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Laser-based coating process of PA12 on stainless steel substrates

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Abstract

Thermoplastic polymers are of great interest for functional coatings due to their good material properties (e.g. chemical and wear resistance, biocompatibility). In the presented study, a laser-based coating process for polyamide 12 (PA12) powder on stainless steel substrates was investigated. To evaluate the influence of the wavelength on the resulting coating characteristics, ytterbium ($\lambda = 1.07$ µm) and thulium fiber laser ($\lambda = 1.94$ µm) were compared for the consolidation of the deposited PA12 powder. Optical microscopy analyses were conducted to characterize the coatings. Furthermore, the degree of particle melt was investigated by differential scanning calorimetry. Results show that dense and adherent coatings can be applied on stainless steel substrates. As the PA12 powder reveals a lower absorption at the wavelength of 1.07 µm, PA12 particles were partially melted by the ytterbium fiber laser. In case of thulium fiber laser, a substrate heating is a crucial process parameter to improve wetting as well as adhesion.

Keywords: laser polymer deposition; thulium fiber laser; ytterbium fiber laser; polymer coating; PA12

1. Introduction

Powder coatings based on thermoplastic polymers such as polyamides or polyether ether ketones offer great potential due to their excellent chemical resistance, biocompatibility, low sliding-friction coefficients and

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abrasion resistance even in dry running conditions. The good price/performance ratio creates furthermore a considerable market share. Thus, thermoplastic coatings are ideally suited to protect surfaces of metals against corrosion and wear. In addition, the use in medical devices such as implants is feasible [1, 2].

Thermoplastic polymers are conventionally applied onto metallic components by means of powder spraying or dispersion coating (dipping, spray gun). Subsequently, the complete workpiece is heated above the melting temperature in a furnace with holding times of at least 30 min [3, 4].

Flame sprayed coatings generally do not require a furnace post-treatment [5]. However, it has to be taken into account that these coatings have a large porosity and weak adhesion strength. Zhang et al. [6, 7] investigated a laser-based post treatment of flame sprayed coatings. Both Nd:YAG and CO_2 lasers were appropriate to remelt the as-sprayed polymer coatings. However, due to the low optical penetration depth, pores near the coating-substrate interface could not be completely eliminated by using a CO_2 laser.

In order to enable a location-selective coating and to reduce the thermal load of the base material, Sändker et al. [4] developed a laser-based coating process. This consists of a laser-based pre-treatment of the metallic substrates, deposition of a hydrous dispersion based on a polyether ether ketone (PEEK) powder by knife coating and laser-based consolidation of the PEEK powder with a diode laser system ($\lambda = 980$ nm). The investigations showed that the process chain represents a promising approach for dense and adherent coatings. The adhesion was significantly increased by a pre-treatment of the substrates with pulsed laser radiation [8]. However, the commercially not available PEEK powder contained additives to enhance the absorptance of the polymer particles.

Admixing additives is often undesirable because it is an additional process step which requires time as well as increases the total manufacturing costs. Furthermore, using additives, like carbon black, poses a risk to the biocompatibility and inhibits the use in particular industries such as the medical sector [9–12].

Due to the aforementioned disadvantages, the presented work is primarily focused on consolidating polyamide 12 (PA12) powder on stainless steel substrates by a laser-based coating process without use of any absorbing additives. It is assumed, that an adequate heating of the coating-substrate interface is a decisive factor to reach adherent coatings [7]. As CO_2 laser radiation exhibits a low optical penetration depth of 103 µm in PA12 powder [13], CO_2 lasers with a wavelength of 10.6 µm are not suitable to consolidate homogeneously polymer powder layers with good adhesion to the substrate. Due to the higher transparency of PA12 in the near-infrared spectrum and thus increased heating of the coating-substrate interface, an ytterbium ($\lambda = 1.07$ µm) and a thulium fiber laser ($\lambda = 1.94$ µm) were investigated for the application in a laser-based coating process. The overall aim of this work is to understand the influence of the emitted wavelength as well as process parameters on the resulting coating characteristics.

