DED Type Laser Additive Manufacturing Technology of Oxide Ceramics

산화물 세라믹스의 DED 방식 레이저 적층 제조 기술

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Abstract

DED laser additive manufacturing is a simpler, more reproducible technology than conventional sintering for fabricating ceramics because it is not restricted by size limitations or location and thus could be utilized for the maintenance and repair of parts. When this method, which applies locally high energy, is employed with ceramics with high melting points and brittleness, defects such as pores and cracks are likely to occur. Therefore, various studies have been conducted to reduce defects and increase toughness. Herein, the effects of the parameters and additives in the DED process for oxide ceramics are summarized, and the influence of using auxiliary devices such as ultrasonic vibration is introduced. This work aims to provide ideas for the design of ceramic materials and systems for DED additive manufacturing, and it summarizes the issues that must be addressed for researchers interested in ceramic manufacturing using the DED method.

Key Words : Directed energy deposition, Oxide ceramic, Additive manufacturing, Laser engineered net shaping

1. Introduction

Ceramics have high strength and modulus, excellent abrasion and chemical resistance, and particularly outstanding thermal resistance^{1,2)}. They are mainly applied to parts used in extreme environments such as severe friction or high stress load conditions at high temperatures. They can be applied to structures and parts in aerospace, automobile and energy fields that require high working temperatures such as gas turbines, engines, batteries, and heat exchangers^{3,4)}. Applying ceramics to these applications can improve efficiency by increasing the operating temperature and reducing losses in the system⁵⁾.

Sintering, a traditional method of manufacturing ceramics, is performed in the following order: 1) powder preparation (granulation), 2) compression molding, 3) machining of green body, 4) sintering, 5) post annealing and finishing, etc. (Fig. 1). Powder preparation refers to a process of granulating to facilitate densification by adding addi-

tives such as a binder and a lubricant. After that, molding is performed by compressing the powder to produce

Fig. 1 Comparison of commercial sintering process and additive manufacturing processes

a green body. Since shaping becomes difficult after sintering due to increased strength, the green body is machined primarily to form the desired shape beforehand. Such machining work requires consideration of the shrinkage that occurs in the subsequent sintering process, and more detailed features are made in the finishing process after sintering. Sintering, which is the main step, is a process of producing a densified sample while decomposing organic material, facilitating grain growth and removing pores through spontaneous reactions using variables such as temperature, time, pressure, and atmosphere. Currently, the process of manufacturing a commercial ceramic involves many steps.

In order to improve the quality of ceramics and simplify the complex process, additive manufacturing using a laser has recently been studied. The additive manufacturing process uses a laser heat source and powder, and the manufacturing takes place layer by layer as the head moves to form a designed 3D structure⁶⁾. Since the commercial sintering process is a process performed in a chamber, there are restrictions in place and size of parts, whereas additive manufacturing can be performed freely in a space where robots can move and be utilized for maintenance and repair of parts. Additive manufacturing can be divided into two groups according to the configuration of the process: indirect additive manufacturing (I-AM) that integrates the powder preparation, compression molding and green body machining steps; and direct additive manufacturing (D-AM) that integrates the processing and sintering steps as well (Fig. 1)⁷⁾. The former, I-AM, includes processes such as fused deposition modeling (FDM), stereolithography (SLA), direct inkjet printing (DIP), layer-wise slurry deposition (LSD), and laminated object manufacturing (LOM). In the I-AM method, after manufacturing a 3D-molded body with a binder, densification is performed through a commercial sintering process. On the contrary, D-AM is classified as directed energy deposition (DED) by ASTM, and laser engineered net shaping (LENS) developed by Optomec is a well-known example. Depending on the company, it is also used in various names such as direct metal deposition (DMD), 3D laser cladding, and laser based metal deposition (LBMD). Nonetheless, D-AM forms a melt pool using a high-power laser heat source without a binder and coaxially sprays the powder to produce a densified deposition at once. With no separate sintering process required, parts can be manufactured quickly through fewer steps using D-AM.

However, since ceramic materials are sensitive to thermal shock and have low fracture toughness, the level of technical difficulty for applying to additive manufacturing is higher than that of metal or polymer materials.

With increasing demand of DED in manufacturing of parts and the rapid development of related technology, studies are being conducted to apply the DED method to oxide ceramics overseas. In South Korea, there have been reports on additive manufacturing of metal or metal matrix composites using the DED method⁸⁻¹⁰⁾, but there have been no domestic studies on AM only using ceramic powders reported so far. Therefore, this study aims to summarize the issues that need to be addressed for domestic researchers in ceramic manufacturing by the DED method.

2. Results & Discussion

2.1 Ceramics Manufactured by DED: Effects of Process Parameters

The DED process system delivers the laser beam and powder simultaneously as shown in Fig. 2. The laser beam creates a melt pool on the surface of the base material, and the powder is fed into the melt pool. The process parameters include powder feeding speed, laser power, scan speed and hatch spacing, and such parameters affect the shape, thermal profile and microstructure of the deposited layer. Al_2O_3 is a representative oxide ceramic. Since it has a melting point of 2072°C , the temperature of the melt pool is higher than that of general metal materials. In addition, the thermal conductivity of Al_2O_3 is $6\text{ W/m}\cdot\text{K}$ at 1000°C , whereas that of metal materials tends to fall in the range of 40 to $500\text{ W/m}\cdot\text{K}$ at the same temperature¹¹⁾. Moreover, Al_2O_3 has a higher laser absorption rate than general metals with a laser absorption rate of 0.77 ¹²⁾. Due to their low thermal conductivity and high laser absorption, oxide ceramics can be melted and deposited with a relatively lower laser power than metals. However, ceramics typically have significantly lower tensile stress than compressive stress. When shrinkage occurs in the peripheral portion

Fig. 2 Schematic of the DED manufacturing system

Fig. 3 Sample appearance Images fabricated with a constant power of 700 W (a)-(b); and with a modulated power pattern (c)-(d)

solidifying faster a tensile stress is applied to the central portion solidifying more slowly, resulting in cracking. The studies conducted on the effects of the process parameters for additive manufacturing of shapes and the effects of the process parameters for reducing the cracks caused by stress are as follows.

