Microstructures formation on titanium plate by femtosecond laser ablation

M Tsukamoto 1, T Kayahara 2, H Nakano 3, M Hashida 4, M Katto 5, M Fujita 6, M Tanaka 1 and N Abe 1

1Joining and Welding Research Institute, Osaka University, Ibaraki, Osaka 567-0047, Japan
2Graduate School of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565-0871, Japan
3School of Science and Engineering, Kinki University, Higashi-Osaka, Osaka 577-8502, Japan
4Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan
5Cooperative Research Center, Miyazaki University, Gakuen Kibanadai Nishi, Miyazaki 889-2192, Japan
6Institute for laser technology, Suita, Osaka 565-0871, Japan
E-mail: tukamoto@jwri.osaka-u.ac.jp

Abstract. Microstructure formation of cone-like protrusions (CLP) on titanium (Ti) plate by the femtosecond laser ablation is reported. The number of the laser pulses to irradiate the Ti plate was varied from 10 to 230 at average laser fluence of 0.75 J/cm 2 per pulse on the plate. The onset of CLP creation was observed with exposure of 70 pulses, and yielding CLP with a height from the bottom of the irradiation area of about 9 μm after 230 pulses. The formation process of the CLP was found to depend on the laser produced periodic microstructures oriented parallel to the direction of the laser polarization vector.

1. Introduction
Titanium (Ti) is a useful and important material in many industrial applications because of low density, strong tensile strength, high melting temperature and good chemical stability. In the field of clinical orthopedics, the Ti or hydroxyapatite-coated Ti is presently used as a biomaterial. The tribological, frictional, flow and hydrophilic properties, bioactivity, biocompatibility and adhesion of the film to the Ti depend on surface morphology of the Ti.

Femtosecond laser ablation offers precision material processing, such as drilling, cutting and grooving into metals [1]. The conventional method using the nanosecond laser gives a heat-affected zone to the metal workpiece [2, 3]. With such long pulses, laser plume, including molten metal, vapor and plasmas is generated from the laser irradiation spot, extending the heat-affected zone and causing morphological change of metal surface. The heat-affected zone and the morphological change limit the precision of metal microstructure formation. It has been reported that the femtosecond laser provides considerable advantages for hole formation in comparison with nanosecond lasers [2, 3]. The advantages are based on very rapid creation of vapor and plasma phase, negligible heat conduction, and the absence of a liquid phase. In addition to these advantages, periodic nanostructures are often produced in the femtosecond laser irradiated area [4-10]. The periodic nanostructures (grooves) lie perpendicular to the laser electric field polarization vector. Thus, the grating vector of the periodic nanostructures are parallel to the projection of the electric field vector E 0 of the laser onto the material surface. The periodic nanostructures formed by the femtosecond laser ablation were similar to results observed for long pulse ablation [11-14]. It was postulated that such gratings were produced by an
intensity modulation which arose from the interaction of the incident and scattered wave with a surface wave created from any modulation in the surface. The observed period was $d_s = \frac{\lambda_L}{\cos \theta_i}$ with s-polarization and $d_p = \frac{\lambda_L}{1 \pm \sin \theta_i}$ with p-polarization, where $\lambda_L$ and $\theta_i$ were the laser wavelength and the incident angle of the laser, respectively [4]. When the incident angle of the laser is 0 degree, the period was shown by $d_s = d_p = \lambda_L$.

In this paper, we report the formation of parallel periodic microstructures together with cone-like protrusions (CLP), in the regime over the laser fluence required for the formation of the periodic nanostructures. Generation mechanisms of parallel periodic microstructures might be related to the periodic nanostructures formation mechanisms.

2. Experimental condition
A commercial femtosecond Ti : sapphire laser system was employed in our experiments, which was based on the chirped pulse amplification technique. Wavelength, pulse length, repetition rate and beam diameter of the laser were 800 nm, 100 fs, 1 kHz and approximately 4 mm, respectively. Pulse duration was measured by a background free second order autocorrelator. An attenuator to reduce the output energy of the laser composed of polarizing filters. The laser beam was focused on the Ti plate surface at normal incidence ($\theta_i = 0$) by a lens with a focal length of 100 mm, installed in a processing chamber. Thickness and surface roughness (Ra) of the Ti plate were 500 $\mu$m and 0.05 $\mu$m, respectively. The Ti plate’s position was controlled with XYZ stages connected to a computer. The processing chamber was pumped down with a rotary pump to produce vacuum conditions. A collimator and a mechanical shutter were installed on the laser beam axis. Number of laser pulses for irradiation was varied by controlling the opening time of the mechanical shutter. Laser beam profile on the Ti plate surface was measured with a monitoring system. The beam diameter of the laser was changed from 4 mm to 2 mm with a collimator to improve the beam profile and provide a Gaussian laser beam profile on the Ti plate surface. The Gaussian laser beam took the shape of a circular with diameter of 50 $\mu$m at $1/e^2$ in intensity. In the first experiment, 10 and 230 pulses of the laser were irradiated on the Ti plates at the average laser fluence of 0.25, 0.75 and 1.5 J/cm$^2$, respectively. In the second experiment, laser fluence was fixed at 0.75 J/cm$^2$ and number of the laser pulse was varied in the range of 25 to 190. These experiments were performed under vacuum (13.3 pa). Microstructures produced by the laser irradiation were observed with an optical microscope, a laser microscope profilometer and a scanning electron microscope (SEM).

