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Femtosecond Laser-induced Ripple Structures on Magnesium

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Abstract:

Two types of periodic surface structures including micro-ripples and nano-ripples were observed on magnesium after femtosecond laser irradiation, and color effect was reported by scanning single laser beam over a large area at near damage threshold fluence. Optical reflectance measurement revealed that the color effect was mainly attributed to the nano-ripples as diffraction gratings, and intensity of the color was affected by morphology of the micro-ripples. AFM and SEM images showed that orientation of the micro-ripples was parallel to laser polarization and period of the micro-ripples increased with scanning numbers, while orientation of the nano-ripples was perpendicular to laser polarization and period of the nano-ripples kept constant as laser sub-wavelength with the increasing scanning numbers. These results suggested that formation of the micro-ripples was due to the combined effect of initial surface roughness and near-field interference, while formation of the nano-ripples was caused by the near-field interference between incident light and surface plasmons being excited in the air and metal interface. Potential application of such effect was further proposed.

PACS: 81.16.c; 42.70.Hj; 61.82.Bg; 68.47.De; 78.66.Bz

1. Introduction

Laser-induced coloration at material surfaces provides an alternative approach to many promising applications, such as decorations, product identification, biocompatible implants and photocatalysts. In picosecond and femtosecond ranges of laser pulse duration, structured color caused by ripples acting as

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diffraction grating has attracted much attention in current years [1-5].

Ripples, also called as periodic surface structures, have been widely reported on different materials, and their periods are smaller than wavelength of incident laser beam. It is widely accepted that these sub-wavelength ripples are as a result of interaction between the incident light and surface scattering wave [6-10]. However, the nature of ripples is still quite controversially discussed in the literature. An increasing number of experimental results show that non-uniform free electron density due to surface roughness plays a significant role for ripples formation [11-13]. In certain situations, such as on metals and around specific scattering centers, the classical scattering model also should be modified to take into account the effect of surface plasmons (SPs) [8, 12, 13].

Mg alloys are important engineering materials, and they are widely used in automobile, communication and aerospace industries due to low density and high specific strength. In order to improve their poor surface-related properties, it has been demonstrated that laser surface treatment can be used to further extend the applications of Mg alloys [14, 15].

In this study, we firstly report both micron size ripples and nano scale ripples on surface of Mg irradiated by femtosecond laser in atmospheric environment. Structure color caused by ripples is also demonstrated by scanning single laser beam over a large area. Special attention was paid to understand mechanism of ripples formation during laser-material interaction.

2. Experimental procedures

The material studied was high purity magnesium (99.99 wt. %). The dimensions of specimens were 20 mm by 30 mm by 3 mm, and they were ground with progressively finer SiC paper (180, 400, 800, 1200, 2400 and 4000 grit), polished using 1.0 μm and 0.5 μm liquid diamond suspensions, cleaned with alcohol, and then irradiated with laser at atmospheric pressure and room temperature in air.

A Ti:Sapphire femtosecond laser (Clark-MXR, CPA-2010) with wavelength of 775 nm was used under following parameters: single pulse energy 20 μJ, frequency 1000 Hz, and pulse duration 150 fs. The number of laser pulses was varied from 1 to 1000 at single spot. Hatched mode in the controlling software was used for large area scanning, and the laser-irradiated area was set as a square of 20×20 mm2. The laser scan number was varied from 1 to 100. The polarization of the incident laser radiation is horizontal. The sample surface was irradiated under normal incidence by focused linearly polarized laser.

After laser irradiation, optical reflection of the irradiated area was measured using Ocean optics DT-Mini-2 system and Spectrometer Operating Software. All specimens were exposed to white light source via an adapter. Reflected light from the surface was guided to HR4000 High-Resolution spectrometer for characterization. Each reflection measuring test was repeated three times. Before each test, environment factor including fluorescent light and natural light were excluded as reference. Microstructural feature of the irradiated area was examined by a scanning electron microscope (SEM, JEOL 5600 LV), and surface topography was inspected by an atomic force microscope (AFM).