Fig. 3 shows two samples produced by additive manufacturing using an oxide ceramic material, MgAl_2O_4 , under the same conditions (scan speed, total heat input, hatch spacing, and powder feed rate) except for laser power. A wall-shaped sample was fabricated by continuously moving the nozzle left and right alternately as shown in the deposition pathway in Fig. 2, using a 6-axis robot. The longer the interlayer idle time is, the more energy is consumed for reheating, thereby increasing the total energy applied to the deposited layer. This in turn increases residual stress and deformation, resulting in cracking in the ceramic material. Therefore, performing the process continuously using residual heat without idle time helps to reduce cracking.

The samples in Fig. 3 (a) and (b) are fabricated with a constant laser power of 700 W; the samples in Fig. 3 (c) and (d) are fabricated with a modulated power pattern while maintaining the same total heat input. The

power pattern is shown in Fig. 4, and the modulated power exerted a higher power to the lower layer in consideration of the thermal conductivity of the ceramic material. At the lower layer, heat is relatively easily released to the base material, but once a deposited layer is formed, the passage through which heat can be transferred is limited. Due to the low thermal conductivity of the ceramic, residual heat remains in the previous layer. Therefore, under constant speed and power conditions, the width of the wall widened toward the upper layer as shown in Fig. 3 (b). This means that an increase in temperature of the melt pool reduced the viscosity and expanded the size of the melt pool. Since the feeding of the powder was constant, the height of one layer decreased as the width of the melt pool expanded. Based on the design, a wall with a height of 20 mm was supposed to be formed by regularly stacking 40 layers with a hatch interval of 0.5 mm. However, as it proceeded up to the upper layer, the width of the melt pool increased due to accumulation of residual heat, unable to ensure a sufficient height. As the distance from the tip of the nozzle to the surface of the deposited layer increases, melting and deposition of the powder became more difficult (Fig. 3(a) to (b)). When using a modulated pattern in which the power is reduced in the upper layer while maintaining the total heat input, it was possible to carry out deposition according to the designed shape as shown in Fig. 3(d). Therefore, it is necessary to control the process parameters in consideration of the thermal conductivity of the ceramic material and the shape of deposition.

The study by Niu manufactured a sample with almost no cracks with a layer thickness of 0.8 mm or more by depositing the Al_2O_3 material using the DED method¹³⁾. Table 1 shows the DED process conditions and the number of cracks observed on the side of each sample. As the layer thickness increases, the number of required layers and the total energy input decrease. Cracking can be suppressed primarily by reducing thermal stress.

Fig. 4 Laser power profile

Table 1 Various process parameter conditions and the number of surface cracks in each sample¹³⁾

	1	2	3	4	5
Hatch distance (mm)	0.2	0.4	0.6	0.8	1.0
Number of layer	50	25	17	13	10
Scanning speed (mm/min)	500	500	500	500	500
Powder feed rate (g/s)	0.0189	0.0378	0.0567	0.0756	0.0945
Laser power (W)	380	422	463	505	547
Energy consumption (J)	34227	18995	18915	11379	9856
Number of cracks	> 10	6	4	1	1

Suppressing the diffusion and aggregation of impurities can reduce cracking by improving the solidification rate of the melt pool. In other literature, cracking decreased with increasing scan speed, and wall structures without cracks were fabricated at scan speeds of 700 mm/min or higher. As the scan speed increased, the thermal stress decreased, and the fracture strength increased¹⁴⁾.

The study by Yu analyzed the effect of scan patterns on the deformation and quality of parts¹⁵⁾. The raster pattern and offset from inside to outside patterns in Fig. 5 (a) and (b) showed larger thermal gradient and thermal deformation than the offset from outside to inside and fractal patterns in Fig 5 (c) and (d). Research on deposition patterns to reduce thermal gradient and thermal deformation is also required.

The process parameters of DED also affect the microstructure¹⁶⁾. The microstructure formed by solidification of the melt pool is quite different from the microstructure formed by the general sintering process^{17,18)}. As the melt pool solidifies, heat escapes in the direction opposite to the scan direction within the layer, and most of the heat is lost by heat conduction toward the base metal¹⁹⁾. According to the solidification theory, the grains grow in the opposite direction to the heat flow. During the solidification process, small grains disappear and large grains grow resulting in the final microstructure

with the distribution of columnar grains stretched in the height direction of deposition. The size of the columnar grains is tens of μm in the width direction and several hundred μm in the height direction, which is larger than that in the structure made of a metal material manufactured by the DED method^{20,21)}. According to the primary dendrite spacing model proposed by W. Kurz, the grain size is proportional to $G^{-0.5}$ (where, G is the temperature gradient)²²⁾. Since ceramics tend to accumulate significant amount of heat due to its lower thermal conductivity than metals, the temperature gradient appears relatively smaller than that of metals at the solid-liquid interface, and larger grains are formed.

Thus, various process parameters in DED affect not only the macroscopic shape, but also the defects such as cracking and porosity, the microstructures, and the mechanical properties. Therefore, it is important to control and optimize the process parameters, and real-time monitoring technology is required for this²³⁾. Although the makers of additive manufacturing equipment provide the modules for real-time monitoring, but in many cases, the modules only store the generated data in real-time and do not immediately reflect them to the process through feedback. In order to improve the quality of manufactured parts, the technology to control of the process parameters such as heat input in real-time by analyzing the size of the melt pool is required. Also, in order to improve the precision of the parts, the working distance from the tip of the nozzle to the surface of the melt pool must be controlled in real-time. In addition, research on the technology for modifying the scan patterns to suppress cracks and deformations through monitoring of temperature gradients and thermal profiles is required. Since the process parameters of DED are diverse and related to one another, further studies should be conducted to understand the effects of the process parameters.

