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Removal of doped poly(methylmetacrylate) from tungsten and titanium substrates by femto- and nanosecond laser cleaning

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Abstract

The influence of different laser pulse lengths on the removal of a polymer layer from metal substrates was investigated. As model systems, doped poly(methylmetacrylate) (PMMA) on titanium and tungsten substrates were selected.

The ablation threshold and irradiation spot morphology of titanium and tungsten were compared for femtosecond (fs) and nanosecond (ns) laser irradiation and different pulse numbers. Nanosecond laser treatment resulted in a non-homogeneous surface morphology for both titanium and tungsten substrates. Femtosecond irradiation of tungsten revealed a homogeneous ablation spot with little changes in the surface morphology. For titanium, the formation of columnar structures within the irradiation spot was observed.

Two different dopant concentrations were used for PMMA to achieve an equal linear absorption coefficient for the femto- and nanosecond laser wavelengths of 790 and 1064 nm. The best results were achieved for the removal of doped PMMA by femtosecond laser irradiation, where only a minimal modification of the metal surface was detected. In the case of nanosecond laser exposure, a pronounced change of the structure was observed, suggesting that damage-free cleaning of the selected metal may only be possible using femtosecond laser pulses. Different experimental parameters, such as laser fluence, pulse repetition rate and sample speed were also investigated to optimize the cleaning quality of doped PMMA from tungsten substrates with femtosecond laser pulses.

Keywords: Poly(methylmetacrylate); Laser treatment; Tungsten; Titanium; Femtosecond

1. Introduction

The removal of a polymer layer from any substrate plays an important role in areas, such as laser cleaning [1] and laser micromachining [2,3]. The ablation of polymers with ultraviolet, nanosecond (ns) lasers has been studied for the last 20 years [4]. The scope of this work was to investigate the influence of the pulse length on the removal of a polymer layer from metal substrates. As a model polymer, poly(methylmetacrylate) (PMMA) was selected, due to its well-known properties [4]. It was demonstrated that PMMA doped with an IR-dye can be structured in the near IR range with femtosecond (fs) and nanosecond laser pulses, while pure PMMA could only be processed with fs laser irradiation in the near IR range [5]. For doped PMMA, the ablation threshold fluence (F_{th}) for ns laser irradiation is about two times higher than for fs laser treatment. For pure PMMA, the ns laser fluence had to be at least 10 times higher and still no clean ablation could be achieved.

Titanium was selected because of its reactive surface and detailed data [6–9] for femto- and nanosecond laser ablation and laser surface modification, due to its utilization in biomedical applications [10]. Tungsten was chosen as reference material with a less reactive surface, but similar properties, e.g. hardness, temperature resistance, but with a higher melting point than titanium and the formation of a stable oxide layer. First of all, ablation experiments on the pure metal substrates were performed. Their ablation thresholds and possible surface modifications for nano- and femtosecond laser irradiation were

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tested in order to apply them as models for the comparison of the different pulse lengths. One boundary condition was that the ablation threshold fluence should be higher than for doped PMMA [5].

2. Experimental

A nanosecond Nd:YAG laser (Brilliant BW from Quantel) and a femtosecond Ti:sapphire laser (Femtopower Compact Pro from Femtolasers) were used for all ablation experiments under ambient conditions.

The ns laser emits a 6 ns pulse at 1064 nm with a repetition rate of 10 Hz. It has a Super-Gaussian beam profile with some hotspots in the beam intensity profile. The pulse energy was measured with a pyroelectric detector QE50 and a SoloPe Display unit (GenTec).

The fs laser provides 790 nm central-wavelength pulses with a bandwidth-limited duration of 30 fs at a repetition rate of 1 kHz and a Gaussian beam profile. The pulse duration was determined by means of a dispersion-minimized autocorrelator (Femtolasers). The laser pulse energies were varied using a rotatable half-wave plate in front of the compressor unit of the Ti:sapphire laser. The Brewster prisms of the compressor acted as analyzer. The pulse energy was measured employing a pyroelectric detector J25LP series with a display unit 3Sigma (Molectron).

In both cases, the sample was mounted on a x–y–z translation stage with the surface perpendicular to the incident laser beam. The laser beams were focused to a diameter of approximately 200 μm on the sample surface. Different pulse numbers from 1 to 1000 were applied to the sample.