3. Results and discussion

3.1 Color effect

Figure 1 displays color effect on Mg surface after femtosecond laser irradiation. The irradiated surface exhibits different colors, mainly including blue, green, orange and some yellow color in the transition region between green and orange, at different viewing angles by naked eyes. It is well known that surface structures aligned in arrays can separate mixed "white" light into light of different wavelengths due to diffraction grating behavior. Moreover, variations in periods of these structures result in an iridescent effect, as seen in peacock feathers, soap bubbles, films of oil, and mother of pearl, because the reflected color depends upon the viewing angle. Correspondingly, we suggest that iridescent effect has been achieved at Mg surface after femtosecond laser scanning.

The iridescent effect takes place at all irradiated surfaces after laser scanning at different times from 10 to 100. When the number of laser scan time is above 50, the brightness of the color by naked eyes was reduced significantly with the increasing number. No color but randomly spots or small patterns were observed when the number is below 10. Such iridescent effect was also observed on the irradiated surface of AZ31B alloy and AZ91D alloy following similar laser processing. Here we focus on analyzing Mg due to its predominant microstructure and property.

Typical optical reflectance of Mg surfaces before and after laser irradiation is showed in Figure 2. Before laser irradiation, the reflectance of polished surface was nearly 100% in the visible spectral range from 475 nm to 750 nm. After laser irradiation, three dominate peaks appeared in the spectra at 485 nm, 540 nm and 610 nm, and the corresponding wavelength of colors were blue, green and orange, respectively. Small and wide peak was also observed between 570 nm and 600 nm, and this belonged to yellow color wavelength range. This is in agreement with the observation of Figure 1. It should be noted that the spectra pattern for all irradiated surfaces was the same, but the reflectance decreased to 10%-70% when laser scan times increased from 10 to 100, compared that of non-irradiated surface. The reduction of reflectance at large laser scan times was possibly due to light trapping at rough surface when laser irradiation time was long.

3.2 Morphology evolution

In order to study effect of surface morphology of laser-irradiated Mg on the optical reflectance, SEM investigation of morphological evolution at Mg surface with progressive laser parameters was performed, as shown in Fig. 3 and Fig. 4. When number of laser scan was 10, nano-sized ripples were produced on top of micro-size ripples, as shown in Fig. 3(a). Orientation of micron ripples was found to be parallel to the laser polarization direction, while orientation of nano ripples was perpendicular to the laser polarization direction. Fig. 3(a) also shows that the micron ripples were irregular and the space was around 1-3 μm, while the nano ripples had regular shape and the period was in the range of 480 nm to 520 nm, which was appreciably less than the wavelength of incident light 775 nm. In addition, the nano ripples were found to be formed above the micron ripples. When number of laser scans increased to 30 and 50, micro-ripples expanded and micron size clusters structure was developed inside individual micro-ripple. The orientation of nano-ripples kept the same as pervious direction, but the period decreased slightly (Figs. 3(b)-(c)). Compared to that of Fig. 3(a) and Fig. 3(b), Fig. 3(c) reveals that features of micro-ripples and nano-ripples become unclear, which is likely attributed to melting effect at high fluence. For laser scan time at 100, more cluster structures occurred, resulting in rough surface at the irradiated area. Moreover, both micro-ripples and nano-ripples disappeared gradually.

Development of micro-ripples and nano-ripples at single spot on laser-irradiated Mg surface with progressive number of laser pulses is further investigated in Fig. 4. Fig. 4(a) reveals random nanostructures produced after 50 laser pulses. When number of laser pulses increased to 200, random nanostructures grew and coalesced into initial feature of micro-ripples and nano-ripples, as shown in Fig. 4(b). The size and the orientation of two ripples were the same as laser scans in Figure 3. Fig. 4(c) shows that laser irradiated area expanded at 300 laser pulses, and the feature of micro-ripples and nano-ripples developed correspondingly. Morphology of the nano ripples was more obvious than the previous structure in Fig. 4(b). When number of laser pulses further increased to 500, the irradiated area expanded significantly, as shown in Fig. 4(d). The nano ripples were clear and straight above the micron ripples, while the micron ripples became smooth and the spacing increased slightly. Again, the size and the orientation of two ripples did not change. Moreover, cluster structures were observed in the peripheral area of the irradiated surface. The nano ripples were less obvious above the cluster structures, while the spacing of micron ripples decreased. As number of laser pulses increased larger than 500, surface features became coarse and poorly defined.

