening relative to other materials, while the research on the printing of hard composite materials with low Co content is very few, and lack of in-depth analysis, just stay at the macro-density index level [19-21].

4. Research on monitoring of molding quality of SLM hard composite

The disadvantage of the current selective laser melting technology is that the components will produce some inherent defects during the manufacturing process, such as residual stress, cracks, spheroidization, and pores. Due to the process characteristics of material accumulation molding, laser additive manufacturing of hard composite materials is difficult to avoid the above-mentioned inherent defects, which affects the performance and application of components.

In the laser additive manufacturing process, the temperature of the hard composite powder changes greatly, and it is easy to form thermal stress remaining in the components. Experimental studies have found that the factors that have a greater impact on residual stress include material properties, component height, powder layer thickness, scanning strategy and related process parameters [22-24]; internal cracks are also typical laser additive manufacturing component defects. It is mainly caused by thermal stress, which has a great impact on the performance of the component; process parameters are the factors that affect the generation of cracks in the component, and the direction of the grains in the component determines the growth direction of the crack. Cloots M et al. [25] studied the crack formation mechanism and found that during the cooling process of the component, the emerging particles grow in a certain way along the vertical direction. Due to the fast cooling rate, in the critical temperature range, the liquid alloy can't be completely homogenized, which leads to cracks. The metal balls formed by spheroidization are independent of each other, and the pores are easily generated in the process of scanning layer by layer, resulting in higher porosity and reducing the mechanical properties of the component. Chen J et al. [26] formed a thermal gradient of the actual sintering temperature in the thickness direction of the carbide processed by SLM through the interaction of the carbide particles and the laser beam, as shown in figure 5. Kuai Z et al. [27] used SLM technology to form CoCrW powder, and studied the defects, micro-hardness, and corrosion resistance of overlaps during the forming process.

![Figure 5. Thermal gradient when SLM forming laser interacts with carbide particles][26]

Industrial CT (computed tomography) technology is an advanced non-destructive testing method based on two-dimensional or three-dimensional imaging technology. It is suitable for non-destructive testing of different materials and structures, and is especially suitable for the detection and analysis of parts with complex shapes and structures. Zhang X et al. [28] designed and produced industrial CT inspections for laser selective melting additive manufacturing through the analysis of the principle and
characteristics of industrial CT technology and the study of the formation mechanism and characteristics of typical defects in selective laser melting additive manufacturing. Using comparative specimens and defect simulation specimens, the industrial CT inspection research of comparative specimens, defect simulation specimens and actual samples was carried out.

So far, the research on the quality control of laser melting technology for hard composite materials is not thorough enough. Using non-destructive testing technology to control the quality of hard composite materials manufactured by additive manufacturing, CT inspection of SLM molded parts can complete the quality assessment of the workpiece without destroying the integrity and service performance of the workpiece, which can meet the requirements of additive manufacturing.

5. Simulation research on SLM molding process of hard composite

SLM molding is a thermally driven process, and the temperature evolution behavior is the basis of SLM research. However, with the deepening of research, single temperature field simulation is increasingly difficult to meet research needs. Based on the SLM temperature field, the flow field simulation of the molten pool can reproduce the key details of the molten pool during the processing process, which is helpful to study the molten pool behavior, such as the heat distribution, defect evolution, molten splash and spheroidization[29]. SLM stress field simulation can predict the residual stress and deformation of the part, and can be used to optimize the scanning strategy and design support to improve the mechanical performance and dimensional accuracy of the part. SLM molding process simulation is generally realized by coupled finite volume method or finite difference method, commonly used softwares includes Flow-3D, Fluent and Openform, etc. Some flow field models use finite element method, commonly used software is Comsol Multiphysics. Since the warpage deformation of SLM parts has little effect on the temperature field, SLM forming stress simulation is generally realized by non-coupled finite element method, and mostly realized by Abaqus, Ansys, etc.

At present, domestic and foreign scholars have carried out many researches on numerical simulation of SLM temperature field. Literature[30,31] used ZrO₂ powder to perform SLM molding experiments on Phenix PM 100 equipment. The surface microstructure of the molded part is dense and uniform, but contains pores and cracks. Pei W et al.[32] established a three-dimensional numerical model for selective laser melting of AlSi10Mg powder, and studied the effects of laser scanning speed, laser power and hatch spacing on the thermodynamic behavior of the molten pool, as shown in figure 6. Li Y et al.[33] used a combination of finite element analysis and experimental verification to simulate the temperature field of the AlSi10Mg SLM process, and studied the influence of laser power and scanning rate on the temperature field of the SLM process. The above researches show that finite element analysis can be used as an auxiliary research method for SLM forming, but there are few researches on SLM numerical simulation analysis of hard composite materials.

6. Summary and outlook

This paper briefly introduces the material technology of SLM forming hard composite materials, discusses and summarizes the influencing factors such as the optimization process, detection and simulation of SLM forming hard composite materials. At present, there is no mature technology for hard composite WC-Co powder molding. The research focus is on solving cracks and improving molding efficiency, and there is a lack of mechanism research.
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