The Effect of Crystal Structure on Fabrication of Fine Periodic Surface Structures with Short Pulsed Laser

Shuhei KODAMA¹, a *, Shinya SUZUKI², b, Akihiro SHIBATA², c, Keita SHIMADA¹, d, Masayoshi MIZUTANI¹, e and Tsunemoto KURIYAGAWA¹, f

¹Tohoku University, 6-6-01 Aramaki-Aza-Aoba, Aoba-ku, Sendai, Miyagi 980-8579, JAPAN
²Dexerials Corporation, 3-4-1 Sakuragi, Tagajo-shi, Miyagi 985-0842, Japan

a shuhei.kodama.r6@dc.tohoku.ac.jp, b shinya.suzuki@dexerials.com, c Akihiro.Shibata@dexerials.com, d shimada@m.tohoku.ac.jp, e mizutani@m.tohoku.ac.jp, f tkuri@m.tohoku.ac.jp

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Abstract. In recent years, nanostructures have been demanded for industry and medical services to produce functions such as reduction of friction, control of wettability and enhancement of biological affinity. Ultrashort pulsed lasers have been applied to meet these demands and have been actively studied both experimentally and theoretically about phenomena and principles. In this study, to clarify the phenomenon of fabrication of nanostructures and to apply to industry, experiments were conducted on SUS304 by a short pulsed laser that has longer pulse duration, more cost-effective and higher stability than ultrashort pulsed lasers. The results confirmed that a uniform fine periodic structure was not fabricated on the whole irradiated surface and crystal grain boundaries appeared since SUS304 is an alloy composed of Fe, Cr and Ni, and the short pulsed laser has low power and long pulse duration inducing the thermal effect compared to ultrashort pulsed laser. Our research group clarified the effect of crystal structure on fabricating fine periodic surface structures with short pulsed laser.

Introduction

Reduction of energy loss and a safer and more secure society are highly demanded since there are many environmental issues such as global warming and electric power shortage. With this in mind, more interest has been shown in the fabrication of fine structures on material surfaces capable of imparting such functional properties as the reduction of energy loss by reducing friction of automobile sliding parts [1], the improvement of safety of medical care due to enhancement of biological affinity of implants [2] and the improvement of efficiency of solar light power generation by reducing reflection [3]. For use in the fabrication of functional surfaces, ultraprecision cutting, ultrasonic vibration assisted machining and photolithography techniques are often employed, however there are some disadvantages: the long processing time, the complicated work process and the difficult processing with large surface areas. We therefore have chosen the fabrication of fine periodic structures with ultrashort pulsed lasers, hereinafter it is defined as less-than-one-picosecond pulse duration laser, since this method creates nanostructures in self-organizing ways by laser irradiation alone [4]. This method can simplify the working processes, shorten the processing time, and significantly reduce energy loss. It will contribute to mitigating the pace of global warming, and therefore, will help make society safer and more secure.

Figure 1 shows the processing model when an ultrashort pulsed laser is irradiated on the surface of metal. Firstly, laser irradiations induce surface plasmons causing a deviation of the electric field. Secondly, ionized atoms cause Coulomb explosions in the large electric field. Finally, ablation occurs in a heat distribution generated on the surface. As mentioned above, fine periodic surface structures are fabricated in self-organizing ways by laser irradiation in this way.
The pulse length of lasers is a determinant factor to fabricate nanostructures since optical phenomena mainly occur when it is shorter than the collisional relaxation time of the object material [5], so ultrashort pulsed lasers are suitable for fabrication of nanostructures. However, longer pulsed lasers are favorable from the aspects of cost-efficiency of equipment and stability of irradiation. Thus, in this study, a short pulsed laser, whose pulse length is 20 ps, is used to fabricate nanostructures on a stainless steel alloy and to examine effects of a picosecond-long pulse length on processing.

In this paper, the result of consideration is reported that distorted periodic structures and no structure are fabricated on the irradiated surface of the alloy.