The laser-ablated area was analyzed with an optical microscope (SZH10, Olympus) and a surface profilometer (Dektak 8000, Sloan) for the ns laser experiments. To determine the ablation threshold fluence, it was defined, that ablation only takes place, when a clear removal of material was observed with both methods.

For the femtosecond experiments, the measurements of the diameter D of the laser-damaged area were performed with an optical microscope (Eclipse L200, Nikon). F_{th} was identified by a plot of D^2 versus the maximum laser fluence for a fixed pulse duration τ and number of pulses per site N [11].

A scanning electron microscope (SEM; Cambridge Stereoscan 180, acceleration voltage 10–20 kV) was used for a detailed characterization of morphological changes of the laser-irradiated areas.

The titanium samples (99.5%, from Alfa Aesar, USA) with a thickness of 0.25 mm and tungsten foil with a thickness of 0.15 mm (99.95%, from Goodfellows, UK) have been used as delivered. The poly(methylmetacrylate) (Aldrich) was dissolved in a solvent mixture (50 wt% methyl ethyl ketone, 15 wt% n-butylacetate, 15 wt% cyclohexanone and 20 wt% 4-methyl-2-pentanone) by stirring for 12 h to obtain a 10 wt% polymer solution. An IR-dye (IR165) was dispersed in the same solvent and added to the polymer solution by stirring for 30 min. The metal–polymer composite samples were produced by spincoating the polymer–dye solution onto the metal substrates at 1000 rpm for 30 s on a spincoater™ (Model P6700 Series, from SCS). The films were heated to 40 °C to remove remaining solvent after drying for 24 h under ambient conditions.

The linear absorption coefficients were measured with an UV–vis spectrometer (Carry 500, Varian) from polymer films spincoated on quartz substrates.

The IR-dye concentration was chosen to obtain a linear absorption coefficient of 750 cm^{-1} for the doped polymer at the irradiation wavelengths of 1064 nm (1% IR-dye) and 790 nm (5% IR-dye).

3. Results and discussion

The ablation threshold fluence for tungsten decreases from 0.6 J cm^{-2} for a single pulse with 30 fs duration to 0.16 J cm^{-2} after irradiation with 1000 pulses (see Fig. 1(■)).

For fluences of about 0.03 J cm^{-2}, a modification was visible as a ''white'' circular area of 90 μm diameter in the center of the ablation spot (Fig. 2a). The confinement of the surface modification to the center of the ablation spot is caused by the Gaussian beam profile, where the laser energy is decreasing with increasing radius. The modification does not significantly change the surface topography and is caused by damaging or removing the native oxide layer by the fs laser pulses.

The removal of doped PMMA from a tungsten surface should be possible, as F_{th} for tungsten is higher than F_{th} for doped PMMA ($F_{th\ PMMA}$) (from ref. [5]). The ''white'' modification will always be present, as it occurs at fluences below $F_{th\ PMMA}$ and is already formed with the first laser pulse (Fig. 1(●)).

Initially, the fs irradiation of uncoated titanium resulted in the formation of a ''white'' area (shown in Fig. 3a) and at higher fluences in a columnar surface modification (Fig. 3b). The ''white'' modification is caused by damaging or removing the oxide layer on the titanium by the fs laser pulse. The columnar structure is still observed after 1000 pulses at an even lower fluence of 0.6 J cm^{-2}.

Material removal of titanium was observed after multiple pulses on the same ablation spot (see Fig. 4(■)). Titanium reveals a strong incubation behavior as already reported by Mannion et al. [12]. The ablation threshold fluence is higher for

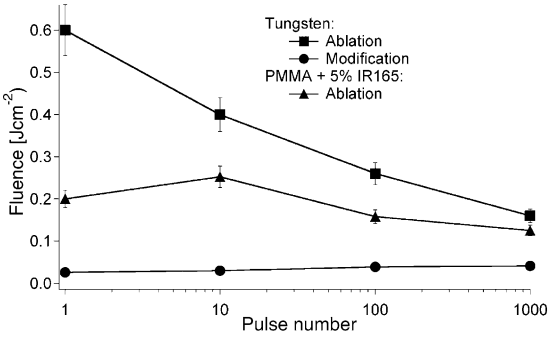

Fig. 1. Ablation threshold fluence for tungsten (■) and doped PMMA (▲) [5] vs. pulse number for fs laser irradiation. Also the onset fluence of the surface modification for tungsten is shown (●).