Fig. 5 Single layer patterns for multilayer additive manufacturing. (a) Raster, (b) offset from inside to outside, (c) offset from outside to inside, and (d) fractal¹⁵⁾

2.2 Ceramics Manufactured by DED: Trend of Material Technology

Ever since Balla¹²⁾ reported the possibility of deposition with the Al_2O_3 ceramic material, various oxide ce-

Fig. 6 $x\text{Al}_2\text{O}_3\text{-}y\text{ZrO}_2$ oxide ceramics fabricated by DED (unit of x, y is mol%). (a) $100\text{Al}_2\text{O}_3$, (b) $95\text{Al}_2\text{O}_3\text{-}5\text{ZrO}_2$, and (c) $90\text{Al}_2\text{O}_3\text{-}10\text{ZrO}_2$ ³²⁾

ramics such as $\text{Al}_2\text{O}_3\text{-ZrO}_2$ ²⁴⁾, $\text{Al}_2\text{O}_3\text{-YAG-ZrO}_2$ ²⁵⁾, zirconate-titanate²⁶⁾, calcium phosphate bioceramics²⁷⁾ and the MgAl_2O_4 transparent ceramics^{28,29)} have been manufactured by the DED method. Since considerable thermal stress is exerted due to the nature of DED involving local heating of the material, research has been conducted to improve the toughness of the ceramic material to overcome the high brittleness. In sintering, additives such as ZrO_2 are used to improve the toughness of Al_2O_3 . When ZrO_2 solidifies in its liquid phase, it changes from $t\text{-ZrO}_2$ to $m\text{-ZrO}_2$ through stress induced phase transformation during cooling, which increases the toughness of the material and suppresses cracking^{30,31)}. Moreover, the residual stress due to the difference in the coefficient of thermal expansion between the Al_2O_3 and ZrO_2 materials plays a positive role in suppressing crack propagation. The study by Wu manufactured $\text{Al}_2\text{O}_3\text{-ZrO}_2$ samples by DED, and addition of ZrO_2 appeared to reduce cracking as shown Fig. 6³²⁾.

Fig. 7 is a binary phase diagram of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ where the location of each microstructure shown in Fig. 8 is

Fig. 7 Binary phase diagram of $\text{Al}_2\text{O}_3\text{-ZrO}_2$

marked in a red dotted line. Fig. 8 shows the photographs of different microstructures with varying ZrO_2 contents, and white arrows indicate build direction³²⁾. In all samples, the grains are vertically stretched. According

Fig. 8 Microstructure of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ ceramics. (a) $100\text{Al}_2\text{O}_3$, (b) $95\text{Al}_2\text{O}_3\text{-}5\text{ZrO}_2$, (c) $90\text{Al}_2\text{O}_3\text{-}10\text{ZrO}_2$, (d) $80\text{Al}_2\text{O}_3\text{-}20\text{ZrO}_2$, (e) $70\text{Al}_2\text{O}_3\text{-}30\text{ZrO}_2$, and (f) $63\text{Al}_2\text{O}_3\text{-}37\text{ZrO}_2$ ³²⁾

to Thakur, the size of grains is considerably reduced compared to pure Al_2O_3 , and the grain growth direction changes depending on the ZrO_2 content³³). In pure Al_2O_3 , grains of Al_2O_3 continuously grow during the solidification process. With ZrO_2 added (Fig. 8 (b) to (e)), an eutectic reaction takes place as primary Al_2O_3 grains are formed first to appear in dark gray and ZrO_2 and Al_2O_3 are formed at the same time below the eutectic temperature to appear in light gray. ZrO_2 is formed at the grain boundaries of primary Al_2O_3 , and in the composition of $63\text{Al}_2\text{O}_3\text{-}37\text{ZrO}_2$ at the eutectic point, the eutectic reaction takes place immediately in the liquid phase, and Al_2O_3 and ZrO_2 form a fine lamellar structure as shown in Fig. 8 (f) with no formation of primary Al_2O_3 grains. The fracture toughness value was the highest in the composition at the eutectic point with $5.1 \text{ MPa} \cdot \text{m}^{1/2}$, which was 17% higher than that of pure Al_2O_3 ³²).

The study by Pappas used MgO powders as an additive to Al_2O_3 for analyzing the effects of the parameters on porosity²⁹. Pore size distribution analysis revealed that the use of MgO nanopowder having an average particle size of 50 nm or less significantly reduced the number of large pores of 30 μm or more in size compared to the use of MgO having a size of several tens of μm . In addition, the use of high laser power of 485 W instead of 275 W reduced the overall porosity. However, changing the laser mode (continuous wave, pulse, etc.)

while maintaining the average power of the laser did not have a significant impact on the porosity. It is thermodynamically stable for Al_2O_3 and MgO to react and form a MgAl_2O_4 phase. Since this material stays transparent despite its polycrystallinity, it has potential as a new method of manufacturing transparent ceramics²⁸).

2.3 Ceramics Manufactured by DED: Ultrasonic Application Technology

Since rapid solidification in the DED process creates a large thermal gradient and results in cracking and degradation of mechanical properties as mentioned earlier, additives such as ZrO_2 and Y_2O_3 were used to refine the grains of Al_2O_3 and improve the toughness. However, it is difficult to ensure local homogeneity as different materials are mixed in. Therefore, the effect of ultrasonic vibration using ultrasonic devices has been proposed by researchers^{5,34-36}). An ultrasonic device is attached to the bottom of the base material to apply ultrasonic vibration during the melting and solidification process of the DED process. Ultrasound creates acoustic streaming in liquid substances absorbing acoustic frequencies and vacuum cavitation. This effectively homogenizes the material dispersion, mitigates thermal gradients and thermal stresses, reduces cracks, and refines grains^{37,38}).