**Experimental Method**

A picosecond pulse laser oscillator (EKSPLA, PL 2250-50P20) was applied in this experiment. Figure 2 and Table 1 show the setup and the laser irradiation conditions, respectively. The work material was stainless steel alloy SUS304, which is equivalent to AISI304 and a widely-used material, which was 15 mm thick and mirror-finished. In a trial in the experiment, laser with a Gaussian beam profile was irradiated at a fixed point on the sample under the conditions where the irradiation number was \( n \) and energy density was \( E_d \), and the irradiated point, \( n \) and \( E_d \) were varied in each trial.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Pulse duration (ps)</th>
<th>Frequency (Hz)</th>
<th>( n )</th>
<th>( E_d ) (J/cm(^2))</th>
<th>Workpiece</th>
</tr>
</thead>
<tbody>
<tr>
<td>1064</td>
<td>20</td>
<td>50</td>
<td>10, 200</td>
<td>0.03, 0.05</td>
<td>SUS304</td>
</tr>
</tbody>
</table>

Fig. 2 Setup of laser processing
Results and Remarks

Irradiated areas. The irradiated areas with low $n$ and $E_d$ were observed. Figure 3 illustrate the scanning electron microscope (SEM) images of the irradiated areas where $n = 10$, $E_d = 0.03$ and 0.05 J/cm$^2$, expressing the surface topographies considered as crystal grain boundaries (CGBs).

CGBs have lower melting point than crystal grains due to impurities [6] and high absorption from disturbed atomic arrangement [7]. Tsukamoto et al. [8] reported that CGB appeared after nanosecond laser irradiation on SUS304 since CGBs melted with low melting point and high absorption, rose to the top surface due to expansion of surrounding crystal grains and became elevated portion after cooling and solidifying. However, as shown in Fig. 4 [8], the result of CGBs appearing from Tsukamoto et al. is confirmed that appearance is different from the results of our experiment. Therefore, the electron backscattered diffraction pattern (EBSD) analysis is performed to confirm if the appeared structure is caused by the crystal orientation.

Figure 5 show the EBSD images of surfaces of Fig. 3. Compared Fig. 3 with Fig. 5, it is confirmed that appeared structures after laser irradiation accord with crystal structures and it is possible to visualize crystal structure of material surface by short pulsed laser with low $n$ and $E_d$. Nevertheless, while a nanosecond laser visualizes CGBs in the previous research, the short pulsed laser expresses crystal structures not CGBs, this reason which is considered later.

Fabrication of fine periodic structures. In order to confirm effects of crystal structures on fabrication of nanostructures with the short pulsed laser, the laser was irradiated on the surface that was preliminarily analyzed with EBSD. Firstly, the laser was irradiated with $n = 10$ and $E_d = 0.03$ J/cm$^2$ to decide the irradiation point, whose SEM and EBSD images are shown in Fig. 6. Next, the laser with $n = 200$ and $E_d = 0.05$ J/cm$^2$ was irradiated on the decided point. Fig. 7 is the SEM image of the result. As shown in this figure, fabricated structures vary with crystal orientation planes. Magnified images of the faces (001), (101) and (111) are shown in Fig. 8, which confirms that pitch length of nanostructures on (001) are shorter than those on (101) and (111) whose pitch lengths are similar to the laser wavelength, and the structure direction on (101) was not perpendicular to the polarization unlike cases of (001) and (111).
Effects of crystal structures on the pitch length of nanostructures. The pitch length of periodic structures is calculated by fast Fourier transformation applied to the luminance profiles of SEM images. While the face (001) had the pitch length of about 500 nm that is half the laser wavelength, the face (101) and (111) had the pitch length of about 900 nm that is 0.85 times the laser wavelength.

The reason why the pitch length is 0.5 – 0.85 times the laser wavelength is explained by the parametric decay by Sakabe et al. [9]: an incident light divides into a surface plasma wave and a scattered wave after changing surface roughness with laser irradiation, a surface plasma wave interferes with the incident light and nanostructures are fabricated with the pitch length of the wavelength of the surface plasma. The wavelength of a surface plasma wave attributes laser power and electron density as expressed by

\[ \omega_L - \omega_{SP} = ck_{SP} - ck_L \]  
\[ \omega_L = ck_L \]  
\[ \omega_{SP}^2 = ck_{SP}^2 - \frac{1}{2} \frac{\omega_P^2}{\omega_P^2 - \frac{1}{4} \omega_P^4} \]

where subscripts L and SP express the incident light and the surface plasmon, respectively, \( \omega \) is the frequency, \( c \) is the velocity of light in vacuum, \( k \) is the wave number and \( \omega_P \) is the electron plasma frequency. From these equations, the wavelength of a surface plasma wave is half laser wavelength with low laser power and electron density, for example, \( \omega_P/\sqrt{2} \approx 0 \), on the other hand, that widens to 0.85 times the laser wavelength with an increase of laser power and electron density, for example, \( \omega_P/\sqrt{2} \approx \omega_L \). It is considered that the pitch length of nanostructures depends on the electron density of each crystal orientation faces.

