

LASER MICROMACHINING OF BIO-ABSORBABLE POLYMERS: IMPACT OF THE LASER PROCESS PARAMETERS ON THE MACHINING THROUGHPUT AND QUALITY

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Abstract

Since their introduction in 1986, stents have transformed the treatment of coronary heart disease and other arterial occlusions. Today, millions of stents are implanted worldwide each year to treat various vascular and endovascular diseases caused by the narrowing or blockage of blood vessels. Nearly all commercially available stents are made from metals. These stents remain in the vessels permanently after implantation and are prone to cause serious medical complications in many cases. One potential solution to avoid such complications is to use stents made out of bio-absorbable materials. Bio-absorbable stents dissolve in the human body after serving their purpose. However, machining of bio-absorbable material is a challenging task. In this paper the influence of the laser process parameters on the efficiency and quality of the machining of bio-absorbable materials using High Q Spirit™ femtosecond laser system is presented.

Introduction

Ultrafast laser systems, with pulse duration in the femtosecond time range, have proven their potential in many material processing applications. The unique advantages of the ultrafast lasers i.e. high ablation efficiency and high accuracy of ablated structures on metal as well as on dielectric targets have been demonstrated in several studies [1-5]. Although the achieved processing quality meets industrial demands, processing speed needs to be improved in order to satisfy an economical industrial use [6, 7]. Ultrafast laser systems with high average power and repetition rate are required in order to overcome this problem. Additionally, ultrashort pulse lasers have to be industrially reliable with compact foot print. With the introduction of femtosecond laser systems such as the Spirit™ platform developed by High Q Lasers, micro-processing of solid targets using femtosecond laser have gained new perspective for industrial applications [8, 9].

Laser fusion cutting was employed in stent fabrication almost from the start, with great success. Early-generation stents were made from stainless steel and, at 2.5 - 4.0 mm diameter, were relatively large. Part geometries and features were relatively simple and feature tolerances could be $\pm 25 \mu\text{m}$ or more [10]. Laser cutting, implemented with nanosecond-duration pulsed infrared lasers, easily met the accuracy requirements for machining at this level.

However, thermal interactions of the nanosecond laser pulses with the metal generally result in non-optimal surface finish on metal parts: burring, melting, and re-cast are standard features of laser fusion cutting. In addition, heat deposition in the material results in a heat affected zone (HAZ) bordering the cut edges. Within the HAZ, material properties or composition are altered. These effects have meant that laser cutting technology could only be scaled to volume stent production with the development and refinement of several post-processing steps to remove rough and modified material edges. Cleaning, deburring, etching, and final polishing are routinely employed to bring the stent's surface properties to the level and consistency required for implantable devices. Some of these post-processing steps could be avoided by fabricating stents using ultra short pulse lasers.

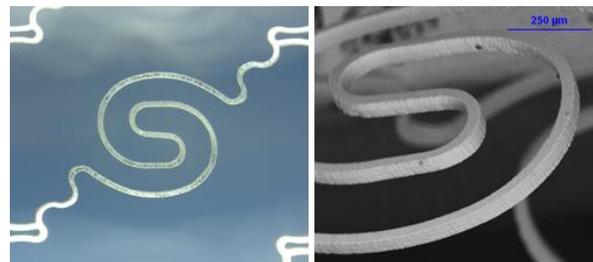


Figure 1. Micro-stent precision machined with Spirit™ 1040-4 fs laser. The material is Nitinol, with tube diameter and wall thickness of 4.25 mm and 45 μm , respectively. Strut width is 35 μm .

Figure 1 shows a Nitinol micro-stent machined by the Spirit™ laser. Key characteristics include tight machining tolerances, absence of HAZ, no heat-

induced distortion of the delicate lattice structure, and very clean cut edges.

Bio-absorbable materials are a very interesting class of compounds due to their ability to be absorbed by the human body over time [11]. The stents made out of bio-absorbable material can help avoid some of the medical complications caused by metal stents. The use of bio-absorbable polymers for production of bio-degradable stents has led to increasing attention to micromachining of bio-absorbable polymer. The choice of laser for production of stents depends on the type of material and cutting details. Because of the low melting temperature (usually below 100 C°) of bio-absorbable polymers any heat load to the surrounding areas during laser processing should be minimized. Therefore, using ultrafast laser pulses for micromachining of bio-absorbable polymers is highly promising due to the non-thermal nature of laser-material coupling and the possibility of structuring very small micron scale features.

