Femtosecond laser microstructuring of nickel foil

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We observe the morphological change and grain structure of Ni foil when it is ablated with femtosecond laser pulses. Scanning electron microscopy and field emission transmission electron microscopy are used to study the nature of the morphology and grain structure of nickel foil and determine the essential features. The results indicate that there are many random nanostructures in the center of the ablated region composed of nanocrystalline grains as well as some core-shell structures. The observed morphologies seem to suggest that phase explosion and extremely high cooling rate are the most probable physical mechanisms responsible for the formation of surface nanostructures.

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As ultrashort pulse duration confines heat diffusion, the femtosecond laser pulses provide a promising tool for the alteration of surface morphology and texture without significant damage to the underlying material. Unique materials modification and surface texturing effects may be achieved through the controlled use of laser irradiation parameters, such as pulse energy and pulse count[1−5]. Physically, these correlate to thermal gradient structure and quenching rates. Thus, it is possible to develop unique phases and surface microstructures through the appropriate combination of laser processing parameters. Her *et al.* have found that silicon surfaces develop an array of sharp conical spikes when irradiated with femtosecond laser pulses[6,7]. Wu *et al.*[8−10] reported that the linearly polarized femtosecond laser pulses produce fine periodic structures with periodicity shorter than the laser wavelength. The studies of Vorobyev *et al.* have shown that random surface nanostructures can be produced following ablation of metals by femtosecond laser pulses[11−14].

In this letter, the morphology and grain structure of nickel ablated with femtosecond laser pulses is studied, using scanning electron microscopy (SEM) and field emission transmission electron microscopy (FETEM) to determine the essential features and their relationships. Based on the thermal evolution of the ablation with femtosecond laser pulses, a mechanism for the formation of the unique surface texturing is proposed.

All samples were processed in the air using a commercially available femtosecond laser micromachining workstation (Clark-MXR, UMW-2110i) equipped with a Ti:sapphire chirped pulse amplification (CPA) system. The laser emitted pulses of linearly polarized light at a central wavelength of 775 nm. The laser pulse width and repetition rate were 130 fs and 1 kHz, respectively, and the maximum energy was 1 mJ per pulse. The laser beam was focused by a long working distance microscopic objective (numerical aperture NA = 0.14). The laser beam was normally focused onto the sample surface. The focused beam diameter was measured to be about 11.5 μm.

A commercially available Ni foil (99.9% purity) was used as the target. All samples had dimensions of 20 × 20 × 0.03 (mm). The morphology of the machined surface was examined by a SEM (Philips XL30E) at an operating voltage of 20 kV. A FETEM (Philips Tecnai G2 F20) with an accelerating voltage of 200 kV was used to characterize the structural properties of the ablated sample. FETEM samples of about 3 mm in diameter were prepared using focused ion beam (FIB) etching with 5-kV voltage and tilt angle of 10°. In order to avoid the residual ionization effect, the FETEM samples were machined using a FIB etching firstly.

Figure 1 shows the evolution of the modification at near-ablation-threshold fluence of 2.6 J/cm^2 after increasing numbers of incident laser shots. In the center of the ablated region, there are large numbers of randomly oriented protrusions of nanoscale dimension, which is a foamlike structure, and periodic surface structures (the well-known 'periodic ripples') in the peripheral of the ablated region. Outside the laser-ablated region, there is a large quantity of debris caused during laser ablation and deposited on the surface of the Ni sample. As the shot number increases, the extent of modification area expands and the periodic ripples grow. This indicates the accumulation behavior of the ablation. If one considers the Gaussian-shaped intensity profile, it becomes clear that the lower intensity outer-edges of the beam cause no ablation, but cause periodic ripples due to the accumulation in the outer regions of the irradiated area.

The morphology in the center of the ablated region is similar to the random nanostructures reported by Vorobyev[12−14] and consistent with rapid expulsion of liquid and vapour droplets which cool quickly[15] and resolidify. This suggests that phase explosion[16] is the most probable physical mechanism responsible for the random nanostructures. For high fluence and sufficiently short pulses, melted material at the irradiated surface is unable to boil because the time scale does not permit the necessary heterogeneous nuclei to form. Instead, it is superheated significantly past the normal boiling point to