2. Material and methods

The utilized polymer material for the laser-based coating process was commercially available PA12 powder (PA 2200, EOS) with an average particle size of 59 µm, according to manufacturer's data sheet. For the experimental investigations, stainless steel substrates (AISI 316L) with a thickness of 1 mm and a quadratic shape (dimension: 50 x 50 mm) were used. The substrate surfaces were grinded with abrasive paper to promote mechanical interlocking between substrate and coating. The average roughness of the surfaces was determined as $S_a = 0.48 \pm 0.1$ µm. All substrates were cleaned with ethanol in an ultrasonic bath for 10 min to remove residues of the grinding process.

Prior to the laser-based coating process, a basic study on the spectral properties of the PA12 powder and stainless steel substrates was performed using an UV-vis-NIR-spectrometer (UV-3600, Shimadzu). In order to investigate the PA12 powder, the polymeric particles were placed in a cuvette with a thickness of 10 mm. The total transmission and total reflection were measured in the wavelength range between 1.0 µm and 2.0 µm. The measurements were used for the calculation of laser light absorption in this spectral range. As the metallic substrates are opaque in the investigated spectral range, only measurements of the reflection were conducted. At least three samples of both the PA12 powder and stainless steel substrate were analyzed.

For the laser-based coating process, the polymeric powder material was deposited manually on the stainless steel substrates with a defined layer thickness by using a metallic sheet of 200 µm thickness and a quadratic centered cutout (10 x 10 mm). The experimental setup for the laser-based consolidation of the PA12 powder on the metallic substrate is shown in Fig. 1. The beam sources used for the experiments were an ytterbium fiber laser (YLR-200, IPG) with a wavelength of 1.07 µm and a thulium fiber laser system (TLR-120, IPG) with a wavelength of 1.94 µm in continuous-wave mode. The incident beam was guided onto the specimen using a laser fiber, mirror system and scanning unit. The laser beam with a Gaussian profile is deflected by the scanning unit in a meander-shaped scanning path. In order to investigate the influence of the substrate temperature on adhesion, a hot plate was used to heat the metallic substrate.

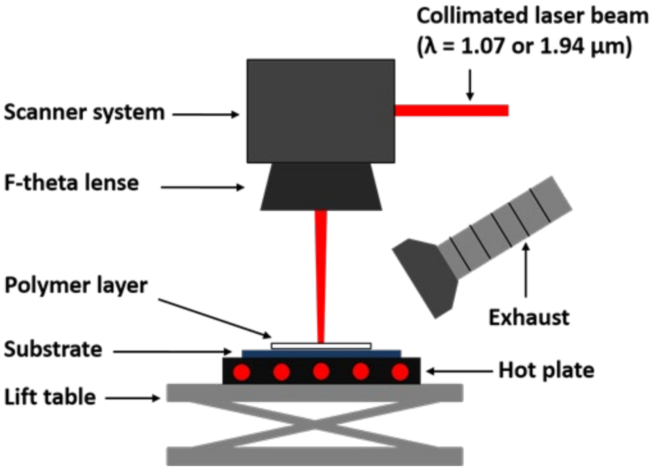

Fig. 1. Experimental setup for the laser-based coating process

Process parameters in previous studies [4, 12] for the laser polymer deposition of PA12 and PEEK were used as a benchmark for expedient values. Table 1 presents the investigated sets of processing parameters and the corresponding energy input per area unit E_a. E_a is given by equation (1), including the three experimental variables of laser power (P_L), scanning velocity (v_s) and hatch distance h_s [14].

$$E_a = \frac{P_L}{v_S \cdot h_S} \tag{1}$$

For an adequate comparison between the ytterbium and thulium fiber laser system, laser power and substrate temperature were adapted systematically for each wavelength without changing the remaining parameters (beam diameter, hatch distance, scanning velocity). Optical microscopy (M80, Leica/ BX53M, Olympus) analyses were performed to characterize the surface morphology and cross sections of the coatings in terms of possible defects. The cross sections were prepared using a disc cutting machine (Discotom-10, Struers) and subsequently grinded as well as polished. In order to evaluate thermal features of both PA12 powder and coatings, differential scanning calorimetry (DSC) tests were conducted using a DSC822e machine

(Mettler Toledo) under nitrogen purge of 40 mL/min. The solidified PA12 layers were removed from the substrate by means of a scalpel and samples with a mass of about 6 mg were placed in 40 µL aluminum pans with covers. The samples were heated from 25 to 250 °C at a rate of 10 K/min with a holding time of 3 min at 250 °C. Therefore, all residual crystals were molten and a thermal equilibrium was achieved. Subsequently, the melt was cooled down to 25 °C at a cooling rate of 10 K/min.