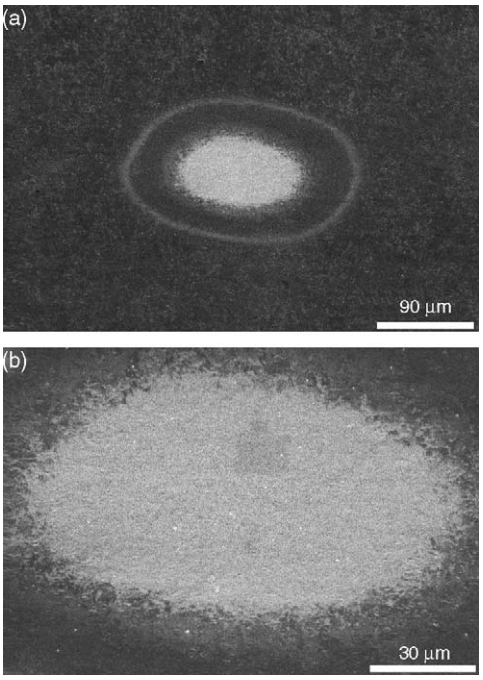

Fig. 2. Scanning electron microscope (SEM) picture of tungsten after fs laser treatment with 100 pulses and 1.6 J cm^{-2} at 1 kHz as overview (a) and detailed view of the "white" surface modification (b).

titanium than for IR-dye-doped PMMA (Fig. 4(▲)) [5], which should allow a removal of the doped PMMA from a titanium substrate.

Due to columnar structure formation on titanium after multiple pulses, a clean removal of a PMMA layer from a titanium substrate without physical modification is not possible. Therefore, tungsten was selected as the more promising substrate to investigate the influence of the laser pulse duration on the removal of doped PMMA.

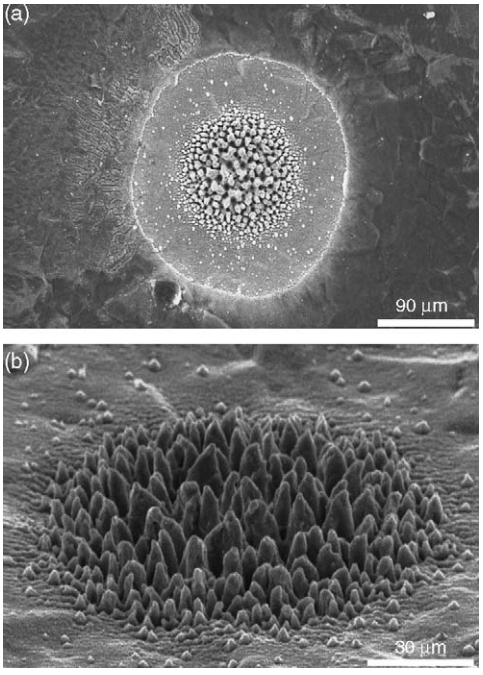

Fig. 3. SEM picture of titanium after fs laser irradiation with 100 pulses and 1.7 J cm^{-2} at 1 kHz as overview (a) and detailed view of the columnar surface modification (b).

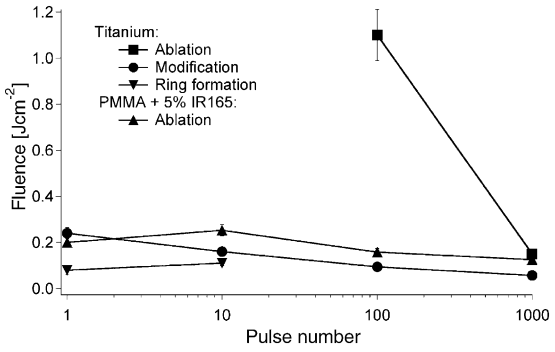

Fig. 4. Ablation threshold fluence for titanium (■) and doped PMMA (▲) [5] vs. pulse number for fs laser exposure. The onset fluence of the surface modification (●) and the ring formation (▼) for titanium are also shown.

The ns laser irradiation at 1064 nm wavelength of tungsten and titanium result both in surface modifications. The irradiation of titanium with a fluence of 1.01 J cm^{-2} (1000 pulses) yielded a modification of the surrounding material by thermal effects. These are visible as a dark zone around the ablation spot (Fig. 5a). A crown-like structure as described by György et al. [6,7] was not observed probably due to the inhomogeneous beam profile of the Nd:YAG laser.

