Surface mico-structures on amorphous alloys induced by vortex femtosecond laser pulses*

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This paper investigates the generation of self-organized surface structures on amorphous alloys by vortex femtosecond laser pulses. The scanning electron microscope characterizations show that the as-formed structures are periodic ripples, aperiodic ripples, and 'coral-like' structures. Optimal conditions for forming these surface structures are determined in terms of pulses number at a given pulse energy. The applicable mechanism is suggested to interpret the formation and evolution of the 'coral-like' structures.

Keywords: femtosencond laser pulse, vortex, ripple, 'coral-like' structures
PACC: 4240E, 4262A

1. Introduction

Femtosecond laser has become a new powerful tool for precise patterning surface structures because of its ultra-high power density and ultra-fast time duration.[1,2] The advantages of femtosecond laser pulses, in comparison with longer laser pulses, are the negligible thermal effects, higher precision, higher repeatability and small amount of debris around the ablated spot.[3−5] Laser-induced periodic surface structures (LIPSSs) on various materials have been observed extensively for decades.[6−9] Normally, the orientations of regular LIPSSs are perpendicular to the direction of the polarization of the laser, and have a spatial period which is very close to the incident wavelength. The underlying mechanism has been attributed to interference between the incident laser radiation and scattered or excited surface waves.[10] The femtosecond laser pulses applied in the previous studies usually show a special Gaussian intensity distribution profile. So during the laser ablation, different temperature fluid state appears on the surface of material due to laser energy deposition.[11]

Compared with the Gaussian intensity distribution, the optical vortex is described as a topological point defect on wavefront and manifests as a 'null' within a light beam because the phase at the defect point is undetermined. Such a phase profile is described by an $\exp(\mathrm{i}\,m\theta)$ multiplier, where the signed integer m called the topological charge is controllable and θ is the azimuthal coordinate. Optical vortex has been applied in many fields, such as optical trapping, optical manipulation, and optical vortex coronagraph. Several methods including mode-converters, phase mask, and computer-generated hologram (CGH) could be used to generate optical vortex. Among those methods, optical vortex generated in femtosecond laser fields by use of CGH has been proved to be feasible.[12−14]

In this paper, we perform a detailed study of surface structures such as periodic ripples, aperiodic ripples, and 'coral-like' structures on amorphous alloys induced by vortex femtosecond laser pulses. We reconstructed the optical vortex beam from the fabricated CGH. As-structured surfaces were examined by scanning electron microscope (SEM) and energy dispersive x-ray (EDX). Surface oxidation was observed in the multi-pulse ablation. To our knowledge, so far, there have been no detailed reports on the ablation of any materials by vortex femtosecond laser pulses.

2. Experiment

The materials used in the experiment were Zr-based amorphous alloy foils, whose composition (at. %) is: Zr62, Cu18, Ni10, Al10. Amorphous alloys have always been optimized candidates because of

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their mechanically isotropic and structurally homogeneous properties. Amorphous alloys are assumed to be free from size effects and structural defects, and have been a promising material for micro-electromechanical systems.[15,16] The low ablation threshold of amorphous alloy[17] is suitable to be processed by the optical vortex because of the low energy of the optical vortex. The samples were prepared as foils with thickness of 50 μm.

In our experiments, a regenerative amplified Ti: sapphire laser (Coherent Co.) system was used, which delivered pulses with a duration of 120 fs, with the central wavelength at 800 nm and a repetition of 1 Hz–1 kHz. We applied a microscope objective lens with a numerical aperture of 0.3(LMPLFL50X, Olympus) to focus the femtosecond laser pulses, and mounted the glass on a computer-controlled XYZ translation microstage with 100 nm resolution. To construct a binary CGH of optical vortex, we numerically calculate the interferogram of two waves: a planar reference wave and an object wave containing the desired optical vortex. The binary CGH was directly fabricated inside glass by femtosecond laser pulses.[12] To reconstruct the optical vortex beam from the fabricated CGH, a collimated femtosecond laser pulse was incident on the CGH, as schematically shown in Fig. 1. For there are muti-levels diffraction, in order to get the optimized effect, a mask was located in the diffraction beam path and only the first order diffraction vortex beam was permitted to impinge on the sample. An achromatic lens with a focal length of 10 cm was used to focus the selected diffractive beam. The spatial profile of the focused vortex femtosecond laser pulses with distinct annular shape was captured by a charged couple device (CCD) camera, as shown in Fig. 1(b).

