Microstructure formation on titanium oxide (TiO$_2$) coatings by femtosecond laser irradiation

Toshiaki OSUGA,* Masayuki FUJITA* and Yo ICHIKAWA**

Research Center for Frontier Medical Engineering, Chiba University, Yayoi, Image, Chiba 263-8522, Japan
*Institute for Laser Technology, 2–6 Yamadaoka, Suita, Osaka 565–0871, Japan
**Department of Systems Engineering, Nagoya Institute of Technology, Gokiso, Showa, Nagoya 466–8555, Japan

Depressions were generated on a titanium oxide coating of 100 nm thickness by irradiation with a femtosecond laser with a pulse width of 100 fs when the laser output was below 10 mW. When the number of pulses was five or less, irregularities were found to be generated on the coating surface in the area corresponding to the periphery of the pulses, where the laser intensity is low, while titanium oxide was removed from the area corresponding to the center of the pulses. The formation of microstructures is expected on the surface of titanium oxide coatings by setting the output of a femtosecond laser in the periphery of the pulses to below a certain value.

Fig. 1. (a) SEM image and (b) PCM image of depression formed by irradiating titanium oxide coating with femtosecond laser. The laser output is 5 mW and the number of pulses is 300.

1. Introduction

In femtosecond laser micromachining, highly reproducible results can be obtained by repeatedly carrying out preliminary experiments while changing various parameters such as laser intensity, the number of pulses, the numerical aperture of focal lenses, the position of focal points, the direction of polarization, and the incident angle. A femtosecond laser can form highly useful microstructures peculiar to a substance, such as interference fringes, within an appropriate range of parameters. Many examples of femtosecond laser micromachining have been reported thus far. It is possible to form microstructures with femtosecond laser micromachining, and the surface characteristics of titanium oxide coatings are expected to be improved by controlling the laser intensity below a certain value, and the surface morphological changes of titanium oxide coatings are induced above a threshold laser intensity. Therefore, we have carried out fundamental experiments on the micromachining of titanium oxide coatings using a femtosecond laser, respectively. The output of the femtosecond laser was 100 mW. The femtosecond laser system used for irradiating the titanium oxide coating was a commercial Ti:sapphire laser (Hurricane, Spectra Physics). The fundamental wavelength was 800 nm and the full width at half maximum of the laser pulse width was 100 fs. The final output energy was about 0.8 mJ per pulse with a repetition rate of 1 kHz. The laser pulse energy was controlled by an energy attenuator composed of a thin-film polarizer and a half-wave plate. The laser pulse was focused on the TiO$_2$ coating by a fused silica plano-convex lens whose focal length was 100 mm.

Scanning electron microscopy (SEM) (VE-8800, Keyence) and phase contrast microscopy (PCM) (ODEO-2222, Iponacology) were used to observe the titanium oxide coating. Figures 1(a) and 1(b) show a SEM image and a PCM image of a depression formed by vertically irradiating a titanium oxide coating with a femtosecond laser, respectively. The output of the femtosecond laser is 5 mW, the number of pulses is 300, and an electric field is applied parallel to the coating. There are gentle undulations at the bottom of the depression formed by irradiation with the femtosecond laser, which are clearer in the PCM image than in the SEM image.
in the SEM image [Fig. 1(a)], although the resolution of the former image is inferior. Moreover, the irregularities and fringes on the titanium oxide coating deposited by evaporation before laser irradiation can be clearly identified by PCM.

3. Effects of laser output and number of pulses on the center and periphery of pulses

A femtosecond laser enables surface machining without damage due to thermal conduction because the energy of each pulse is limited. The number of pulses should thus be increased to apply a higher energy. Figure 2 shows PCM images of a depression formed by irradiating a titanium oxide coating with a 10 mW femtosecond laser for different numbers of pulses [(a) 1, (b) 10, (c) 300, and (d) 1000]. As shown in Fig. 2(c), the diameter of the circle inscribed in the depression (shown by a dashed circle) is defined as the depression diameter. Figure 3 shows the relationship between the depression diameter and the number of pulses when the titanium oxide coating is irradiated with a 10 mW femtosecond laser. Figure 2 reveals that the depression diameter increases with increasing number of pulses of the femtosecond laser. In Fig. 3, the abscissa indicates the number of pulses and the ordinate indicates the depression diameter. Figure 3 shows that although the depression diameter increases with increasing number of pulses, the rate of increase decreases when the number of pulses exceeds 10.