3. Experimental results and discussion
Figure 1 (a) and 1 (b) show SEM images of the irradiation area at the laser fluence of 0.75 J/cm$^2$ for 230 laser pulses at low and high magnification, respectively. Depth from the Ti plate surface to the bottom of the irradiation area was about 11 $\mu$m. As figures 1 (a) and 1 (b) show, cone-like protrusions (CLP) were produced. Bottom widths of the CLP on X (horizontal) and Y (vertical) axes in figure 1(b) were 8.4 $\mu$m and 6.3 $\mu$m, respectively. X and Y axes were perpendicular and parallel to the laser polarization vector, respectively. Height of the CLP from the bottom of the irradiation area was about 9 $\mu$m. Surface of the CLP had microstructures as shown in figure 1 (b). For 0.25 and 1.5 J/cm$^2$, the CLP were not created by 230 laser pulse irradiation.

SEM images of Ti plate surface irradiated with the femtosecond laser for 0.25, 0.75 and 1.5 J/cm$^2$ are shown in figure 2 (a), 2 (c) and 2 (e), respectively. High magnification images of figure 2 (a), 2 (c) and 2 (e), the centre region of the irradiation area, are shown in Figs. 2 (b), 2 (d) and 2 (f), respectively. As figure 2 (b) shows, the periodic nanostructures were formed in the irradiation area for 0.25 J/cm$^2$. The period of the periodic nanostructures was about 700 nm, which was slightly less than the period predicted by $d_s = d_p = \lambda_L$, 800 nm, at $\theta_i = 0$ degrees. For 0.75 J/cm$^2$, there were two regions, outer and centre regions, in the irradiation area as shown in figure 2 (c). In the outer
region of the irradiation area, periodic nanostructures were formed. As figures 2 (c) and 2 (d) show, in the centre area with a radius of about 20 μm, another periodic microstructure was observed in addition to the periodic nanostructures. The grooves of this new periodic microstructure lie parallel to the laser polarization vector (parallel periodic microstructures) and have a period in the range of 1.5 to 3.0 μm, which is 2.0 – 3.7 times longer than the laser wavelength. For 1.50 J/cm², figure 2 (e) shows three periodic microstructures creation. The parallel periodic microstructures might be formed by an intensity modulation, which arose from the interaction of the laser and strongly scattered wave from the periodic nanostructures.

Microstructures produced in the centre region of the irradiation area at 0.75 J/cm² for 25, 50, 70, 90, 110, 130 and 190 pulses are shown in figures 3 (a), 3 (c), 3 (e), 3 (g), 3 (i), 3 (k) and 3 (m), respectively, with high magnification images shown in figures 3 (b), 3 (d), 3 (f), 3 (h), 3 (j), 3 (l) and 3 (n), respectively. As figures 3 (a) and 3 (b) show, parallel periodic microstructures were clearly formed with the smaller periodic nanostructures superimposed on the parallel periodic microstructures. For 50 pulses, figures 3 (c) and 3 (d) show the periodic nanostructures were not observed on the larger profile of the parallel periodic microstructures. Small spheres (dots) were locally generated on the ridges as indicated with an arrow (d1) in figure 3 (d). For 70 pulses, figure 3 (e) indicates the etching of the ridges between the dots. This etching defined the initial CLP formation as indicated with an arrow (e1) in figure 3 (e). At higher magnification, the arrow (f1) in figure 3 (f) suggests that a pair of dots on neighbouring ridges were joined across a groove. For 90 pulses, the arrow (h1) in figure 3 (h) suggests even stronger bridging between dots across a similar groove in the underlying periodic structure. The parallel periodic microstructures were still generated even with the bridging structures as shown in figures 3 (g) and 3 (h), although larger period is observed as compared with the period shown in figure 3 (c). For 110 pulses, the size of a dot indicated with an arrow (j1) in figure 3 (j) was similar to that indicated with an arrow (d1) in figure 3 (d). However, the size of the CLP indicated with an arrow (i1) in figure 3 (i) was bigger than that indicated with an arrow (e1) in figure 3 (e). For 130 pulses, the parallel periodic structures were broken and less ordered as shown in figure 3 (k). As figure 3 (l) shows, the bridging of the CLP caused this disordering of the parallel periodic structures. For 190 pulses, the bonding of the CLP was promoted by the laser ablation as shown.
in figure 3 (m) and, as figure 3 (n) shows, the CLP were similar to that formed with 230 pulses as shown in figure 1 (b). Etching of the ridges between the dots such as shown in figures 3(e), 3(g) and 3(i) suggested that intensity modulations were generated on the hills at a direction parallel to the laser polarization vector.

The base widths of the CLP are plotted in figure 4 as a function of number of laser pulses. Circles and triangles indicate horizontal and vertical widths, which were on axes perpendicular and parallel to the laser polarization vector, respectively. As figure 4 shows, the size of the CLP increased as the number of laser pulses increased. In the range of 25 to 70 pulses, the CLP was generated by the etching of the hills between the dots and the bridging of the dots, as shown in figures 3(e) and 3(f). The size increase of the CLP in the range of 90 to 110 was caused by such increased bridging that joined dots across the grooves as shown in figures. 3(g), 3(h), 3(i) and 3(j). In the range of 130 to 190 pulses, the horizontal base width became longer than vertical base width. As figures 3(k) and 3(l) suggest, the bridging formed between CLPs on neighbouring ridges. By this bonding, the CLP had asymmetric bases with horizontal bases wider than the vertical base. To form such bridges between neighbouring CLPs, forces perpendicular to the laser polarization vector were required. These forces might be generated by the laser produced plume ejected from the valleys of the parallel periodic microstructures.

4. Conclusion
Cone-like protrusions were produced by femtosecond laser ablation of Ti using laser fluence of 0.75 J/cm². Formation of the CLP was induced by creation of periodic microstructures oriented parallel to the laser polarization vector. The initial CLP were formed by the etching of the ridges of the parallel periodic microstructures in the region between two nearby dots. The size of the CLP was increased by the bridging structures formed between neighbour CLP structures.

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