Table 1. Sets of parameters used for the laser-based coating process

Parameter	Variable/fixed	Unit	Value
Wavelength λ	Variable	µm	1.07/1.94
Laser Power P_L	Variable	W	10 – 80
Substrate temperature T	Variable	°C	25/125
Scanning velocity v_s	Fixed	mm/s	10
Hatch distance h_s	Fixed	mm	0.5
Beam diameter d	Fixed	mm	1
Energy input per area unit E_a	Variable	J/mm^2	4 – 16

3. Results and discussion

Fig. 2 shows the absorption spectra of PA12 powder and stainless steel substrates (AISI 316L) in the wavelength range of 1.0 – 2.0 µm. The PA12 polymer reveals about a three times higher absorption at the emitted wavelength of a thulium fiber laser (λ = 1.94 µm) compared to the emitted wavelength of an ytterbium fiber laser (λ = 1.07 µm). The values of absorption were determined as 8.8 ± 0.1 % at a wavelength of 1.07 µm and 29.7 ± 2.6 % at 1.94 µm. This results in a more efficient energy deposition into the polymeric material, but also leads to a decreasing optical penetration depth at a wavelength of 1.94 µm.

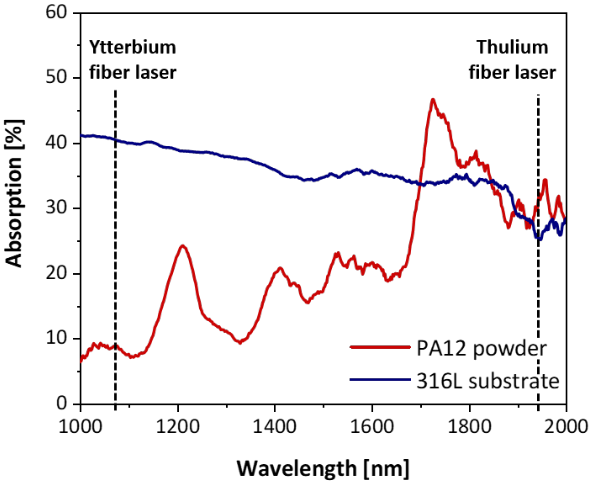

Fig. 2. Absorption spectra of PA12 powder (cuvette thickness of 10 mm) and stainless steel substrate (AISI 316L).

The stainless steel substrate exhibits an inverse behavior regarding the absorption. The values of absorption were 40.5 ± 0.2 % at a wavelength of 1.07 µm and 25.9 ± 1.7 % at 1.94 µm. Due to the lower optical penetration depth in the PA12 layer and lower absorption of the stainless steel substrate at a wavelength of 1.94 µm, it can therefore be concluded that the metallic substrate is heated less in a laser based-coating process by the thulium fiber laser compared to an ytterbium fiber laser.

Microscopic images of the surfaces after laser consolidation by ytterbium and thulium fiber laser with different process parameters are shown in Fig. 3. The coating produced by an ytterbium fiber laser with a substrate temperature of 25 °C leads to only partial coalescence of the PA12 powder particles on the surface (Fig. 3a). In order to reach a closed melting film with an adequate wetting of the metallic substrate by a thulium fiber laser (Fig. 3b), a higher energy input of 16 J/mm^2 at a substrate temperature of 25 °C was required. However, PA12 coatings exhibited a crack structure and yellowing on the surface, which is associated with material aging effects [15, 16]. A possible explanation for the poor wetting (compared to Fig. 3a) is the lower transmission through the PA12 powder layer and the lower absorption of the metallic substrate at a wavelength of 1.94 µm, which results in a higher temperature difference between substrate and polymer layer.