The study by Hu manufactured $\text{Al}_2\text{O}_3\text{-ZrO}_2$ ceramics with and without ultrasonic vibration²). As shown in

Fig. 9 Pore distribution and sample images of $\text{Al}_2\text{O}_3\text{-MgO}$ ceramics manufactured by DED. (a) effect of MgO powder size, (b) effect of laser power, (c) effect of laser mode, (d) as-DEDed sample, and (e) translucent sample after polishing^{28,29}

Fig. 10 Microstructure of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ manufactured by DED without ultrasonic vibration (a), and with ultrasonic vibrations (b)²⁾

Fig. 10, the grain size was refined by ultrasonic vibration and the eutectic structure existing at the grain boundary was homogenized. This change in structure demonstrated enhanced mechanical properties (hardness, wear resistance, and compressive strength) as suggested by the results of the compression test and the fracture surface analysis in Fig. 11. The sample manufactured by DED with ultrasonic vibration had higher compressive strength and ductility than the sample manufactured without ultrasonic vibration. In the fracture surface analysis, only intragranular fractures were observed on the fracture surface of the sample manufactured without ultrasonic vibration, whereas intergranular fractures were observed as well on the fracture surface of the sample manufactured with ultrasonic vibration.

The study by Yan analyzed the effect of ultrasonic vibration on cracking and porosity^{35,36)}. Since the energy of ultrasonic vibration helps reduce the thermal gradient, cracks decreased with increasing power. On the other hand, the porosity decreases until the ultrasonic power is 100 W, but the porosity slightly increases when the power exceeds 100 W³⁵⁾. This is because the adequate power deepens the melt pool and promotes the streaming of the melt pool by the effect of the acoustic streaming while the strong power causes the evaporation of the material and impedes the flow of the melt

Fig. 12 Effect of ultrasonic vibration power on cracks and pores³⁵⁾

pool. The cracks were reported to be refined by ultrasonic vibration with an average eutectic spacing of 70 nm, and the sample demonstrated excellent properties with a hardness of 16.22 GPa and a fracture toughness of $7.67 \text{ MPa} \cdot \text{m}^{1/2}$ ³⁶⁾.

3. Conclusions

While sintering, the commercial manufacturing method of oxide ceramics, involves complex processing steps, the DED additive manufacturing using laser can be performed in simple steps with no limitation in

Fig. 11 (a) Compression test result showing the effect of ultrasonic vibration (marked in UV). Fracture surface of compression test samples without ultrasonic vibration (b), and with ultrasonic vibrations (c)²⁾

terms of space, and the technology can be applied for easy repair, overhaul, and maintenance of parts. However, ceramics have a higher melting point, lower thermal conductivity, and higher brittleness than metals. Therefore, during the DED process involving local heating of materials, ceramics are vulnerable to temperature gradients and thermal stresses and are prone to cracks. Therefore, various studies have been conducted to reduce defects, such as pores and cracks, and increase toughness. The summarized results of the studies are as follows:

1) Various process parameters (laser power, scan speed, powder feeding speed, scan pattern and hatch spacing) affect not only the cracking and porosity, but also the microstructure and mechanical properties. Therefore, the process parameters must be controlled to lower the thermal stress on the manufactured parts. In the future, real-time monitoring technology based on real-time analysis is required to improve the quality of parts.

2) Oxide additives such as ZrO_2 and Y_2O_3 were mixed with Al_2O_3 to reduce cracking and porosity. The additive forms a lamellar eutectic structure at the boundary of primary Al_2O_3 grains through eutectic reaction. The additives refine the grains to improve mechanical properties, and the eutectic structure suppresses the propagation of cracking.

3) Due to the nature of the DED process involving local application of energy and fast solidification, it is difficult to achieve homogenization. Therefore, a technique using ultrasonic vibration has been studied. The acoustic streaming and cavitation affect the behavior of the melt pool; reduce porosity and cracking; and improve toughness and strength at the same time.

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산화물 세라믹스의 DED 방식 레이저 적층 제조 기술

DED Type Laser Additive Manufacturing Technology of Oxide Ceramics

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1. 서 론

세라믹은 높은 강도와 모듈러스 그리고 뛰어난 마모 및 화학 저항성, 그리고 특히 고온에서 우수한 특성을 갖는다^{1,2)}. 따라서, 고온에서 심한 마찰이나 높은 응력이 부하되는 조건 등 극한의 환경에서 쓰여지는 부품에 주로 응용된다. 가스 터빈, 엔진, 배터리, 열 교환기 같이 높은 작업 온도를 필요로 하는 항공우주, 자동차, 에너지 분야의 구조체와 부품에 응용이 가능하다^{3,4)}. 이러한 어플리케이션들에 세라믹을 적용하면, 작동 온도를 증가시켜 시스템의 손실을 줄여 효율을 향상시킬 수 있다⁵⁾.

세라믹을 제조하는 전통적인 방법은 소결(sintering) 공정으로 1) 분말 과립, 2) 성형, 3) 성형체(green body) 가공, 4) 치밀화 소결, 5) 후 공정(열처리, 가공) 등의 순서로 제조된다(Fig. 1). 분말 준비 단계에서는 결합제, 윤활제 등의 첨가제를 넣고 치밀화에 용이하도록 과립화하는 공정을 의미한다. 그 후, 성형

은 분말을 압축하여 성형체를 제조하고, 소결 이후에는 강도가 높아 가공이 어려우므로 사전에 성형체를 일차적으로 가공하여 형상을 만든다. 이 과정에서 소결 공정에서의 수축율을 고려한 작업이 요구되며, 복잡한 형상은 소결 후 피니싱 가공을 통해 제조된다. 본 공정인 소결은 온도, 시간, 압력, 분위기 등을 변수를 이용하여 자발적인 반응을 통해 유기물을 분해하고 입성장 및 기공을 제거하면서 치밀화된 시편을 제조하는 공정이다. 현재 상용 세라믹을 제조하는 공정은 많은 단계를 거쳐 제조되고 있다.