In this work the influence of the processing conditions on the efficiency and quality of laser processing of commonly used bio-absorbable poly-L-lactic acid (PLLA) polymer has been studied. Particularly the influence of pulse duration on the ablation process was investigated. Based on the parameter study, dross- and melt-free cut of stent structures machined by femtosecond Spirit™ laser in PLLA is demonstrated.

Experimental Setup and Materials

Laser source



Figure 2. New Spirit™ 1040-8-SHG femtosecond laser developed by High Q Laser and Spectra-Physics.

During the past decade, it has become possible to produce ultrashort laser pulses ($\tau < 10^{-11}$ s) using laser materials which can be directly pumped by laser diode. The most promising and advanced laser materials for femtosecond generation are ytterbium-doped crystals (e.g. Yb:YAG, Yb:KGW, Yb:KYW) [7]. Besides direct diode pumping, a more reliable and robust laser

system can be achieved by using semiconductor saturable absorber mirrors (SESAM) for passive mode-locking and by intracavity pulse stretching design.

The two near-IR laser systems Spirit™ and picoREGEN™ from High Q Laser GmbH were used in this work. Spirit™ laser system (see Figure 2) is based on a Yb-doped chirped pulse regenerative amplifier [12, 13]. Spirit™ has flexible repetition rates up to 1 MHz and average power of 4 and 8 W at 520 and 1040 nm respectively. Maximum pulse energy of 40 μ J with pulse duration of < 400 fs could be reached at 200 kHz. picoREGEN™ system has the average power of 30W at 1064 nm and a repetition rate up to 1 MHz. The maximum pulse energy is 200 μ J with pulse duration of 10 ps. Both lasers have a very good beam quality factor $M^2 < 1.2$. The intensity of the laser beam was adjusted with an integrated fast (300 kHz) signal attenuator. The laser beam could be expanded up to 16x magnification by a variable beam expander. The lasers spot size was found from the relationship between the laser fluence F and the diameter D of a crater produced by a single laser pulse [14].

Material

The material used in this experiment was a natural PLLA ribbon of 80 μ m thickness. The sample has been kindly provided by Zeus Industrial Products, Inc.

Results and Discussion

Optimization of ablation rate

For laser machining, throughput is an important factor to consider when comparing results achieved using different laser systems or technologies. Also, quality is an important factor and it often competes with speed. Depending on the application, the correct balance between speed and quality must be determined. To determine the removal rate for PLLA in our study we have used the method described by Schille et al. [15].

For the parameter study squares of 2x2 mm were filled with parallel rectangular crossed lines (see Figure 3). The machining outcome was evaluated by the depth of the ablated structures and the heat load i.e. melt formations during the laser processing. To find out optimized processing conditions the influence of laser fluence, repetition rate, lateral pulse distance and pulse duration was investigated. The parameter study was performed using 350 fs and 10 ps laser pulses at wavelengths of 520 and 532 nm, respectively. Repetition rates of 100 kHz and 500 kHz for both the

femtosecond and picosecond lasers were applied in the study.

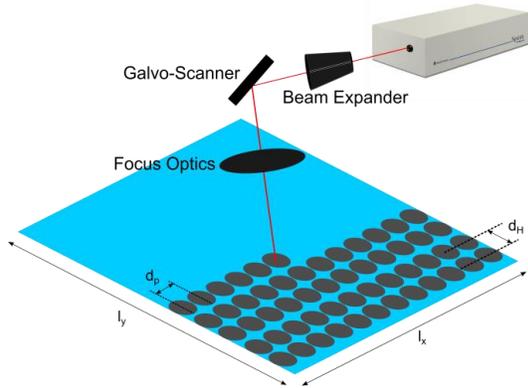
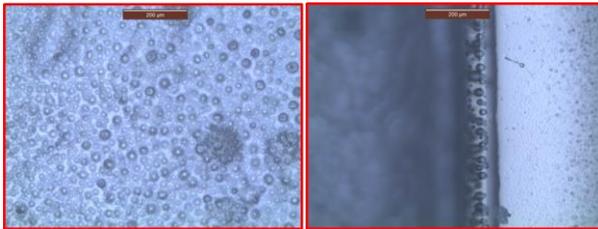


Figure 3 Schematic of experimental setup. Here d_p is the lateral pulse distance, d_h is hatch distance.

Optimal ablation rate was observed at $d_p=d_h=8\mu\text{m}$ for spot radius of ca. $w_0=10\mu\text{m}$. On the other hand, the machining quality, i.e. melt formation, strongly depends on the process strategy and the pulse duration.

