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Considerations of internal void generation process by observation of melting and solidification behavior in low temperature laser sintering of PEEK

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Abstract

Laser sintering of PEEK performed below the crystallization temperature has been achieved in previous study by low temperature process that anchors the part to a rigid base plate to suppress warpage during processing. However, significant surface roughness and large internal voids are sometimes generated in the parts built by low temperature process, and there are problems in stability of parts quality. The purpose of this study is to contribute to quality improvement of laser sintering of PEEK by low temperature process. It was attempted that clarify the process of surface roughness and void generation by observing the melting and solidification behavior of the material during process with a video camera. From these observation results, it was assumed that the amount of volume change from powder to liquid due to melting and the amount of shrinkage due to solidification affect part quality such as surface roughness and internal voids.

Introduction

PolyEtherEtherKetone (PEEK) which is one of the high-performance plastics with high strength, high chemical, and heat resistance, can be used as a feedstock material for laser sintering. General laser sintering process of PEEK requires a powder bed temperature about 300 °C to suppress parts warpage during the process [1-3]. Since 300°C is above the melting temperature of most polymer materials, laser sintering of PEEK is limited to high heat resistant machine. Therefore, enabling laser sintering of PEEK by ordinary machine that does not have high heat resistant is one of challenges. The authors have been proposing low temperature process as a way to achieve laser sintering of PEEK on ordinary machines that are not highly heat resistant.

Low temperature process is the method of anchoring the part to a rigid base plate instead of maintaining the powder bed temperature between the melting point and the recrystallization temperature to suppress warpage during the process. This method can set powder bed temperature lower than recrystallization temperature. In previous study, it has been shown that setting the powder bed temperature lower than the recrystallization temperature improves the material recycling rate [4], and parts with various crystallinity can be obtained in various powder bed temperatures [5].

The authors have succeeded that laser sintering of PEEK at a powder bed temperature of 170 °C that is the same as the laser sintering process for Polyamide12, the most common material for laser sintering by using a low temperature process [6]. However, obtained PEEK parts have had some problems, such as significant rough surface and large diagonal voids [7]. Since voids and rough surfaces cause a reduction in part strength, it is necessary to clarify the mechanisms of voids and rough surface generation. Since it is obvious that generation of rough surface and inner voids are related to the flow behavior of molten polymer powder, in-situ observation is effective. Many in situ observations have been reported for powder bed fusion of metals. The shape of the melt pool, the balling phenomenon, and the generation of fumes due to excessive energy supply have been observed, and the mechanism has been considered [8-10]. On the other hand, report of in-situ observation in powder bed fusion of polymer is few. Gardner et al. used optical coherence tomography to investigate melt pool shape [11] and Klamart et al. showed curling during process by using thermal imaging [12]. Melvin et al. used high-speed microscope and showed vapor bubble formation and entrapment in liquid pool [13]. Sassaman et al. designed laser sintering machine implemented heat resistant high-speed microscope [14]. In this report, it has been found that laser melting of the polymer powder occurs with a delay from the passage of the laser spot and over extended time.

In this study, it is attempted that clarify the process of surface roughness and void generation by observing the melting and solidification behavior of the material during process with a video camera. In addition to observing the parts building process by low-temperature process, the tendency of surface roughness to occur is investigated by laser irradiating different powder layer thicknesses. This study is to contribute to quality improvement of laser sintering of PEEK by low temperature process.

Methodology

In this study, PEEK is used as material and its melting and solidification behavior is observed with video camera. Not only the behavior during low-temperature processes, but also the behavior at various powder thicknesses is observed for understanding the mechanism of rough surface and void generation.

Material and Machine

The material used in this study is PEEK powder (Vestakeep 2000FP, Evonik inc.). Since this powder is not intended for use in additive manufacturing and contains large particles, the powder was sieved with mesh size of 106 μm to remove large particles. Average particle size after sieving was 66 μm.

Table 1 shows the material properties. Thermal properties were determined by differential scanning calorimetry, and densities were obtained from density measurement tests. Material with no thermal history was used.

Table 1. Material properties.

Glass transition temperature	Recrystallization temperature	Melting point	Bulk density	Ture density
Approx. 150℃	299 ℃	343 ℃	0.3 g/cm3	1.3 g/cm3

The machine that modified commercial laser sintering machine (RaFaEl 300C®, Aspect inc.) was used. This machine is equipped with a CO_2 laser and laser spot dimeter can be changed from 350 μm to 1600 μm using defocusing function.