Further investigation of surface topography of micro-ripples and nano-ripples development was carried out using AFM, and the results were shown in Fig. 5 and Fig. 6. Fig. 5(a) and Fig. 6(a) display that the surface has irregular rough topography due to dotlike nanoscale protrusions when the number of laser pulses is small. With the increasing number of laser pulses, these nano protrusions gathered together and grew as coarse and intermediate fine ripples at the surface, as shown in Fig. 5(b) and Fig. 6(b). At large number of laser pulses, the intermediate fine ripples developed into clear nano ripples among the coarse ripples, as shown in Fig. 5(c)-(d) and Fig. 6(c)-(d). The period of nano ripples was estimated as 500 nm, which was in agreement with the SEM results. Surface roughness Ra of measured area was measured as 27.9 nm, 89.6 nm, 107.6 nm, and 119.2 nm, respectively, which was much rougher than that of non-irradiated polished surface 7.6 nm.

Period evolution of micron and nano ripples with the increasing number of laser pulses from 50 to 500 were measured and listed in Table 1. The period of micron ripples is larger than laser wavelength, and it increases with the number of laser pulses significantly. This indicates that surface roughness plays a key role in formation of micron ripples, since the roughness increases with the number of laser pulses. However, the period of nano ripples does not change with the increasing number of laser pulses.

3.3 Formation of micro-ripples and nano-ripples

When Mg surface was initially irradiated by femtosecond laser, rapid ejection of species including electrons, ions or atoms was excited strongly and the excited electrons transferred energy to metal lattice by electron-phonon coupling [17-18]. Meanwhile, plasma including the ejection of species was formed above the irradiated surface. At initial few laser pulses, nano protrusions were produced randomly, which were mainly attributed to laser-ejected species, plasma confinement and material re-deposition within several picoseconds during rapid cooling condensation and plume collapse process [19-21].

With the increasing number of laser pulses, expansion of high energy caused scattering of ejected Mg species, leading to the nano protrusions expanded and occupied in larger irradiated area, as show in Fig. 4(a). Meanwhile, surface plasmons (SPs), both localized and propagating along the surface, would be excited by coupling the incident light to such-nano protrusions [12, 22, 23]. The nano protrusions grew, and the developed nanostructures further excited the SPs when number of laser pulses further increased. Subsequently, the SPs interfered with the incident laser light wave. It has been suggested that the nano-ripples can be explained as the near-field interference between incident light field and the electric field of plasma wave due to the orientation of the nano-ripples being perpendicular to the direction of laser polarization [20-23]. Moreover, combined effect of initial surface roughness and interference of laser and SPs play an important role in forming micro-ripples, According to one dimensional heat conduction model [24], maximum surface temperature of Mg was calculated as 935 ˚C in this work, which is above its melting point as 650 ˚C [14]. Mg surface was heat treated and molted due to high thermal conductivity (418 W/mK at 20 ˚C) [14]. Surface tension of the liquid leads to surface curling, and highly localized heating as well as large thermal gradients caused development of severe strain fields in the peripheral area of the irradiated surface [24, 25], finally results in the formation of micro-ripples and isolated melt (cluster structures) on the surface (Figs. 4-6).

Based on classical scattering model [13], period of parallel-oriented ripples can be obtained as $\Lambda=\lambda/\cos\theta$, and period of perpendicular-oriented ripples can be obtained as $\Lambda=\lambda/(1\pm\sin\theta)$. However, the measured period of micron and nano ripples in Table 1 shows substantial deviations from the classical relationship. This is mainly because surface waves of metals are in the form of SPs that propagate along the metal surface and decay exponentially away from the dielectric/metal interface [26-29]. For a metal/air interface, λsp can be calculated based on dispersion relation $k_0[\varepsilon_a\varepsilon_b/([\varepsilon_a+\varepsilon_b)]^{1/2}$, where k_{sp} and k_0 are wave vectors of the SP and the incident light in vacuum, while ε_a and ε_b are relative dielectric constants of air and the metal, respectively [30, 31]. With help of local field periodically enhanced by the SPs, the interference fringes induce permanent ripples on material surface with Λ equal to λ_{sp}, which is smaller than λ. This is in good agreement with our observations in Figs. 3 and 4, which is the origin of sub-wavelength characteristic of the nano-ripples.