Expansion of the surface of each crystal orientation face. Aforementioned previous study suggest that crystal structures are actualized by different expansions of crystal grains and CGBs due to the difference of melting points. However, the actualizing way in this study was different from that in previous research. Ito et al. reported that heat conductivity depends on crystal orientation, which increases in the order of (100), (110) and (111) making the electric discharge machining speed fast in the order of (111), (110) and (100) [10]. The research gives an expectation that visualizing crystal
structu"es is attributed to the difference of expansion rates and heat conductivities among crystal orientations and (111) has the largest expansion. The difference of expansions according to crystal orientations was confirmed by analyzing the three-dimensional topographies with a laser microscope. Figure 9 is the laser microscope (KEYENCE, VR-3000) image of the irradiated surface before structure fabrication and it also shows that (001) has larger expansion than (101) and (111), which is different from the expectation.

The laser microscope image of the irradiated surfaces after structures fabrication is indicated in Fig. 10, which shows that (001) has the largest expansion coefficient in the same as before. From the result, visualizing crystal structures with the short pulsed laser is due to the different expansion coefficient according to crystal orientations, while the expansion coefficient is different from the expectation.

![Fig. 9 Laser microscope image of the irradiated surface with \( n = 10, E_d = 0.05 \text{ J/cm}^2 \)](image)

![Fig. 10 Laser microscope image of the irradiated surface with \( n = 200, E_d = 0.05 \text{ J/cm}^2 \)](image)

**Effects of crystal structures on fabrication of nanostructures.** It is considered from atomic structures that expansion coefficients are different from the expectation and fabricated nanostructures vary with the crystal orientation. Compared (001) with (111), while the atomic density of (111) surface is larger, that of (001) in a depth direction is bigger, making lattice vibration of (001) easier to transfer in a depth direction. When the ultrashort pulsed laser is irradiated on the faces (100) and (111) of Si, while (100) surface is melted deeper due to large atomic density in a depth direction, evaporation of (111) surface is larger since atoms is easy to move due to the layered structure in a depth direction [11]. A (100) surface has larger heat conductivity as mentioned above, on the other hand, the heat conductivity of (111) in a depth direction is larger [11]. It is considered that expansion of (001) surface is larger since lattice vibration is easy to transform due to low heat conductivity and high atomic density in a depth direction.

Though the pitch length of nanostructures is mainly similar to the laser wavelength, the pitch length of (001) is half the laser wavelength, which is explained by the parametric decay due to low laser power, low electron density and high heat conductivity of surface.

The atomic structure of the face (101) has the periodic structure and the periodic gap. It is considered that the nanostructures on (101) surface are not perpendicular to polarization since coulomb explosion is easy to occur between adjacent atoms and the periodic atomic structure is not perpendicular to polarization.

In conclusion, to fabricate uniformly nanostructures on the whole surface, it is necessary to increase laser energy density or use the sample of a uniform crystal structure, for example, single crystal materials and amorphous materials.
Conclusions

The effect of crystal structures on fabrication of nanostructures with the short pulsed laser was clarified using a SUS304 alloy in this research. Based on the results of experiments and further discussion, the following conclusions were drawn:

1. It is possible to visualize crystal structures by irradiation of the short pulsed laser with less irradiation number and energy density on the mirror surface of SUS304.

2. Fabricated structures vary with crystal orientation as below:
   - (001): Nanostructures have the pitch length of half the laser wavelength and high aspect ratio due to low heat conductivity and atomic density, and large atomic density in a depth direction.
   - (101): Nanostructures whose pitch length of 0.85 times the laser wavelength is not perpendicular to polarization since the periodic atomic structure is not perpendicular to polarization.
   - (111): The pitch length is 0.85 times the laser wavelength perpendicular to polarization.

3. It is effective to uniformly fabricate nanostructures on the whole surface by increasing energy density and using the material of uniform crystal structure such as single crystal materials and amorphous materials.

References