Test Condition of low temperature process

In this study, specimen build tests and single layer tests for various powder thicknesses were performed. Table 2 shows the scan parameters. The powder bed temperature of 170°C is lower than the recrystallization temperature of PEEK. PEEK plate prepared by injection molding were used as base plates for both moldings. The same laser parameters sets and baseplate were used for both experiments.

Table 2. Scan parameters sets.

Spot diameters	Laser power	Scan spacing	Scan speed	Powder bed temperature	Scan strategy	Scan direction
1685 μm	40 W	0.02 mm	5 m/s	170 °C	Laster	Single

In the specimen build test, the specimen shape was half size tensile specimen. Layer thickness was set at 0.1mm and laser scanning direction was the longitudinal direction of specimen as shown Figure 1. Specimen was built on the support structure.

Figure 1. Specimen shape and scan direction of specimen build test.

Figure 2 shows a schematic image of the single layer test for various powder thickness. The powder thicknesses were 0.1 mm, 0.2 mm, 0.3 mm, 0.4 mm, and 0.5 mm. The thickness of the powder was controlled by the layering pitch. Scanning shape was 80mm × 10mm rectangle and scanning direction was the longitudinal direction of the shape.

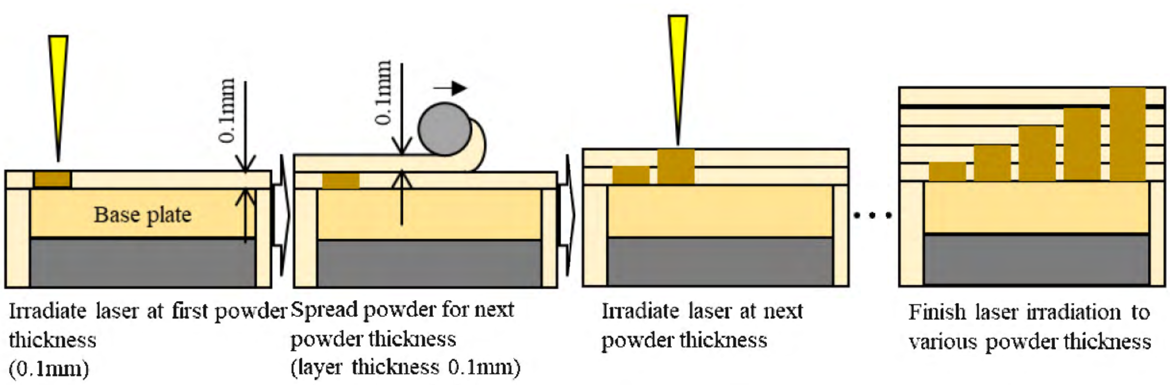

Figure 2. Schematic image of the single layer test for various powder thickness.

Relationship between powder thickness and layer thickness

As reported by Childs et al., the powder thickness that needs to be melted in the laser sintering process is thicker than the layer thickness[15]. The state of the material changes from powder to block through melting and solidification, which also changes the bulk density. The relationship between powder thickness (t_{powder}) and layer thickness (t_{layer}) is showed as equation (1). Here, block density (ρ_{block}) (≅ true density), powder density (ρ_{powder}) are, respectively.

$$t_{powder} = t_{layer} \frac{\rho_{block}}{\rho_{powder}} \tag{1}$$

Observation method during process

Figure 3 shows observation set up. Digital video camera (CANON inc.) with 2.07 million pixels and frame rate of 30 fps was used. A camera was placed outside the machine and the melting and solidification behavior was monitored through the machine window.

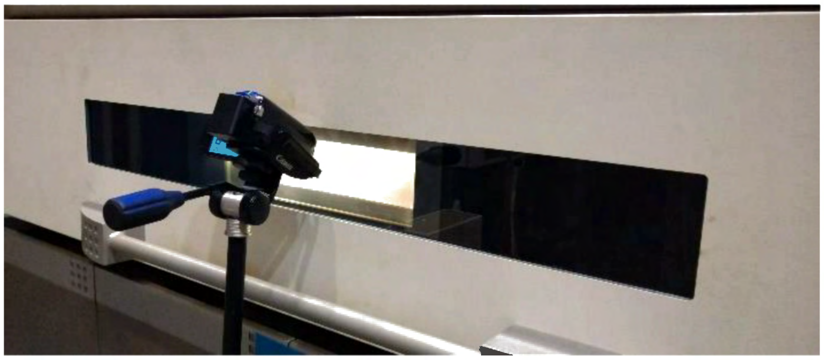

Figure 3. Overview of the observation experiment.