In the case of tungsten, the formation of a rough modification in the center of the ablation spot was found (Fig. 5b). These structures were previously described by

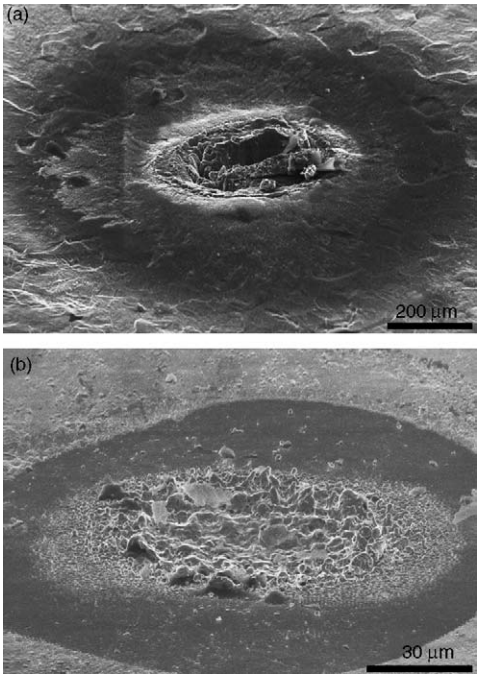

Fig. 5. Scanning electron microscope (SEM) picture of titanium after ns laser irradiation with 1000 pulses and 1 J cm^{-2} at 10 Hz (a) and SEM picture of the ablation spot of tungsten after ns laser irradiation with 100 pulses and 1.3 J cm^{-2} at 10 Hz (b).

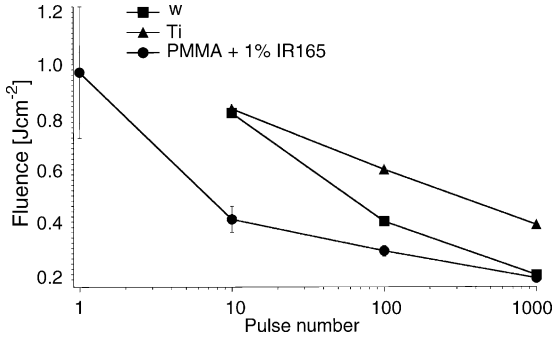

Fig. 6. Ablation threshold fluence for tungsten (■), titanium (▲) and doped PMMA (●) [5] vs. pulse number for ns laser treatment.

Kawakami and Ozawa [13,14] as ''microcones'' formed upon irradiation of tungsten with nanosecond laser pulses.

For both metals, pronounced incubation was observed (Fig. 6(■ and ▲)) [15]. As the ablation threshold fluence for doped PMMA (Fig. 6(●)) [5] is lower than for titanium and tungsten at all pulse numbers, the removal of a doped PMMA layer from both, titanium and tungsten, should be possible. For the further experiments, i.e. the removal of a doped polymer layer from a metal substrate, tungsten was used, as it showed the better results in the fs laser ablation experiments.

A SEM image of the ablation spot of a doped PMMA film on a tungsten substrate is depicted in Fig. 7a for femtosecond laser irradiation and in Fig. 8a for ns laser exposure. A clean removal of the doped PMMA is possible at a fluence of 1.87 J cm^{-2} employing the fs laser. Even though the irradiation fluence was three times higher than the single shot tungsten ablation threshold, no physical damage to the tungsten is observed. A reason for this finding is the absorption of the main part of the pulse energy in the polymer during the ablation process. The ''white'' modification, which was also found on uncoated tungsten is also visible, but the surface morphology seems to be unchanged. In the outer regions of the laser beam, the laser fluence is not high enough (due to the Gaussian beam profile) to ablate the polymer. The same phenomenon can be observed in Fig. 7b, where the fluence of 0.45 J cm^{-2} was not sufficient to completely remove the polymer from the substrate and some molten and solidified ''fibers'' remain in the ablation spot. The fluence of 0.45 J cm^{-2} is in the explicit working range for the removal of doped PMMA from tungsten, as it is higher than the F_{th} for doped PMMA, but still lower than F_{th} for tungsten at the given pulse number.