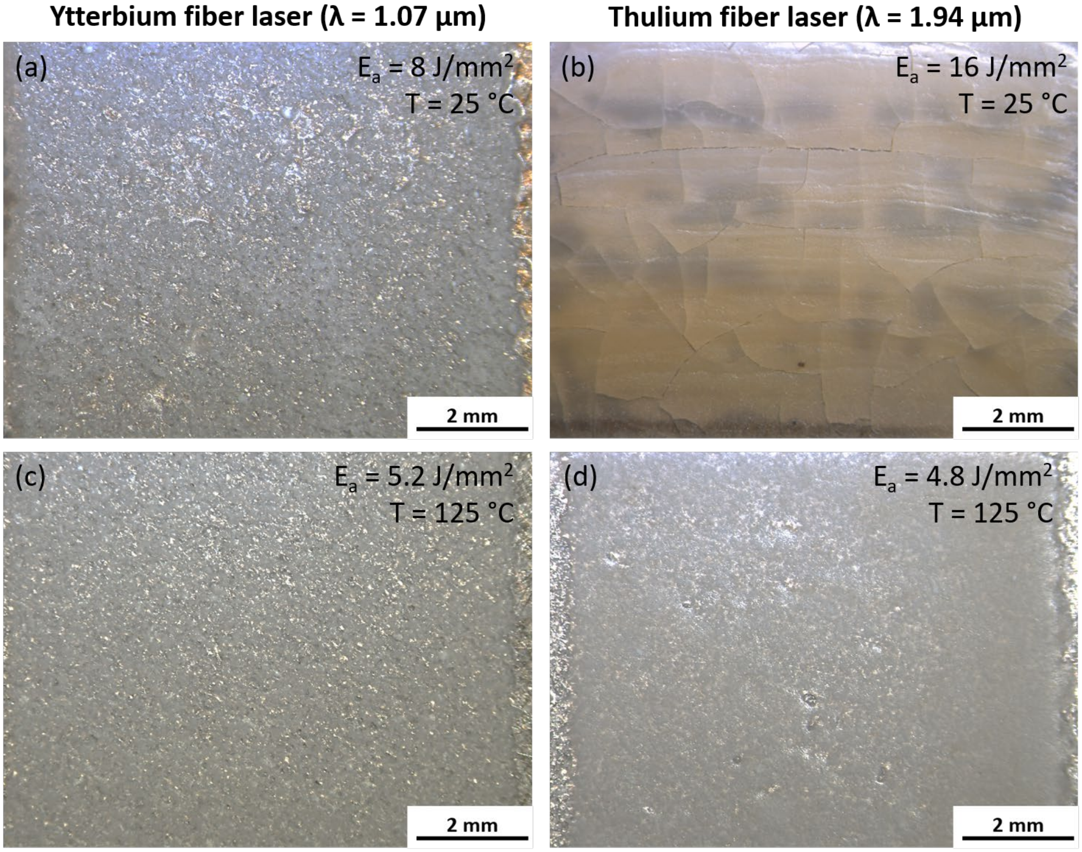

Fig. 3. Microscopic images of the surfaces after laser consolidation by ytterbium and thulium fiber laser.

An additional substrate heating with a hot plate at a temperature of 125 °C (Fig. 3c) did not significantly affect the resulting PA12 layer consolidated by an ytterbium fiber laser (compared to Fig 3a). In contrast, a substrate heating at 125 °C improved the coating consolidated by a thulium fiber laser crucially (Fig. 3d). A closed melting film was achieved and neither a crack structure nor a yellowing of the surface could be observed. By heating the substrate at a temperature of 125 °C with a hot plate, it is assumed, that the temperature difference between substrate and PA12 layer is sufficiently low to avoid rapid solidification. Thus, the duration of the molten phase increases and the metallic substrate can be wetted adequately with a good adhesion.

Fig. 4 shows cross-sections of PA12 coatings consolidated by ytterbium and thulium fiber laser with different process parameters. Both ytterbium and thulium fiber laser are appropriate to process dense coatings. However, we found differences concerning the adhesion and the surface topography.