Experimental result

Figure 4 shows a tensile specimen (top) and its cross section (bottom). It is showed that the surface of the specimen was significantly roughened like a wave. The wave spacing was more than 1 mm, which was larger than the scan spacing. The cracks extended diagonally from the surface across each layer, and the slopes of the cracks were tilted in the laser sweep direction.

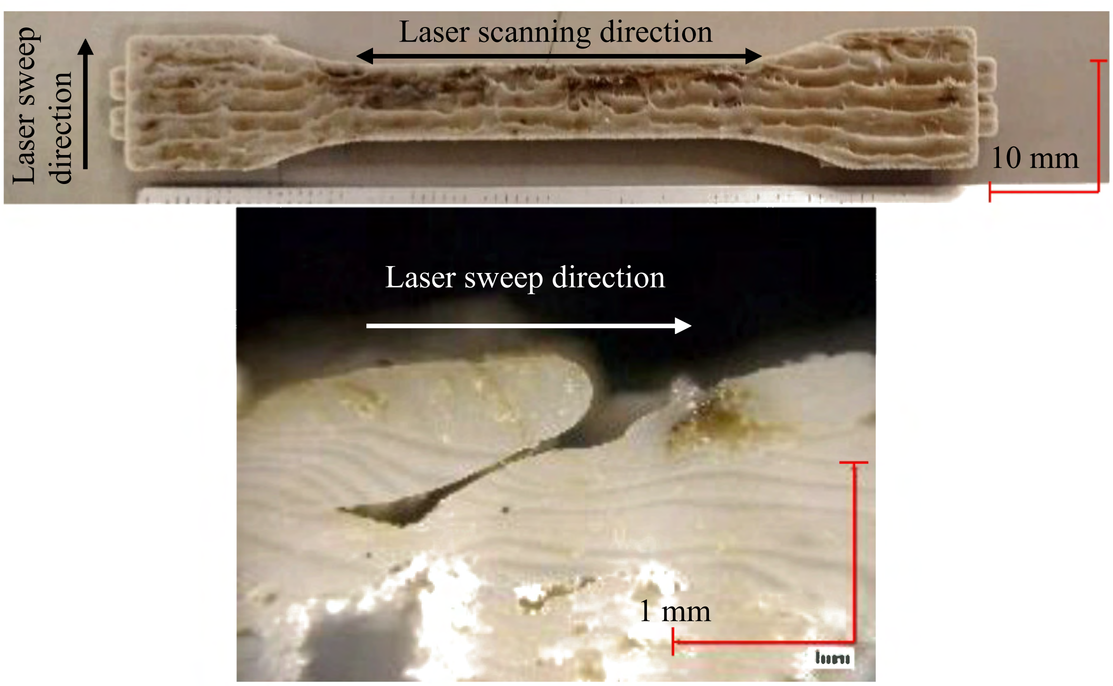

Figure 4. Specimen built by low temperature process.
Top is the whole specimen, and bottom is cross section of specimen.

Figure 5 shows the state of laser irradiation during specimen build test. This picture shows how the powder near the boundary between the melted and unmelted powder was drawn into the melted region like an "avalanche" during laser scanning. This avalanche phenomena occurred periodically during laser scanning.

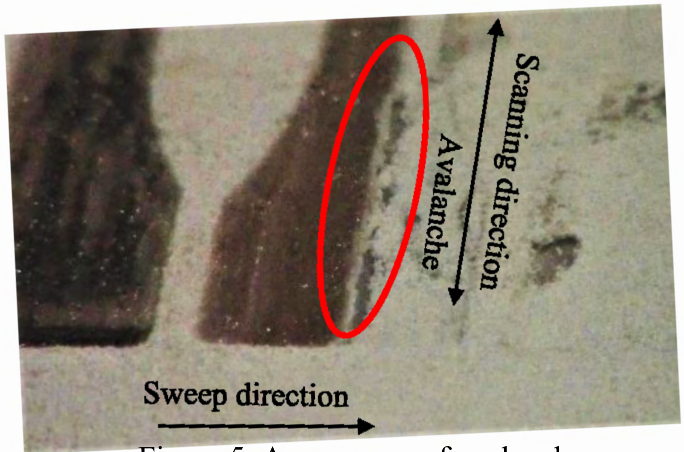

Figure 5. Appearance of avalanche.