세라믹의 품질을 개선하고 복잡한 공정을 단순화 하기 위해 최근에 레이저를 이용한 적층 제조(Additive manufacturing)가 연구되었다. 적층 제조 공정은 레이저 열원과 분말을 이용하며, 디자인된 3D 구조를 형성하기 위해 헤드가 움직이면서 한층 씩 반복하여 제조한다⁶⁾. 상용 소결 공정은 챔버 안에서 이뤄지는 공정이기 때문에 장소와 부품의 크기에 제약이 있지만, 적층 제조 공정은 로봇이 이동할 수 있는 공간에서 자유롭게 제조가 가능하고, 부품의 수정 및 유지/보수도 가능하다. 적층 제조는 공정 구성에 따라 두 그룹으로 나눌 수 있으며, 분말 준비, 성형 그리고 성형체 가공 단계를 통합한 간접 적층 제조(Indirect additive manufacturing, I-AM) 공정과 소결까지 포함하는 직접 적층 제조(Direct additive manufacturing, D-AM)로 분류된다(Fig. 1)⁷⁾. 전자인 I-AM은 Fused deposition modeling (FDM), Stereolithography (SLA), Direct inkjet printing (DIP), Layer-wise slurry deposition (LSD), Laminated object manufacturing (LOM) 과 같은 공정이 대표된다. I-AM 생산 방식에서는 결합제와 함께 3D 형상의 성형체를 제조한 후 치밀화는 상용 소결 공정을 통해서 제조된다. 이와 반대로 D-AM은 ASTM에 의해서 Directed energy deposition(DED)로 분류되며, 대표적으로 Optomec에서 개발한 Laser engineered net shaping(LENS)이 알려져 있다. 업체에 따라 Direct metal deposition

Fig. 1 Comparison of commercial sintering process and additive manufacturing processes

(DMD), 3D laser cladding, Laser based metal deposition (LBMD) 등과 같이 다양한 명칭으로도 쓰인다. 그러나, D-AM은 결합제 없이 고출력 레이저 열원을 통해서 용융풀을 형성하고 동축으로 분말을 분사하여 단번에 치밀화된 적층부를 제조한다. 따라서, 소결 공정은 별도로 진행하지 않으며, D-AM은 적은 공정을 통해 신속하게 부품을 제조 가능하다.

그러나, 세라믹 소재는 열충격에 민감하고, 파괴 인성이 낮은 본질적인 특성으로, 적층 제조에 적용하기 위한 기술적 난이도가 금속이나 고분자 재료에 비해서 높다. DED를 활용하는 부품이 증가하고 및 관련 기술이 빠르게 발달함에 따라, 국외에서는 DED 기술을 산화물 세라믹에 적용하는 연구들이 이뤄지고 있다. 국내에는 DED 기술을 활용한 금속 및 금속기지 복합체(Metal matrix composites)의 적층 제조에 대한 보고는 있지만⁸⁻¹⁰⁾, 세라믹 분말만으로 AM에 적용한 국내 연구 보고는 전무하다. 따라서, 본 논문에서는 국내 연구자들이 이 분야에서 중요하게 다뤄야 할 이슈들을 빠르게 파악하고 이해할 수 있도록 결과들을 정리하여 소개한다.

2. Results & Discussion

2.1 DED 공정 제조 세라믹: 공정 매개 변수의 영향

DED 공정 시스템은 Fig. 2와 같이 레이저 빔과 분말을 동시에 전달하며, 레이저 빔은 모재 표면에 용융풀을 만들고 분말은 용융풀로 공급된다. 공정 매개변수로는 분말 송급 속도, 레이저 파워, 스캔 스피드, 해치 간격 등이 있으며, 이러한 매개변수들은 적층부의 형상, 열 프로파일, 미세조직에 영향을 준다. 대표적인 산화물 세라믹으로 Al_2O_3 이 있으며, 2072 °C의 녹는 점을 가지므로, 이는 일반적인 금속 소재보다 용융풀의

Fig. 2 Schematic of the DED manufacturing system

온도가 높다. 또한, Al_2O_3 의 열전도율은 1000 °C에서 6 W/m·K를 나타내며 금속 소재는 같은 온도에서 대략 40 - 500 W/m·K에 해당한다¹⁾. 게다가, Al_2O_3 은 0.77의 레이저 흡수율로 일반적인 금속보다 높은 레이저 흡수율을 가진다¹²⁾. 따라서, 산화물 세라믹은 낮은 열전도율과 높은 레이저 흡수로 인하여 금속보다 비교적 낮은 출력 조건에서 용융 및 적층 제조가 가능하다. 그러나, 세라믹은 전형적으로 압축응력에 비하여 인장응력이 상당히 낮은 특성을 가지고 있다. 우선적으로 응고되는 주변부에서 수축하게 되면 상대적으로 늦게 응고되는 중앙부에 인장응력이 부하되어 균열이 발생하기 쉽다. 따라서, 적층 형상을 제조하기 위한 공정 변수들의 영향 및 응력에 의한 균열을 저감시키기 위한 공정 변수의 영향을 다룬 연구들을 다음과 같다.

Fig. 3은 $MgAl_2O_4$ 산화물 세라믹 소재를 레이저 출력을 제외하고 동일한 조건(스캔 속도, 총 입열, 해치 간격, 분말 송급 속도)에서 적층 제조한 두 시편을 나타낸다. Fig. 2에 나타난 적층 패스와 같이 6축 로봇을 이용하여 좌우를 번갈아 연속적으로 움직여 벽 형태의 시편을 제조했다. 층간 휴지 시간이 길어질수록

Fig. 3 Sample appearance Images fabricated with a constant power of 700 W (a)-(b); and with a modulated power pattern (c)-(d)

재가열에 에너지가 소모되므로 적층부에 가해지는 총 에너지가 많아진다. 이는 곧 잔류응력 및 변형을 증가시키며 이는 세라믹 소재에 균열을 일으키기 쉽다. 따라서, 휴지시간 없이 잔열을 이용하여 연속적으로 공정을 진행하는 것이 균열을 감소시키는데 도움이 된다.