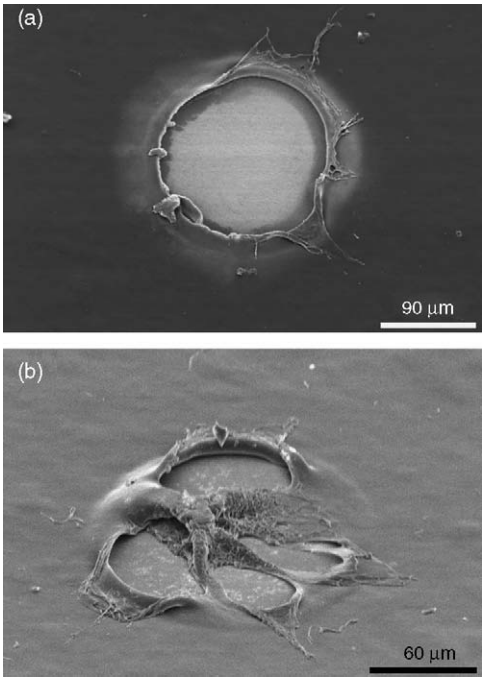

Fig. 7. SEM picture of the ablation spot of doped PMMA on tungsten after fs laser irradiation with two pulses 1.87 J cm^{-2} (a) and 0.45 J cm^{-2} (b).

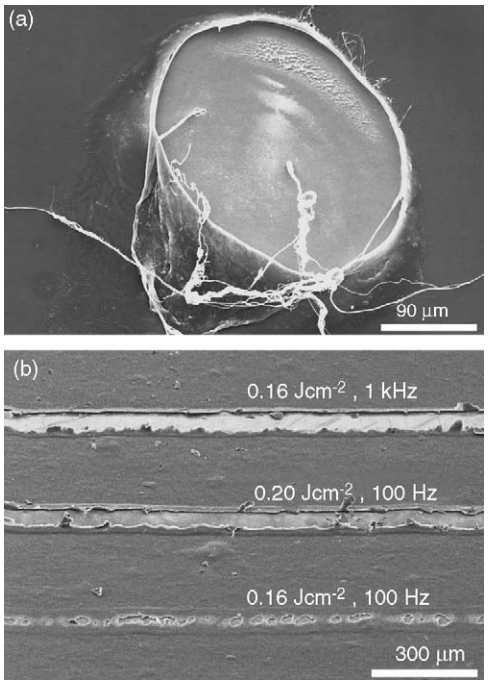

Fig. 8. SEM picture of the ablation spot of doped PMMA on tungsten after ns laser irradiation with 100 pulses and 1.95 J cm^{-2} (a) and in (b) the influence of the pulse repetition rate and the irradiation fluence for fs laser irradiation of doped PMMA on tungsten is shown.

A SEM image of a ns ablation spot is shown in Fig. 8a. A clear damage to the tungsten surface is visible as white ripples in the upper half of the ablation spot. Thermal effects are also detected in the lower left corner of the image. The doped PMMA seems to be not completely removed from the surface, but merely flipped out of the ablation spot. In and outside the ablation crater, ''nanofibers'' as reported by Weisbuch et al. [16,17] are also observed. A clean removal of a doped PMMA film from tungsten is therefore not possible with a ns laser at 1064 nm wavelength.

The influence of the pulse repetition rate and the irradiation fluence on the results of fs laser processing of doped PMMA on tungsten is shown in Fig. 8b. The three lines in the SEM image were fabricated with a (sample) scanning speed of 200 µm s^{-1}. The irradiation fluence generating the top and the bottom line was 0.16 and 0.2 J cm^{-2} for the middle line. The bottom and middle lines were produced with a pulse repetition rate of

100 Hz, the top line with 1 kHz. Only for the upper lines, a comparatively clean removal of the doped PMMA can be achieved.

4. Conclusions

The influence of different laser pulse lengths on the removal of a polymer layer from metal substrates was investigated. A Nd:YAG (1064 nm, 6 ns) and a Ti:sapphire laser (790 nm, 30 fs) were employed as irradiation sources. Two different dopant concentrations were used for PMMA to achieve an equal linear absorption coefficient for the femto- and nanosecond laser wavelengths (790 and 1064 nm). The fs laser irradiation of uncoated titanium revealed that a clean removal of PMMA would be impossible due to a columnar surface modification of the titanium. The best results were achieved for the removal of doped PMMA from a tungsten substrate by femtosecond laser treatment, where only a small modification of the metal surface was detected. In the case of nanosecond laser irradiation, a pronounced change of the substrate structure was observed, suggesting that damage-free cleaning of the selected metal is impossible.

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