Although dielectric constant of Mg is not publically available to our best of knowledge, current nano-ripples have a broad distribution of spatial periods, and it indicates that the effective dielectric constants of both air and Mg alloy surfaces may vary significantly during laser processing, thus affect the overall effective refractive index of the SPs and lead to the various periods of nano-ripples [32]. However, the period of the nano ripples did not change. Further effort is needed to elucidate the detail relationship between the SPs and these two ripples.

4. Conclusions

Formation of micro-ripples and nano-ripples was observed on Mg surface following femtosecond laser irradiation in atmosphere, and color effect occurred after large area scanning due to the nano-ripples as diffraction gratings. It is suggested that near-field interference between surface plasmons and incident laser light plays an important role in the formation of the nano-ripples, and initial surface roughness combing with such interference leads to the formation of the micro-ripples. This technique has potential application for Mg, such as bio-optical devices and color display, and it can be applied to other types of materials by adjusting laser parameters according to thermal properties.

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Figure captions

Figure 1 Photographs of color effect on irradiated surface of Mg after femtosecond laser scan 10 times at random viewing angles.

Figure 2 Reflectance spectra of irradiated areas at Mg surface with progressive laser scan times.

Figure 3 SEM images showing morphological evolution of Mg surface after irradiation with progressive laser scan times in Figure 2: (a) 10; (b) 30; (c) 50; (d) magnified image for (c). High magnification images of micro-ripples and nano-ripples as well as cluster structures were also shown.

Figure 4 SEM images showing morphological evolution of Mg surface after irradiation with progressive number of laser pulses: (a) 50 pulses; (b) 200 pulses; (c) 300 pulses; (d) 500 pulses. High magnification images of micro-ripples and nano-ripples as well as cluster structures were also shown.

Figure 5 (Color online) AFM images showing topographical evolution on Mg surface in Figure 4: (a) 50 pulses; (b) 200 pulses; (c) 300 pulses; (d) 500 pulses. The probed areas were about 10×10 μm^2 for all the measurements. The detail of surface roughness was described in the text.

Figure 6 AFM images of surface profile measurement in Figure 5: (a) 50 pulses; (b) 200 pulses; (c) 300 pulses; (d) 500 pulses.