Thermal Laser Machining



Athermal Laser Machining

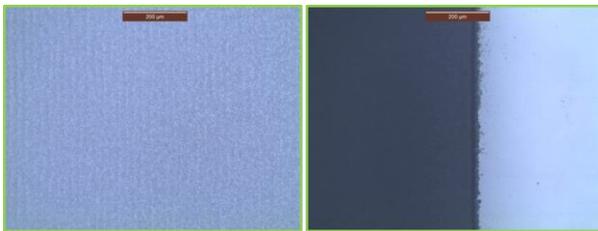


Figure 4. Optical microscope images of bottom surface and edge of test structures ablated with ultrashort pulse laser in PLLA polymer obtained upon thermal (upper row) and athermal (lower row) laser machining regime.

Figure 4 shows microscope images of bottom and edge of test structures ablated in PLLA polymer obtained in thermal (upper row) and athermal (lower row) laser machining regime. Thermal laser ablation leads to strong melting, followed by re-solidification of the polymer material in the machining region. The melting

of the PLLA changes the mechanical and chemical properties of the polymer and therefore also decreases the precision of the laser machining; these are all undesired effects in stents production. In contrast to thermal ablation, athermal machining provides melt free features with nearly no heat affected zone (HAZ).

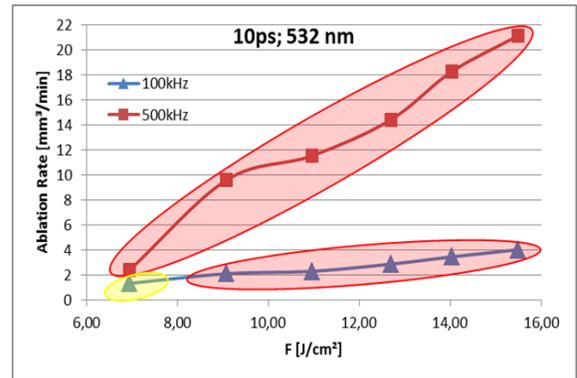
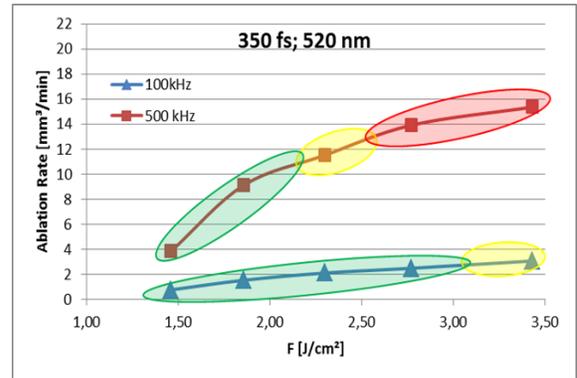


Figure 5. Ablation rate for a PLLA polymer as a function of the applied peak fluence for 350 fs (top) and 10 ps (bottom) laser pulses at wavelength of 520 and 532 nm, respectively. The experimental conditions at which athermal/thermal machining is observed are marked in green and red zone. The transition zone between athermal/thermal machining is marked in yellow.

The dependence of the removal rate for the femtosecond and picosecond laser pulses on the laser fluence at repetition rate of 100 and 500 kHz is shown in Fig. 5. For the femtosecond laser pulses the ablation study was performed with peak fluence between 1.5 and 3.5 J/cm^2 . Because of higher ablation threshold fluence of 5 J/cm^2 for 10 ps laser pulses in comparison to the threshold fluence of 2 J/cm^2 for 350 fs pulses, much higher peak fluences were necessary for micro-machining of PLLA with the picosecond laser i.e. between 6.0 and 16.0 J/cm^2 . The ablation rate increases with increasing of applied laser fluence for both laser pulse widths. Maximum ablation rate of up to ca. 16 mm^3/min was achieved using 350 fs laser pulses,

corresponding to an ablation efficiency of 4.2 mm³/min/W. Although a higher maximum ablation rate of up to 22 mm³/min was observed for ps pulses, the ablation efficiency was lower by as much as a factor of 2 compared to fs laser pulses (2.1 mm³/min/W).