Fig. 3(a)-(b)의 시편은 700 W의 일정한 레이저 출력으로 제조되었으며, Fig. 3(c)-(d)는 총 입열은 동일하게 유지하면서 변조된 출력 패턴을 이용하여 제조한 시편이다. Fig. 4에서 출력 패턴을 나타내었으며, 변조된 출력은 세라믹 소재의 열전도율을 고려하여 하단부에 더 높은 출력을 주었다. 하단부에서는 모재로 열이 비교적 쉽게 빠져나가기만 적층부가 형성되면 열이 전달될 수 있는 통로가 제한된다. 그리고 세라믹의 낮은 열전도율로 인하여 이전 층에 잔열이 상당히 남게 된다. 따라서, 일정한 속도와 출력 조건에서는 Fig. 3(b)와 같이 상층으로 갈수록 벽의 폭이 넓어졌다. 이는 용융 풀의 온도의 증가로 용융 풀의 점성이 감소하고 크기가 확장되었음을 의미한다. 분말의 공급량이 일정했기 때문에, 용융 풀 폭의 확장되면 한 층의 높이의 감소한다. 설계 형상은 0.5 mm의 해치 간격을 두고 일정하게 40층을 적층하여 20 mm 높이의 벽을 형성하는 것이다. 그러나, 상층부로 올라갈수록 잔열이 누적되어 용융 풀의 크기가 커지고 높이가 확보되지 못하면서,

Fig. 4 Laser power profile

노즐 끝에서 적층부 표면까지 거리가 멀어져 분말의 용융 및 적층이 어려워진다(Fig. 3(a)-(b)). 반면에, 총 입열을 유지하면서 상층부에 출력을 감소시킨 패턴을 이용할 경우, Fig. 3(d)와 같이 설계된 형상대로 적층이 가능했다. 따라서, 세라믹 소재의 열전도성과 적층 형상을 고려한 공정 매개변수의 제어가 필요하다.

Niu 에 의한 연구에서는 Al_2O_3 소재를 DED 방식으로 적층 제조하였으며, 층의 두께가 0.8 mm 이상에서 균열이 거의 없는 샘플을 제조하였다¹³⁾. Table 1에 DED 공정 조건을 나타냈으며, 각 시편의 옆면에서 관찰되는 균열 개수를 표기했다. 층 두께가 증가함에 따라 필요한 층의 수가 줄어들고 투입된 총 에너지도 감소한다. 균열은 일차적으로 열응력을 줄임으로써 발생을 감소시킬 수 있으며, 용융 풀의 응고속도를 향상시켜 불순물의 원소 확산 및 응집을 억제함을 통해 균열을 저감할 수 있다. 다른 문헌에서는 스캔 속도가 증가함에 따라 균열이 감소하였으며, 700 mm/min 이상의 스캔 속도에서 균열이 없는 벽 구조물이 제조되었다. 스캔 속도가 증가할수록 열응력이 감소하고 파괴강도가 증가했다¹⁴⁾.

Yu에 의한 연구에서는 스캔 패턴이 부품의 변형 및 품질에 미치는 영향에 대해 분석했다¹⁵⁾. Fig. 5(a)-(b)

Fig. 5 Single layer patterns for multilayer additive manufacturing. (a) Raster, (b) offset from inside to outside, (c) offset from outside to inside, and (d) fractal¹⁵⁾

Table 1 Various process parameter conditions and the number of surface cracks in each sample¹³⁾

	1	2	3	4	5
Hatch distance (mm)	0.2	0.4	0.6	0.8	1.0
Number of layer	50	25	17	13	10
Scanning speed (mm/min)	500	500	500	500	500
Powder feed rate (g/s)	0.0189	0.0378	0.0567	0.0756	0.0945
Laser power (W)	380	422	463	505	547
Energy consumption (J)	34227	18995	18915	11379	9856
Number of cracks	> 10	6	4	1	1

의 Raster 패턴과 Offset from inside to outside의 패턴은 Fig. 5(c)-(d)의 Offset from outside to inside와 Fractal 패턴에 비해서 더 큰 열구배와 열변형을 나타냈다. 열구배 및 열변형을 줄이기 위한 적층 패턴에 관한 연구도 필요하다.

DED 적층 공정 매개변수는 미세조직에도 영향을 미친다¹⁶⁾. 용융 풀의 응고에서 형성되는 미세조직은 일반적인 소결 공정에서 형성되는 미세조직과는 상당히 다르다^{17,18)}. 용융 풀이 응고하면서 열은 층 내에서는 스캔 방향과 반대 방향으로 열이 빠져 나가고, 대부분의 열은 모재 방향으로 열전도에 의해서 손실되는 것이 전형적인 특징이다¹⁹⁾. 응고 이론에 따라, 결정립의 성장 방향은 열의 흐름과 반대 방향으로 성장한다. 응고 과정에서 작은 결정립들은 사라지고 큰 결정립들이 성장하는 과정을 통해 최종적으로 적층 높이 방향으로 늘어난 주상 결정립이 분포하는 미세조직을 가진다. 주상 결정립의 크기는 폭 방향으로 수십 μm 이고 길이 방향으로 수백 μm 으로, DED 방식으로 제조된 금속 소재의 조직보다 더 크게 나타난다^{20,21)}. W. Kurz에 의해 제안된 Primary dendrite spacing model에 의하면 결정립의 크기는 $G^{-0.5}$ (G 는 온도구배)에 비례한다²²⁾. 따라서, 세라믹은 금속보다 낮은 열전도율로 상당한 열 축적이 발생하므로, 고액계면에서 온도구배는 금속보다 상대적으로 작게 나타나며, 보다 큰 결정립을 형성할 수 있다.

따라서, DED 적층에서 다양한 공정 변수들은 거시적 형상뿐만 아니라, 균열 및 기공과 같은 결함, 그리고 미세조직 및 기계적 특성에도 영향을 미친다. 따라서, 공정 매개 변수를 제어하고 최적화 하는 것은 중요하며, 이를 실시간 모니터링 기술이 필요하다²³⁾. 적층 제조 장비 업체들은 실시간 모니터링 모듈들을 제공하지만, 많은 경우 생성된 데이터들이 실시간으로 저장될 뿐, 피드백을 통해 즉각적으로 반영되지 않는다. 부품의 품질을 향상시키기 위해서 용융 풀의 크기를 실시간으로 분석하여 입열과 같은 공정 매개변수들을 실시간

제어할 수 있는 기술이 필요하다. 또한, 부품의 정밀도를 향상시키기 위해서는 노즐 끝에서 용융 풀 표면까지 작업 거리가 실시간으로 제어되어야 한다. 추가적으로, 온도구배 및 열 프로파일 모니터링을 통해서 균열 및 변형을 억제할 수 있도록 스캔 패턴을 수정하는 기술에 관한 연구도 필요하다. 추가적으로, DED 공정 매개 변수들은 다양하고 서로 연계되어 있기 때문에 공정 변수의 영향을 이해하기 위한 추가적인 연구들이 지속되어야 한다.