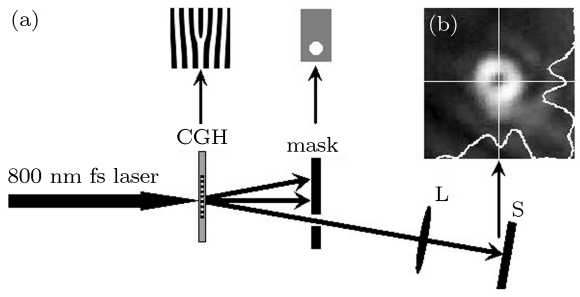


Fig. 1. (a) The schematic setup of femtosecond laser inducing microstructures. (b) The spatial profile of the focused vortex femtosecond laser pulses.

It could be clearly seen that the field does not vanish to zero at the centre due to the rather large spectrum width (10 nm) of the femtosecond laser pulse. The pulse energy irradiated at the sample surface was 14 μJ, which was measured by an energy metre.

All experiments were performed in air under atmospheric pressure. The morphologies of the laser irradiated regions were characterized by SEM (Hitachi S-4800). The material composition of the laser ablated surface was analysed by EDX analysis.

3. Experimental results and discussion

Figure 2(a) shows the SEM image of the amorphous alloys surface before laser irradiation. Figures 2(b)–2(d) correspondingly show the surface morphology induced by femtosecond laser with different pulses number. Figure 2(b) shows the characteristic surface features after one pulse irradiation and we can see that random particles distribute with the size ranging from tens to one hundred nanometres. After exposure to 10-pulses with the same condition, as shown in Fig. 2(c), ripples with direction perpendicular to laser polarization begin to appear. The spatial period of the ripples is measured to be about 800 nm. The morphology of the laser-induced surface structures could be controlled by the pulse numbers. When the number of pulses is increased to 100, as shown in Fig. 2(d), two kinds of irregular periodic structures are formed on the irradiated areas with different period of 800 nm (the originally formed ripples) and several micrometres (new formed ones). We define them as compound ripples in following. The original ripples whose orientations are perpendicular to the polarization direction are overlapped by the longer a periodic structures which are slightly curved and roughly aligned to the polarization direction. Moreover, some deep micro-holes are generated in their overlapped areas. Normally, the orientations of regular LIPSSs are perpendicular to the direction of the laser polarization, and have a spatial period which is very close to the incident wavelength.[6–9] The underlying mechanisms have been commonly attributed to interference between the incident laser beam and the surface-scattered wave. The original ripples formed under ten shots irradiated belong to the regular LIPSSs. Previous studies showed that the compound ripples could be produced on several materials.[18,19] The local field enhancement of transient surface air nanoplasmas, resulting in a nonthermal ablation of the metal targets, has been presented to explain the formation of compound ripples. However, the detailed mechanisms of the novel compound surface structures induced by vortex femtosecond laser pulses in our experiments are still unclear.