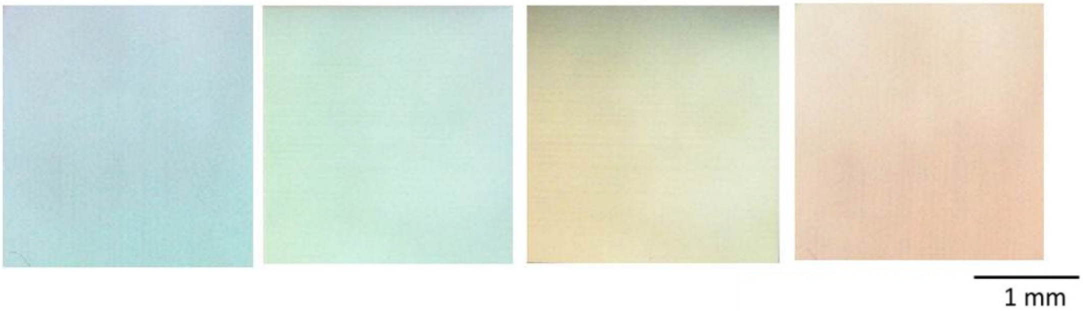


Figure 1

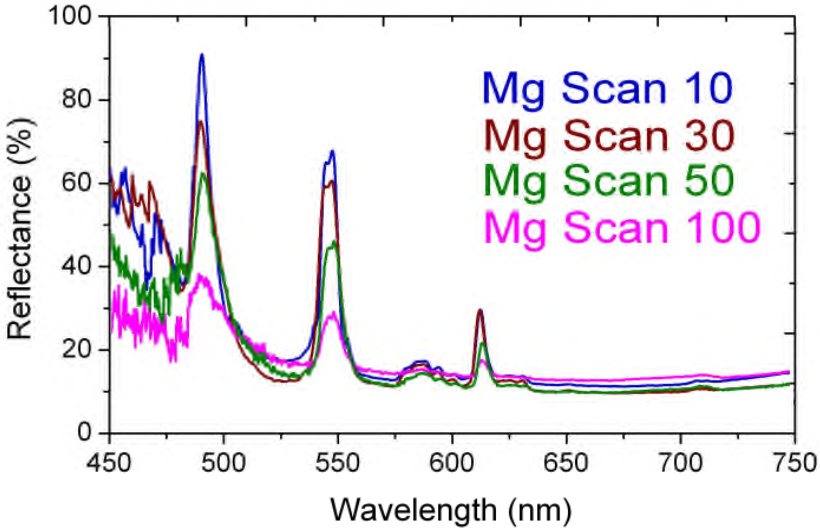
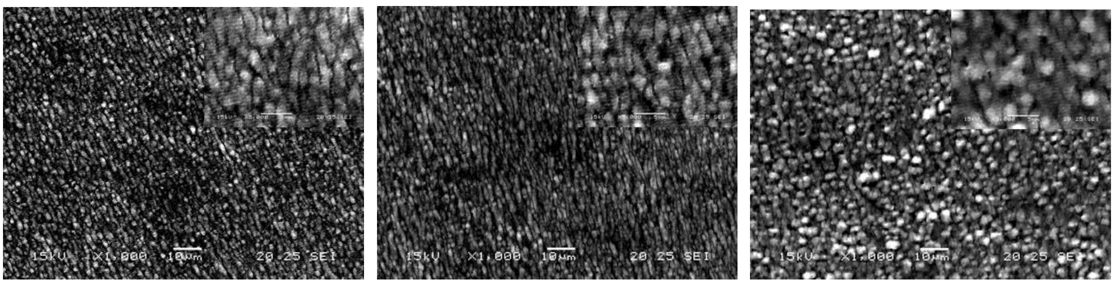
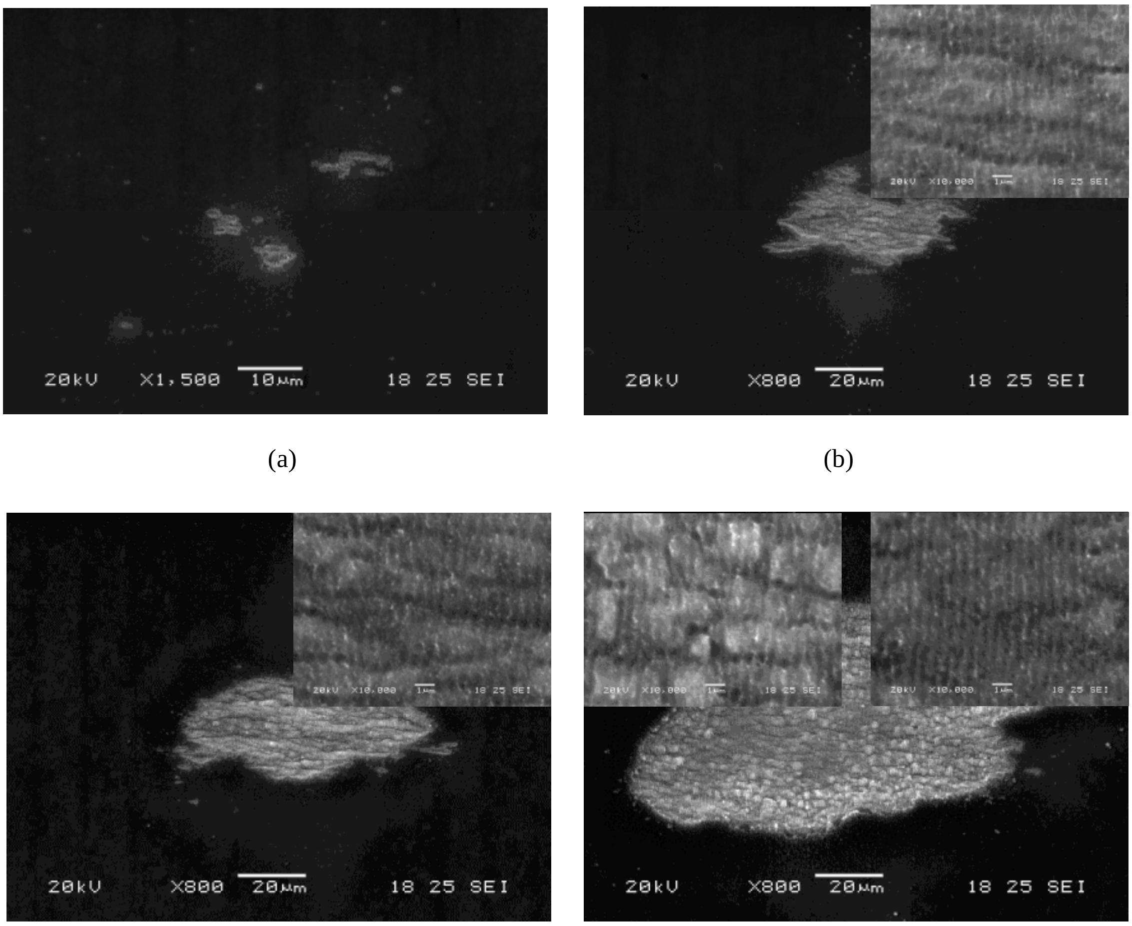