Figure 6 shows the state of the solidification process from the end of laser irradiation in 10 seconds interval and its schematic image. At the end of laser irradiation (0 second), solidification has already started on the left side of the specimen, which is the beginning of irradiation. 10 seconds after the end of irradiation, the right side of the specimen, which is the last irradiated area, began to solidify, but the center of the specimen had not yet solidified. Then, 20 seconds after the end of irradiation, solidification was completed.

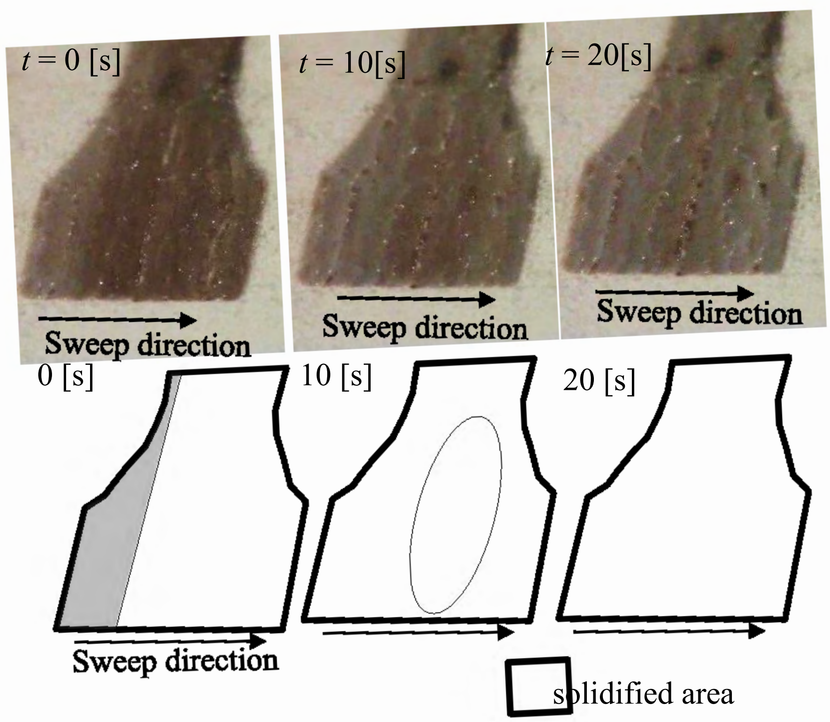

Figure 6. Solidification process of specimen.
Top is photo during laser irradiation, bottom is schematic image.

Figure 7 shows the results of single-layer tests for various powder thicknesses. Waveform rough surface and thermal decomposition were observed at powder thicknesses of 0.4 mm and 0.5 mm. Figure 8 shows the state of melting behavior at each powder thickness. Avalanche phenomena were observed at powder thicknesses of 0.4mm and 0.5mm where waveform roughness occurred.

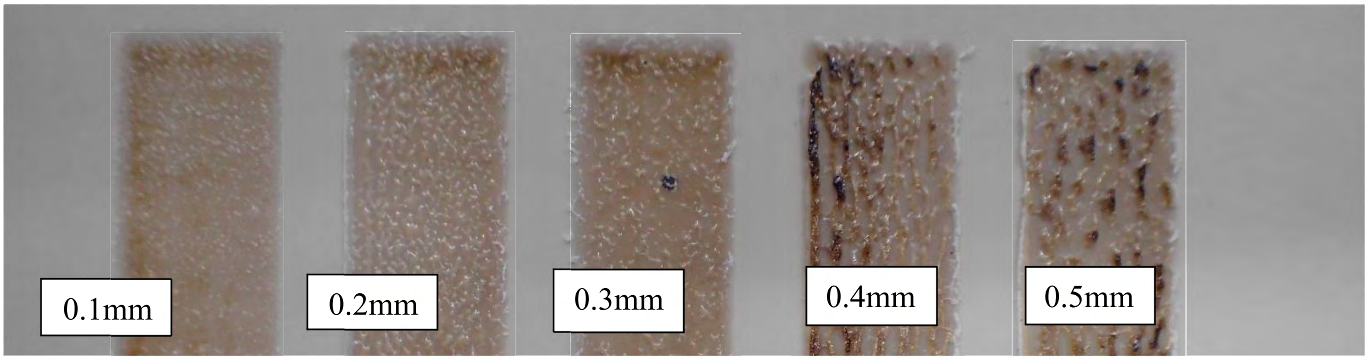

Figure 7. Result of difference powder thickness melting test.
Thermal decomposition and rough surface was observed in thickness 0.4mm and 0.5mm.