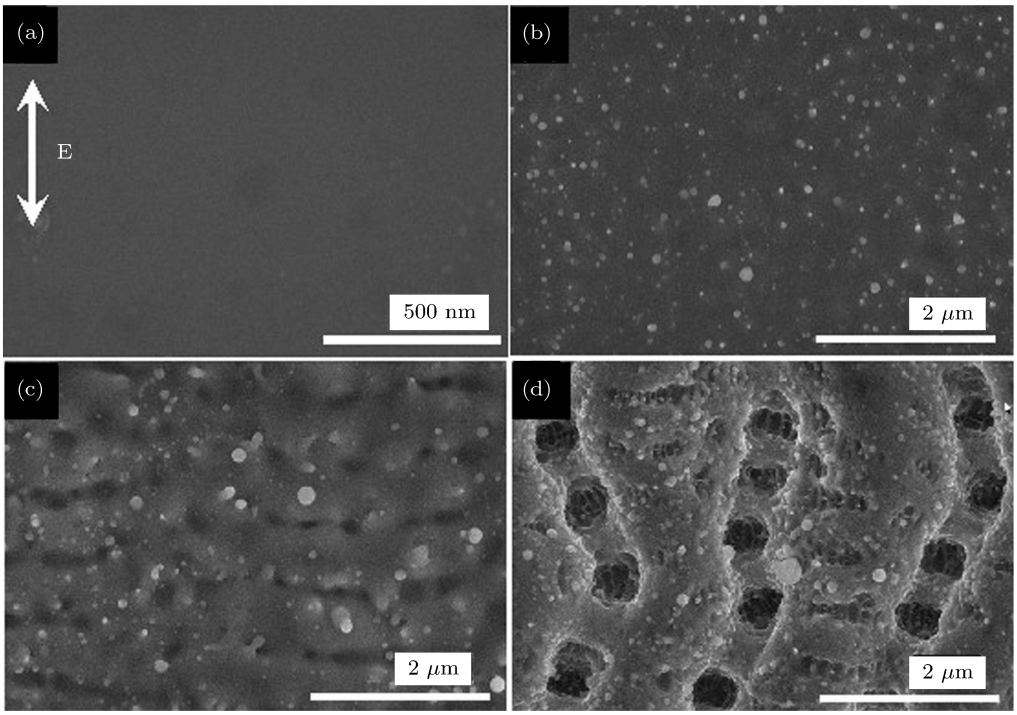


Fig. 2. SEM images of induced surface structures on the amorphous alloys surface following femtosecond laser treatment with the energy of 14 μJ. (a) Sample surface before irradiation; (b)–(d) after 1, 10, 100 shots treatment. The laser beam polarization direction is represented by white arrows on the figure.

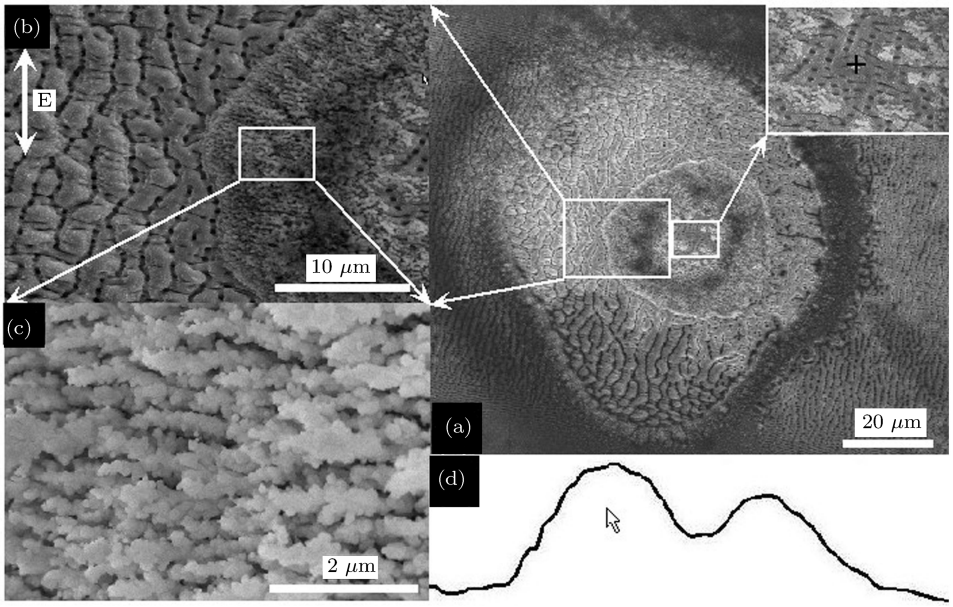


Fig. 3. SEM images of induce surface structures after 1000-shot treatment with the energy of 14 μJ. The curve (d) indicates the spatial energy profile of the focused vortex laser pulse. The laser beam polarization direction is represented by white arrows on the figure.

Figure 3 shows the surface morphology of sample after irradiation by 1000 laser shots. We can observe that the ring-like structure is formed as shown in Fig.3(a). The spatial energy profile of the focused vortex laser pulse is shown in Fig. 3(d). Apparently, the ring-like structure indicates a close relation between surface profile of as-formed structures and the spatial energy profile of the focused vortex laser pulse. Figures 3(b) and 3(c) show the magnified images of different regions in the ring-like structure. The compound ripples are formed