By using an ytterbium fiber laser (Fig. 4ac), the interface of the substrate and the PA12 layer shows, regardless of the substrate temperature, a form-fitting connection. After consolidation by the thulium fiber laser at a substrate temperature of 25 °C (Fig. 4b), delamination was observed at the interface between substrate and PA12 layer that indicates a weak adhesion. By heating the substrate to a temperature of 125 °C (Fig. 4d), a form fitting connection was observed, which is comparable with the interfaces in Fig. 4a and Fig. 4c. Hence, substrate temperature is a decisive factor that affects the adhesion between coating and substrate in a laser-based coating process.

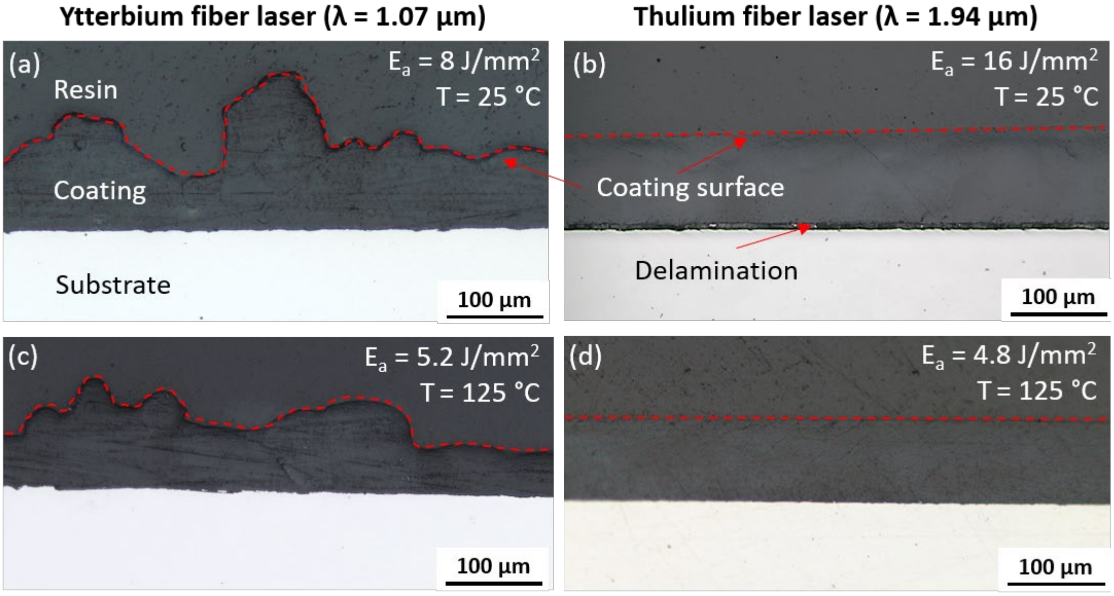

Fig. 4. Microscopic images of polished cross sections of PA12 coatings consolidated by ytterbium and thulium fiber laser.

Besides the evaluation of adhesion, it can be seen that the coatings consolidated by the ytterbium fiber laser (Fig. 4ac) exhibit an increased roughness in comparison to layers, which were consolidated by a thulium fiber laser (Fig. 4bd). A possible explanation for the observed behavior is a different consolidation mechanism by the ytterbium fiber laser. Due to the low absorption of laser light by PA12 at a wavelength of 1.07 µm, the thermal energy to melt the polymeric powder particles is delivered mainly by means of heat transfer from the metallic substrate to the polymer layer. The low thermal conductivity of PA12 particles (< 0.2 W/mK [17, 18]) causes a non-uniform temperature distribution between the upper and lower section of the PA12 layer. Therefore, it is assumed that the upper section of the layer is only partially melted.

In order to study the melting behavior of powder material and processed coatings, DSC analyses were conducted. Fig. 5 presents heating curves of raw PA12 powder and two coatings consolidated by both ytterbium and thulium fiber laser with identical process parameters (E_a = 8 J/mm^2, T = 25 °C). The curve of the PA12 powder depicts sharp single endothermic melting peaks at 189 °C for the first heating cycle and at 176 °C for the second heating cycle.