Figure 2



(a) (b) (c)

Figure 3


20kV X1,500 10µm 18 25 SEI
20kV X800 20µm 18 25 SEI
(a)
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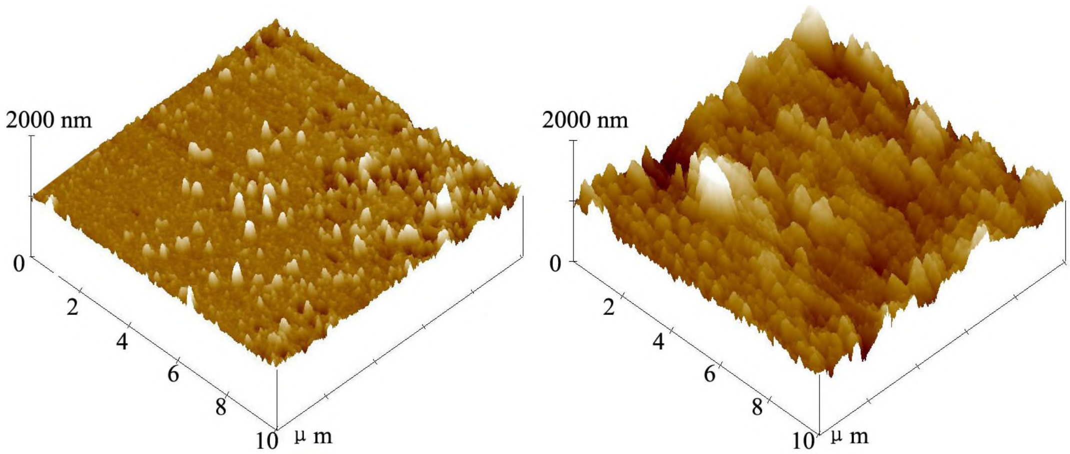
20kV X800 20µm 18 25 SEI
(c)
(d)

Figure 4


2000 nm
0
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8
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µ m
2000 nm
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2
4
6
8
10
µ m
(a) (b)