in the central region where the laser intensity is low, labeled as '+' in Fig. 3(a). A magnified image of the section is insetted in Fig. 3(a). As we can see, one type ripples are oriented perpendicularly to the polarization of the laser with the period about 800 nm; the other ones are aligned along the polarization direction. As shown in Fig. 3(b), a unique pattern appeared on the sample surface, where two kinds of different structures were formed: one kind is compound ripples with different periods; the other is much resembling 'coral' whose magnified image is shown in Fig. 3(c). We define them as 'coral-like' structures. These 'coral-like' structures are irregularly positioned, and individual branch shows length of several micrometres and width of about 200 nm. The 'coral-like' structures are formed around the location where the vortex laser has the maximum intensity and distributes in the ring-like configuration as shown in Fig. 3(a). The experimental results show that the formation of the 'coral-like' structures is dependent on the number of laser shots. When the applied laser pulses was less then 1000-shot, the 'coral-like' features are smaller in length and less regular, while when we increase the laser shots, the 'coral-like' structures became more obviously and more regularly distributed.

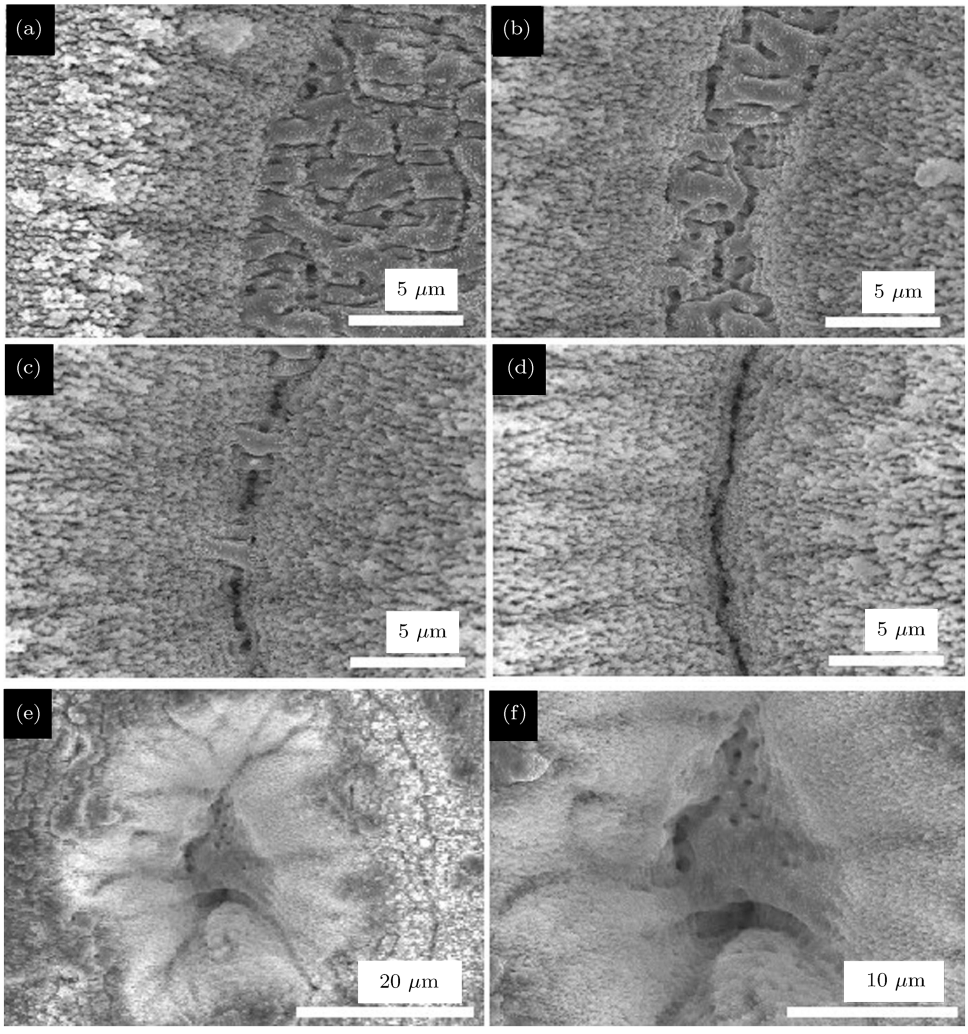


Fig. 4. The SEM images of multi-pulses ablation region: (a)–(d) typical structures following 2000, 3000, 4000, 5000-shot treatment, respectively; (e)–(f) typical structures following 4000-shot treatment of Gaussian profile pulses.