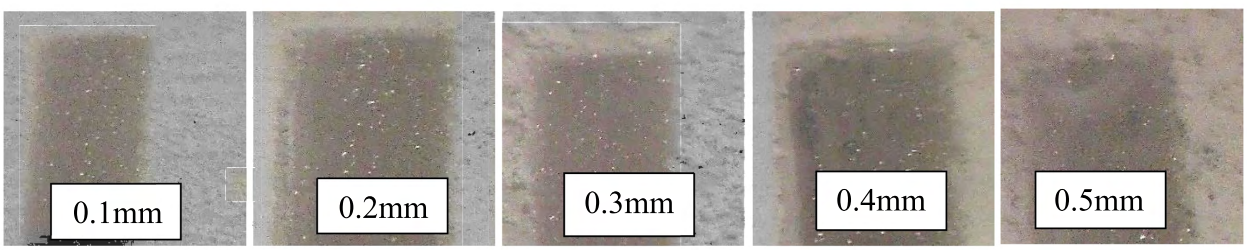

Figure 8. Behavior of each powder thickness during laser irradiation.
Thermal decomposition smoke generated in thickness 0.4mm and 0.5mm and avalanche was observed in thickness 0.5mm.

Discussion

The cross section shown in Figure 4 shows that diagonal voids were generated from the rough waveform surface. The period of the waveform was larger than the scan spacing and did not occur with each laser scan. The behavior shown in Figure 5 confirms the separation of the molten region due to avalanche that occurred during laser scanning. Therefore, the waveform surface was formed by periodic powder avalanches separating the molten region, and it is assumed that the occurrence of diagonal voids was the effect of the remaining internal waveform surface irregularities.

The solidification behavior was not completely dependent on order of laser irradiation, region of shorter laser scanning length was solidified faster than the region of longer scanning length. This is related to the cooling rate of each part, and it is indicated that the solidification behavior of low temperature process has a shape dependence. In addition, even at a powder bed temperature that was more than 100 °C lower than the recrystallization temperature, it took about 20 seconds from the end of laser irradiation to complete solidification. This was due to the low thermal conductivity of the powder and heating from the already formed underlying layer.

Solidified surface was rougher as powder layer thickness increasing. Especially, waveform surface appeared at a powder thickness of more than 0.3 mm. This is because the movable range of the melted polymer increased as the thickness of the powder layer increased, causing polymer flocculation and flow. The reason for the thermal decomposition in the thick powder layer is assumed as follows. In thin powder layer, the surface temperature does not increase because the polymer adhered to the base plate as soon as it melted and dissipated heat to the base plate. On the other hand, in the case of a thick powder layer, the melted polymer flowed downward and then adhered to the base plate, so it is assumed that the surface temperature increased as more heat was received from the laser irradiation before it was diffused to the base plate.

In considering to specimen building test, due to the powder thickness that is melted is about 0.4 mm in the case of layer thickness of 0.1 mm from equation (1), the avalanche has occurred and generated significant rough surface. In addition, diagonal void is generated from this rough surface as starting point. From these results, it is assumed that powder thickness is needed to keep below 0.3mm to avoid from rough surface and large inner voids. To reduce the thickness of the powder layer, it is effective to reduce the layer thickness or increase the bulk density of the powder. In the case of this study, from equation (1), It is assumed that lamination layer thickness must be below 0.07 mm or bulk density of PEEK powder must be over 0.43 g/cm^3 to achieve below 0.3 mm powder thickness that is melted.

It is assumed that the avalanche phenomenon, which causes surface roughness and internal voids, is affected not only by polymer fluidity, but also by temperature distribution and shrinkage during transition from powder to block. In the future, more detailed investigations such as high speed camera observations and thermal analysis are required to understand and resolve this phenomenon.

Conclusion

This study attempted observation of melting and solidification behavior in low temperature process by using digital video camera. As a result, it was found that avalanche, which occurs during laser scanning with thick powder layers, is the cause of the large rough surface. To suppress this phenomenon, the thickness of the powder layer, which is different from the layering pitch, must be kept at a value that does not cause avalanche. The knowledge from this study is not only contribute to the quality improvement of low temperature process, but also provide important information regarding the requirements for the materials.

Acknowledgments

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