Figure 4 shows phase contrast microscopy images of depressions formed by irradiating a titanium oxide coating with five pulses of the femtosecond laser for different laser outputs [(a) 6 mW, (b) 8 mW, and (c) 10 mW]. Figure 5 shows the relationship between the laser output with five pulses (abscissa) and the depression diameter (ordinate). The depression diameter increases with increasing output of the femtosecond laser. It is expected from Figs. 2–5 that titanium oxide is removed from the area corresponding to the center of the pulses, where the laser intensity is high, and when the number of pulses exceeds 10.

4. Formation of irregularities on titanium oxide coatings in the periphery of pulses

It was found that the electrical resistance of titanium oxide coatings was reduced by irradiation with a femtosecond laser when the laser intensity was set below a certain value, and the surface morphological changes of titanium oxide coatings were induced above a threshold laser intensity, leading to the electrical resistance of the titanium oxide coatings being maintained. The existence of the region with suitable intensity bounded by the lower and upper thresholds was revealed in order to improve the function of titanium oxide coatings by femtosecond laser irradiation.3)

Figure 6(a) shows an SEM image of a titanium oxide coating with a thickness of 100 nm deposited on a glass substrate by evaporation. The titanium oxide coating has undulations with a height of approximately 100 nm, which is almost the same as the
coating thickness. Figures 6(b)–6(e) show enlarged SEM images of the top, left, bottom and right edges (corresponding to the edges of the pulses) of the depression of the titanium oxide coating shown in Fig. 1(a), respectively. Although titanium oxide is removed from the area corresponding to the center of the pulses, where the laser intensity is high, irregularities are generated on the coating in the area corresponding to the periphery of the pulses, where the laser intensity is low. Figure 7 shows PCM images of depressions formed by irradiating a titanium oxide coating with a single pulse of a femtosecond laser for different laser outputs [(a) 7 mW, (b) 8 mW, (c) 9 mW]. When the number of pulses is five or less, a double-ring structure is observed at the periphery of the depressions on the titanium oxide coatings. As seen from the PCM images in Fig. 7, irregularities can be formed in the area corresponding to the periphery of the pulse on the surface of a titanium oxide coating, where the laser intensity is low.

5. Conclusions

Micromachining characteristics were examined by irradiating titanium oxide coatings with a femtosecond laser while varying the laser output between 5 and 10 mW. Titanium oxide is removed from the area corresponding to the center of the pulses, where the laser intensity is high, when the number of pulses exceeds 10, whereas irregularities are generated on the coating surface in the area corresponding to the periphery of the pulses, where the laser intensity is low, when the number of pulses is five or less. Microstructures can be formed on the surface of titanium oxide coatings by setting the output of a femtosecond laser in the periphery of pulses to below a certain value, thus giving the coatings a functional surface.

References

1) Y. Izawa, S. Tokita, M. Fujita, M. Nakai, T. Norimatsu and Y. Izawa, J. Appl. Phys., 105, 064909 (2009).
2) Y. Ichikawa, K. Setsune, S. Kawashima and K. Kugimiya, Jpn. J. Appl. Phys. Part 2, 40, L1054–L1057 (2001).
3) M. Tsukamoto, N. Abe, Y. Soga, M. Yoshida, H. Nakano, M. Fujita and J. Akedo, Appl. Phys., 93, 193–196 (2008).
4) Y. Ohko, T. Tatsuma, T. Fuji, K. Naoi, C. Niwa, Y. Kubota and A. Fujishima, Nat. Mater., 2, 29–31 (2003).
5) T. Osuga, S. Kitagawa, H. Sakamoto and T. Tsuda, Jpn. J. Appl. Phys. Part 1, 39, 4143–4147 (2000).