However, more important than the overall maximum ablation rate is the maximum rate at which athermal machining occurs. As can be seen in Figure 5, when using 350 fs laser pulses at 520 nm, athermal ablation rates in PLLA polymer of up to 12 mm³/min can be achieved, while the maximum ablation rate decreases by as much as a factor of 6 to a value < 2 mm³/min when the pulse duration is increased from 350 fs to 10 ps. Heat accumulation is considered as main effect influencing the melt formation. Although the main part of the pulse energy absorbed by the material goes into plasma generation, bond breaking and also some gets carried away by the ablated particles, a significant fraction of energy remains in the irradiated region. The results presented in Figure 5 emphasize the importance of the correct choice of laser repetition rate and pulse duration for micro machining of PLLA. For high repetition rate the time between successive pulses is not long enough for the heat to diffuse out of the focal volume. Consequently, the energy from successive pulses accumulates and the temperature of the material increases from pulse to pulse. Local heating of the PLLA polymer leads to melt formation upon laser processing. On the other hand, melting effects can be strongly reduced by decreasing pulse duration from 10 ps to 350 fs. Therefore the pulse duration is the key parameter when choosing a proper laser system for laser micro-machining of bio-absorbable polymers.

Micromachining of PLLA bio-absorbable polymer

The femtosecond laser (Spirit™) at wavelength of 520 nm was used to cut a stent structure in 80 μm thick PLLA ribbon. Figure 6 shows the optical microscope and SEM images of the laser processed PLLA ribbon. A high speed, multi-pass processing with a scanning galvanometer was used to produce the stent structures. The PLLA ribbon of 80 μm thickness can be cut with the processing speed of several mm/s with low thermal effects and high resolution (struts width < 100 μm) by using femtosecond laser pulses at 520 nm. No melting zone, no microcracks, and no heat-induced distortion are detectable.

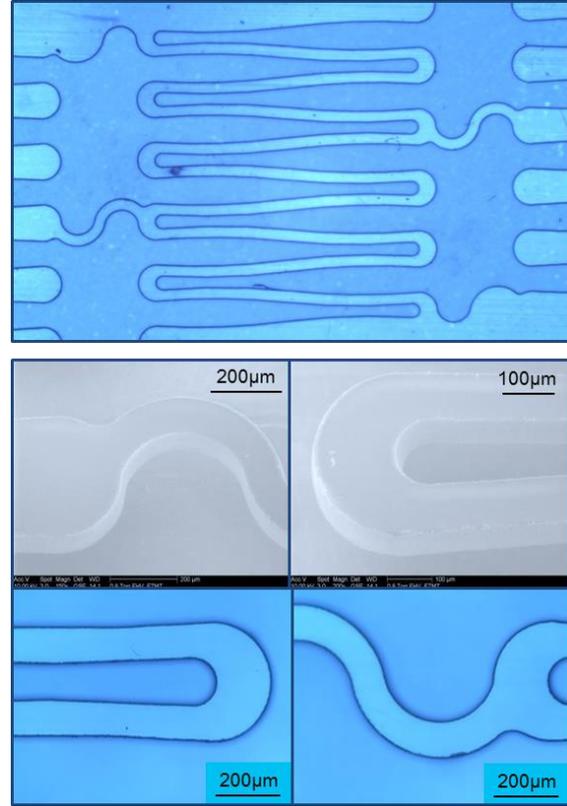


Figure 6. Stent structures machined by femtosecond laser pulses in PLLA. The material is 80 μm thick and struts are 100 μm wide.

Conclusions

Bio-absorbable materials are becoming increasingly popular for manufacturing of stents. Laser micro-machining of bio-absorbable PLLA polymer was examined using femtosecond and picosecond laser pulses. It has been shown that a maximum ablation rate for PLLA polymer of up to 12 mm³/min can be achieved in the athermal machining regime by using 350 fs laser pulses at 520 nm. This is a factor of six higher than the maximum ablation rate observed for 10 ps laser pulses. From this point of view, shorter pulses (ca. 350 fs) are very promising for laser micro-machining of bio-absorbable polymers with respect to reduced melt production and heat affected zones.

The femtosecond laser at wavelength of 520 nm were used to demonstrate feasibility of laser cut of PLLA materials. The preliminary results show that a compact, robust and reliable femtosecond laser, such as Spirit™ is a good choice for machining heat sensitive bio-absorbable materials such as PLLA.

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Meet the Author(s)

Victor Matylitsky received his Ph.D. degree in 2004 in Physical Chemistry from the Goethe-University Frankfurt/Main, Germany. Since 2010 he is employed with High Q Laser GmbH, Austria. Currently Dr. Matylitsky fills the position of business development manager at High Q Laser GmbH. He is author or coauthor of over 20 articles in scientific journals and presentations at international conferences.

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