2.2 DED 공정 제조 세라믹: 재료 기술 동향

Balla¹²⁾에 의해서 Al_2O_3 세라믹스 소재의 적층 가능성에 대하여 보고된 이후, $\text{Al}_2\text{O}_3\text{-ZrO}_2$ ²⁴⁾, $\text{Al}_2\text{O}_3\text{-YAG-ZrO}_2$ ²⁵⁾, Zirconate-Titanate²⁶⁾, Calcium phosphate 바이오 세라믹²⁷⁾, MgAl_2O_4 투명 세라믹^{28,29)} 등 다양한 산화물 세라믹들이 DED 기술로 제조되었다. 국부적으로 가열하는 DED 특성상 상당한 열응력이 부하되고 세라믹 소재 자체의 높은 취성으로 인하여 인성을 향상시키기 위한 연구가 진행되었다. 소결에서는 Al_2O_3 의 인성을 향상시키기 위해서 ZrO_2 과 같은 첨가제를 사용한다. 이는 ZrO_2 가 액상에서 응고할 때, 냉각 중 응력유기 상변태(Stress induced phase transformation)를 통해서 t- ZrO_2 에서 m- ZrO_2 로 변화하는데, 이는 재료의 인성을 높이고 균열을 억제하는데 도움을 준다^{30,31)}. 또한, Al_2O_3 와 ZrO_2 재료간에 생기는 열팽창계수 차이로 인한 잔류응력은 균열 전파를 억제하는데 긍정적인 역할을 한다. Wu에 의한 연구에서 DED로 $\text{Al}_2\text{O}_3\text{-ZrO}_2$ 가 제조되었으며, ZrO_2 의 첨가가 Fig. 6과 같이 균열을 저감하는 효과가 있었다(Fig. 6)³²⁾.

Fig. 7은 $\text{Al}_2\text{O}_3\text{-ZrO}_2$ 2원계 상태도이고, Fig. 8에 미세조직 사진이 포함된 조성의 위치를 빨간 점선으로 표시하였다. Fig. 8은 다양한 ZrO_2 함량에 따라 다른 미세조직을 나타내며, 하얀색 화살표는 적층 방향을 나타낸다³²⁾. 모든 샘플에서 결정립은 수직방향으로 늘어

Fig. 6 $x\text{Al}_2\text{O}_3\text{-yZrO}_2$ oxide ceramics fabricated by DED (unit of x, y is mol%). (a) $100\text{Al}_2\text{O}_3$, (B) $95\text{Al}_2\text{O}_3\text{-5ZrO}_2$, and (c) $90\text{Al}_2\text{O}_3\text{-10ZrO}_2$ ³²⁾

Fig. 7 Binary phase diagram of $\text{Al}_2\text{O}_3\text{-ZrO}_2$

진 모양을 보인다. Thakur에 의하면 순수 Al_2O_3 에 비하여 결정립의 크기가 상당히 감소하였으며, ZrO_2 함량에 따라 결정립 방향이 변화한다³³⁾. 순수 Al_2O_3 는 응고 과정에서 연속적으로 Al_2O_3 의 결정립이 성장한다. 반면에, ZrO_2 가 첨가되면(Fig. 8(b)-(e)) 공용반응(Eutectic reaction)이 형성되고, 초정 Al_2O_3 가 우선적으로 결정화되어 진한 회색으로 나타내고, 공용은도 이하에서는 ZrO_2 와 Al_2O_3 가 동시에 생성되어 밝은 회색으로 나타난다. ZrO_2 는 초정 Al_2O_3 의 결정립계에 형성되어 있으며, 63 Al_2O_3 -37 ZrO_2 의 공용점 조성에서는 Fig. 8(f)와 같이 액상에서 바로 공용반응이 이뤄지므로, 초정- Al_2O_3 가 사라지고 Al_2O_3 와 ZrO_2 가 미세한 층상 구조(Lamellar structure)를 가지는 미세조직을 보인다. 파괴인성 값은 공용점 조성에서 가장

높게 나타났으며, 순수 Al_2O_3 에 비해서 17% 향상된 $5.1 \text{ MPa} \cdot \text{m}^{1/2}$ 이다³²⁾.

Pappas에 의한 연구에서는 Al_2O_3 의 첨가제로서 MgO 분말을 이용하였으며, 기공에 미치는 매개변수의 영향을 분석하였다²⁹⁾. 수십 μm 크기의 MgO 에 비해서 평균입도가 50 nm이하인 나노 분말을 사용하였을 때, 기공 크기 분포 분석결과 30 μm 이상의 큰 기공들이 현저히 줄었다. 또한, 275 W의 출력 대신에 485 W의 높은 레이저 출력을 사용했을 때 전반적으로 기공이 감소하였다. 그러나, 레이저의 평균 출력은 유지하면서 레이저 모드(연속파, 펄스)를 변경하였을 때, 기공률에 큰 영향을 주지 못했다. Al_2O_3 와 MgO 은 반응하여 열역학적으로 MgAl_2O_4 상을 형성하는 것이 안정하며, 이 소재는 다결정에서도 투명한 특성을 가지고 있어 투명세라믹의 새로운 제조 방법으로도 응용가능성을 보였다²⁸⁾.