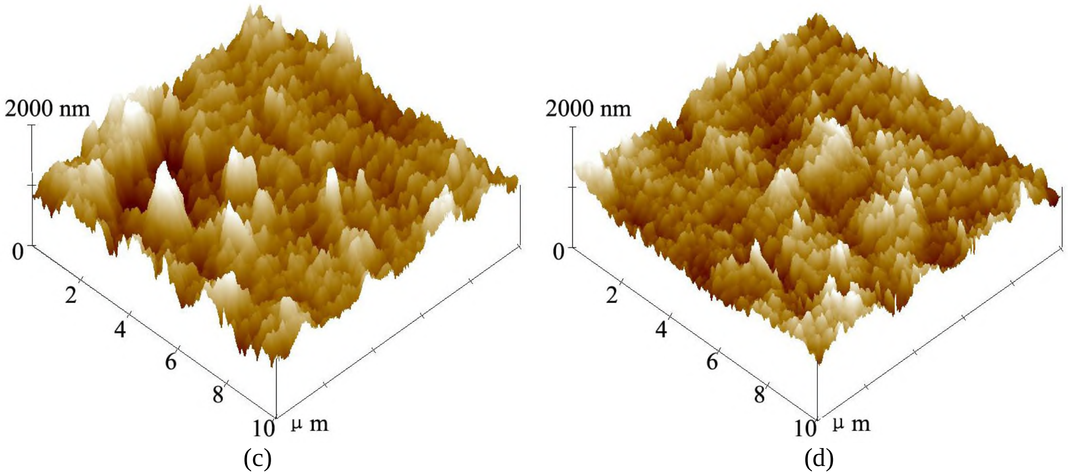

Figure 5

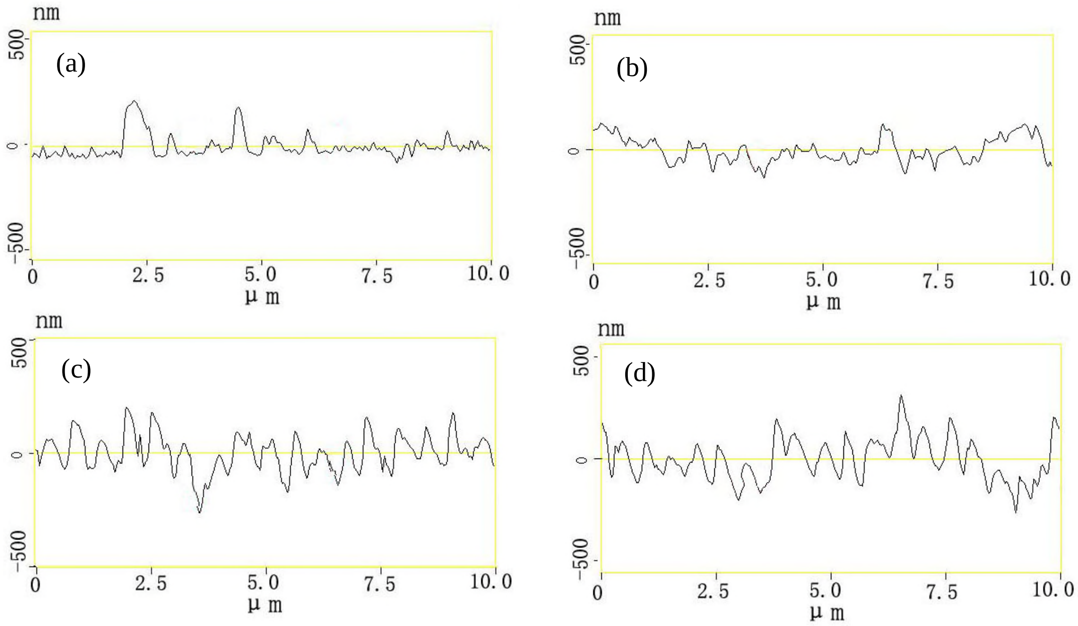

Figure 6

Tables

Table 1 Period evolution of micron and nano ripples on Mg with progressive number of femtosecond laser pulses at wavelength of 775 nm

Number of laser pulses	Micron ripples period (nm)	Nano ripples period (nm)
50	1000	-
100	1200	-
150	1500	501
200	1800	501
250	2100	503
300	2300	502
400	2400	503
500	2600	501