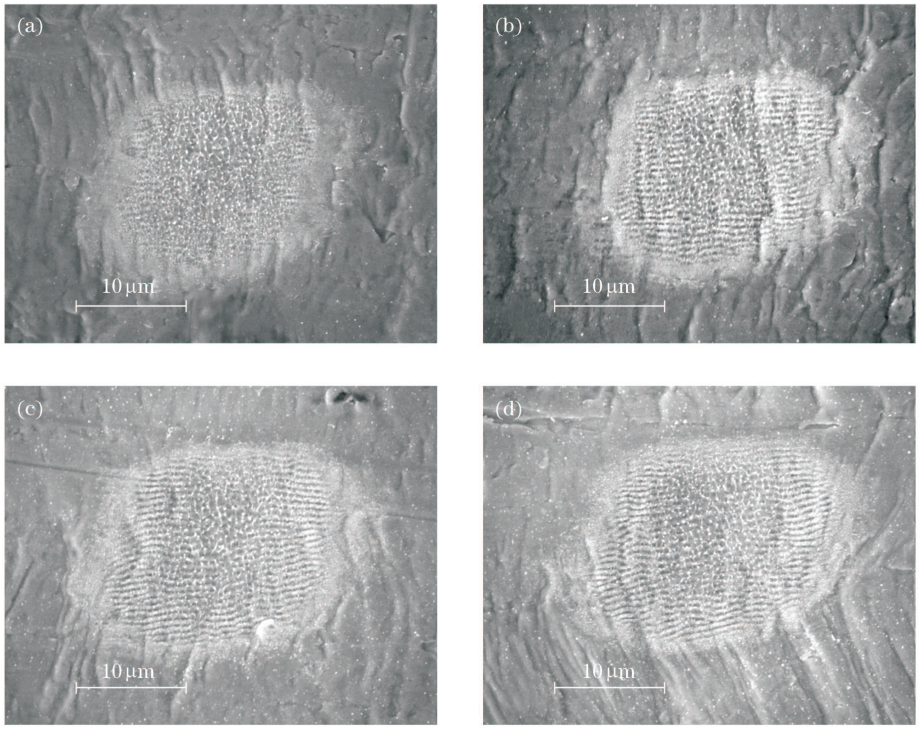

Fig. 1. SEM images of Ni surface ablated at a fluence of 2.6 J/cm^2. (a) 10 shots, (b) 20 shots, (c) 50 shots, and (d) 100 shots.

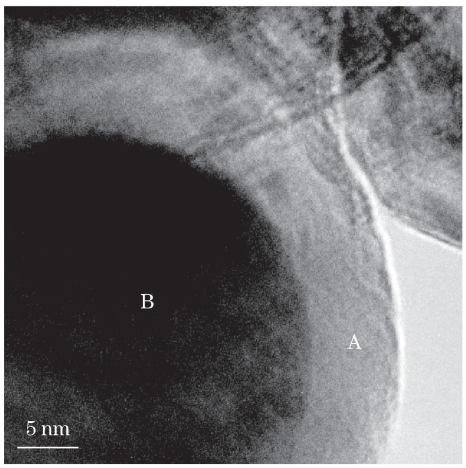

Fig. 2. FETEM image of the rim of the laser-ablated hole with 1000 shots at a fluence of 2.6 J/cm^2.

$0.9T_{\rm tc}$ ($T_{\rm tc}$ is the thermodynamic critical temperature, for Ni, $T_{\rm tc} = 9400$ K)[17−19]. The phase explosion of the overheated material leads to the formation of a foamy transient structure of interconnected liquid regions that subsequently decomposes into a mixture of liquid droplets, gas phase molecules, and small clusters[20]. The observed morphologies are consistent with the rapid expulsion of liquid and vapour droplets which then freeze at an extra high cooling rate[21].

Dou *et al*. found that the nanostructure only appeared when the metal was ablated with femtosecond laser, but no nanostructure appeared on the metal surface ablated with nanosecond laser[1,2]. It appears that the condition of phase explosion could not be achieved during subtle laser ablation with nanosecond laser[17,22].

To directly observe the post-ablation re-cast structure, a grid of holes was drilled over an area of 1×1 (mm) on the FETEM samples using femtosecond laser pulses. Each hole (the hole diameter was about 20 μm and the hole space was 50 μm) was exposed to 1000 consecutive pulses at a fluence of 2.6 J/cm^2. A FETEM study was performed in the rim of a laser-ablated hole. There are large numbers of grains with the size of several tens of nanometers, and few particles with core shell structure on the microstructures were formed by femtosecond laser irradiation. The presence of a nanocrystalline grain adjacent to the ablated region means that there must have been liquid Ni created by the femtosecond laser ablation, and the melting Ni abruptly cools down and re-crystallizes. This mechanism would be the same as the melt-quenching generally used as the fabrication method of nano-crystalline metals[23]. Figure 2 shows a TEM image of a core (labeled B) shell (labeled A) structure existing in the rim of laser-ablated hole. The core-shell structure corresponds to oxidized metal particle. Because amorphous Ni has nearly the same density of free electrons as crystalline one, there would be no contrast between crystalline core and amorphous shell. Since laser exposure is carried out in air, it would be quite evident to assign the observed core-shell nanoparticle to oxidized Ni drop sputtered from the ablated area. The oxide looks brighter than corresponding metal under TEM imaging due to the low density of the electrons in it. The formation of the few core shell structures, as well as nanocrystalline grains, shows that the growth time of the nanoparticles from the molten Ni layer is very fast. When a number of Ni drops are ejected from the center of ablated area and quickly resolidify, random surface nanostructures will occur.

In conclusion, the changes in the morphology and grain

structure of nickel produced following ablation by femtosecond laser pulses have been investigated. The phase explosion happens in the ablated region, and large numbers of Ni drops are sputtered from the ablated area and then resolidify quickly due to a very high cooling rate. It is observed that random surface nanostructures form in the center of laser ablation region. The phase explosion and extremely high cooling rate are the most probable physical mechanisms responsible for the formation of random surface nanostructures.

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