2.3 DED 적층 제조 세라믹: 초음파 응용 기술

앞서 언급했던 것처럼 DED 공정에서의 급속한 응고는 큰 열구배를 만들고, 균열이 형성되어 기계적 특성이 저하되므로, ZrO_2 , Y_2O_3 등의 첨가제를 이용하여 Al_2O_3 의 결정립을 미세화시키고 인성을 향상시켰다. 그러나, 다른 소재들의 혼합으로 인해 국부적인 균질성까지 보장하기 어렵다. 따라서, 연구자들에 의해서 초음파 기기를 활용한 초음파 진동의 효과가 제안되었다^{5,34-36)}. 모재의 하단에 초음파 기기를 부착하여 DED 공정 동안 용융 및 응고과정에 초음파 진동을 가한다. 초음파는 액체 물질이 음향 주파수를 흡수하여 생기는

Fig. 8 Microstructure of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ ceramics. (a) 100 Al_2O_3 , (b) 95 Al_2O_3 -5 ZrO_2 , (c) 90 Al_2O_3 -10 ZrO_2 , (d) 80 Al_2O_3 -20 ZrO_2 , (e) 70 Al_2O_3 -30 ZrO_2 , and (f) 63 Al_2O_3 -37 ZrO_2 ³²⁾

Fig. 9 Pore distribution and sample images of Al_2O_3 - MgO ceramics manufactured by DED. (a) effect of MgO powder size, (b) effect of laser power, (c) effect of laser mode, (d) as-DEDed sample, and (e) translucent sample after polishing^{28,29)}

음향 흐름(Acoustic streaming)과 진공의 공동(Cavitation)을 발생시킨다. 이는 재료 분산을 균질화하고 열구배와 열응력을 완화시켜 균열을 정제하고 입자를 미세화시키는데 효과가 있다^{37,38)}.

Hu에 의한 연구에서 초음파를 보조로 활용하여 DED 공정으로 Al_2O_3 - ZrO_2 세라믹을 제조했다²⁾. 초음파에 의해서 결정립 크기가 Fig. 10과 같이 미세화되고 결정립 계면에 존재하는 공용 조직이 균질화 된 것을 볼 수 있다. 이러한 조직의 변화는 더 높은 기계적 특성(경도, 내마모성, 압축강도)에서 더 우수한 특성을 나타냈다. Fig. 11은 압축시험 결과 및 시험편의 파면 분석 결과이다. 초음파 진동을 활용한 샘플은 압축 강

도 및 연성 모두 초음파 진동을 사용하지 않은 경우보다 높다. 파면 분석 결과에서 초음파 진동 없이 제작된 샘플의 파면은 입내 파괴만 발생한 반면에 초음파를 활

Fig. 10 Microstructure of Al_2O_3 - ZrO_2 manufactured by DED without ultrasonic vibration (a), and with ultrasonic vibrations (b)²⁾

Fig. 11 (a) Compression test result showing the effect of ultrasonic vibration (marked in UV). Fracture surface of compression test samples without ultrasonic vibration (b), and with ultrasonic vibrations (c)²⁾

본 논문은 독자의 이해를 돕기위하여 영문논문을 국문으로 번역하여 게재한 논문입니다. 저자는 본 논문으로 연구업적과 같은 실적에 중복으로 지원받거나 인정받을 수 없음을 알려드립니다.

Fig. 12 Effect of ultrasonic vibration power on cracks and pores³⁵⁾

용한 경우에 입계 파괴도 같이 발생한다.

Yan에 의한 연구에서는 초음파 진동의 출력이 균열과 기공에 미치는 영향을 분석하였다^{35,36)}. 초음파 진동 에너지가 열구배를 감소시키는데 도움을 주기 때문에, 균열은 출력이 증가하면서 감소했다. 반면에, 기공률은 초음파 출력이 100 W까지는 기공률이 감소하다가 100 W 이상의 출력에서는 기공률이 다소 증가한다³⁵⁾. 이는 적절한 출력은 용융풀의 깊이를 깊게 만들고, 음향 흐름 효과에 의해서 용융 풀 흐름이 촉진되는 반면에, 강한 출력은 물질의 증발을 유발하고, 용융 풀의 흐름을 방해하기 때문이다. 균열은 공융 조직의 평균 간격이 70 nm로 초음파 진동에 의해 미세화 되는 것이 보고되었고, 이 샘플의 경도는 16.22 GPa, 파괴인성은 $7.67 \text{ MPa} \cdot \text{m}^{1/2}$ 의 우수한 특성을 보였다³⁶⁾.

3. Conclusions

산화물 세라믹의 상용 제조방식인 소결은 공정 단계가 복잡한 반면에, DED 방식 레이저 적층 제조 기술은 공정이 간편하고 장소에 제약이 없으며 부품의 수정, 교체 및 유지보수가 용이하다. 그러나, 세라믹은 금속보다 녹는점이 높고 열전도도가 낮으며 취성이 존재한다. 따라서, 국부적으로 가열하는 DED 방식에서,

세라믹은 온도구배 및 열응력에 취약하여 균열이 발생하기 용이하다. 따라서, 기공 및 균열 결함을 줄이고 인성을 높이기 위해 다양한 연구가 진행되었으며, 결과는 다음과 같다.

1) 다양한 공정 매개 변수(레이저 출력, 스캔 속도, 분말 송급속도, 스캔 패턴, 해치 간격)는 균열, 기공 형성에 영향을 줄뿐만 아니라 미세조직과 기계적 특성에도 영향을 미친다. 그러므로, 공정 매개 변수들은 부품에 부하되는 열응력을 낮출 수 있도록 제어되어야 한다. 앞으로, 부품의 품질을 향상시키기 위해서 실시간으로 분석을 통한 실시간 제어 기술이 요구된다.

2) Al_2O_3 에 ZrO_2 , Y_2O_3 등의 산화물 첨가제를 혼합하여 균열 및 기공을 저감하였다. 첨가제는 공융 반응을 통해서 초정 Al_2O_3 결정립 계면에 라멜라 구조의 공융 조직을 형성한다. 첨가제는 결정립을 미세화하여 기계적 특성을 향상시키며, 공융 조직은 균열 전파를 억제한다.

3) 국부적으로 에너지를 가하고 급속히 응고되는 DED 공정 특성상 균질화가 어렵다. 따라서, 초음파 진동을 활용한 기술이 연구되었다. 음향 흐름과 공동은 용융풀의 거동에 영향을 주며, 기공 및 균열을 저감하고 인성과 강도를 동시에 향상시킬 수 있었다.

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