The coating generated by the ytterbium fiber laser presents three visible melting peaks. Peak 1 at 188 °C is associated with unmolten particle cores that have a higher melting temperature than surrounding spherulite crystalline structures (Peak 2 at 178 °C) [19]. It is described by previous authors [19] that these unmolten particle cores are caused by an incomplete melting of the PA12 powder due to insufficient heat absorption. At a temperature of 168 °C a third peak was observed. Wu et al. [20] concluded that an excessive energy input can lead to chain scission, which results in a lower melting point of the crystalline structures.

The layer fused by a thulium fiber laser exhibits a sharp single endothermic melting peak at 177 °C. This behavior is comparable to the second heating cycle of the PA12 powder which was subjected to complete melting. This observation indicates that the PA12 particles were fully melted by the thulium fiber laser [19]. It is reported by previous authors [21] that a higher amount of nonmolten regions reduces the mechanical properties. Due to the complete fusion of PA12 powder particles at an emitted wavelength of 1.94 µm, improved mechanical properties of the PA12 coatings can be expected. Under these conditions, the suitability of a thulium fiber laser for the consolidation of PA12 powder is confirmed. Furthermore, it is shown that the additional use of additives for improving the absorption of the polymer powder is not required.

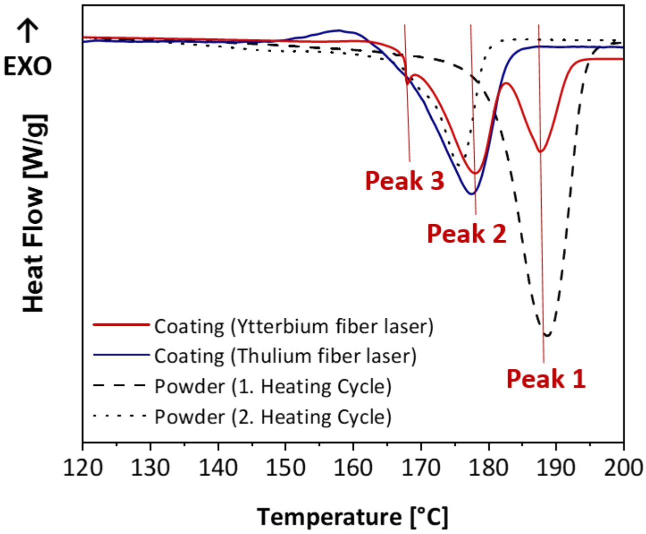

Fig. 5. DSC heating curves of PA12 powder (1. and 2. heating cycle) and coatings processed by both laser beam sources with identical parameters (E_a = 8 J/mm^2, T = 25 °C).

4. Summary and Conclusion

In the present study, two near-infrared laser beam sources, ytterbium (λ = 1.07 µm) and thulium fiber laser (λ = 1.94 µm), were systematically compared in a laser-based coating process to evaluate the influence of the emitted wavelengths on the resulting coating characteristics. The conclusions can be drawn as follows.

Both ytterbium and thulium fiber laser were appropriate to process dense coatings. The substrate temperature is a crucial factor that affects the wetting behavior and adhesion between coating and substrate in a laser-based coating process. Due to the high optical penetration depth in PA12 powder at a wavelength of 1.07 µm, the heating of the stainless steel substrate by the ytterbium fiber laser was adequate. By using a thulium fiber laser, an additional substrate heating at 125 °C with a hot plate improved the wetting and adhesion significantly.

An incomplete melting of the PA12 powder particles and increased roughness of layers consolidated by the ytterbium fiber laser is observed, which can be attributed to the low absorption at a wavelength of 1.07 µm. As the PA12 powder particles were fully melted by the thulium fiber laser, the suitability of this laser beam source for the consolidation of polymer powders is indicated.

The main focus of future works will comprise the adaption of the laser process parameters to improve the adhesion of coatings consolidated by a thulium fiber laser. In this context, a quantitative evaluation of the coating adhesion is required. Furthermore, investigations should be performed for other thermoplastic coating (PEEK) as well as substrate materials (titanium, ceramics).

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