As shown in Figs. 4(a)–4(d), when the pulses number is increased to 2000, 3000, 4000, and 5000, respectively, the evolvement of the 'coral-like' structures distribution becomes clearer. The 'coral-like' structures are formed instead of original compound ripples when the of number applied pulses is increased to 5000, as shown in Fig. 4(d). As a comparison, the collimated femtosecond laser pulse without passing through the CGH is used as an irradiated source, and the resulted surface structures is depicted in Figs. 4(e) and 4(f). Figure 4(e) shows

the SEM images of the ablation region by 4000-shot treatment with the laser energy of 14 μJ and Fig. 4(f) gives an enlarged vision of the selected region in Fig. 4(e). Similar as previous experiments, the 'coral-like' structures are still observed on alloys and are closely related to the special energy distribution of the laser. For vortex femtosecond laser, it is known that the spatial energy distribution is controllable, therefore, compared with normal femotosecond laser with Gaussian profile, we can use the vortex femtosecond laser to precisely control the spatial distribution of micro-or nano-structures on amorphous alloys.

It has been reported previously that the formation of pillars, spikes and conical microstructures induced by ultrafast laser on silicon or germanium in an SF_6 atmosphere is a mixed process of laser ablation and chemical reactions at the sample surface.[20,21] The vapour-liquid-solid growth mechanism was first suggested to explain the growth of columnar Si structures.[22,23]

In order to investigate the mechanism of the formation of the 'coral-like' structures in our results, the material composition of the ablated surface is analysed by EDX at the depth of 0.5–5 μm by point scanning mode. Figure 5(a) shows EDX results of non-ablated region and Figs. 5(b) and 5(c) shows the EDX results of the compound ripples and 'coral-like' structures, respectively. Oxygen component was both observed in the two types of structures. Comparing Fig. 5(c) with Fig. 5(b), we can see that oxygen component in 'coral-like' structures is higher than that in ripples structures. Simultaneously, carbon element is also detected in the 'coral-like' structures but not in other structures. Based on above analysis, an applicable mechanism is suggested to interpret the formation and evolution of the 'coral-like' structures. When the material is exposed to femtosecond laser pulses, the surface layer will be vapourized, the oxygen and carbon in the air are absorbed. The as-vapourized species will further deposit on the surface. Therefore, the structures are formed by the repeated ablation and deposition process.

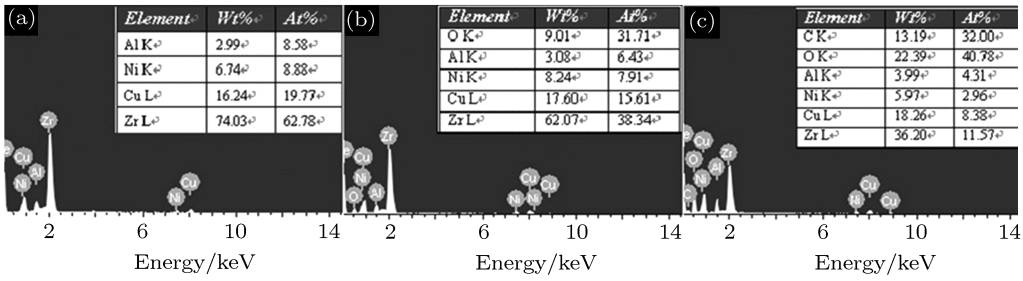


Fig. 5. The EDX analysis of (a) the un-ablated surface of sample; (b) compound ripples structures; (c) 'coral-like' structures under 1000-shot irradiation.

In particular we indicate that topological charge m described above determines the dimension of dark hole centred at the middle of the diffracted beam. So the distribution of the structures induced by vortex femtosecond laser could be further controlled by the topological charge m.

Laser modified surface with micro-or nano-structures always present new properties such as decreasing the light reflection and increasing the absorption.[24] These characteristics widen the applied range of materials. So the 'coral-like' structure formed in our experiments could be promisingly applied in the fabrication of photodetector devices and sensors.

4. Conclusions

In summary, compound structures such as periodic ripples, aperiodic ripples, and 'coral-like' structures are formed on the surface of amorphous alloys by a vortex femtosecond laser. The results show that the as-formed surface mophorlogy depends on the number of applied laser pulses. Modified surface structures might find potential applications in the fabrication of photodetector devices and sensors.

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