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Fundamentals of layered nanoparticle covered pyramidal structures formed on nickel during femtosecond laser surface interactions

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ABSTRACT

The formation of nanoparticle covered pyramidal structures using femtosecond laser pulses with a fluence near the ablation threshold is reported for the first time. These unique structures form through a combination of preferential ablation of flat regions around the pyramids and redeposition of nanoparticles created during the ablation process. The structures are demonstrated on nickel and stainless steel 316. When produced by rastering Gaussian pulses across the sample, layers of nanoparticles join together by sintering to form unique layered shells.

1. Introduction

Femtosecond laser surface processing (FLSP) is a rapidly developing technology that can be utilized for creating specialized micro/nanostructures on the surface of various types of materials. The wide range of and precise control over the surface morphologies enable precise tailoring for specific applications. A large variety of micro/nanostructured morphologies fabricated by FLSP have been reported in the literature, including pillars [1–5], cones [6–11] spikes [3,12–14], and mounds [15]. All of these surface morphologies share similar characteristics, namely microstructures with a height to width aspect ratio of at least 2:1, widths around 2–10 μm, and either nanoripples or nanoparticles covering the surface. In this work, we present for the first time a new surface morphology fabricated via FLSP that is referred to as nanoparticle covered pyramids (NC-pyramids). NC-pyramids have a pyramidal shape and are covered with a thick layer of nanoparticles (typically >2 μm thick). The NC-pyramids have an aspect ratio near 1:1 and can grow to be more than 50 μm in height and width. In a recent publication covering FLSP, we demonstrated that different values of the laser fluence lead to dissimilar formation processes for mound-shaped structure growth and therefore unique surface morphologies [15]. NC-pyramids are another unique surface morphology that result from using FLSP at much lower fluences (near the ablation threshold of the material). NC-pyramids form through a series of different processes than either of the mound structures previously reported [15].

The pyramids discussed in this paper are similar in formation and shape to pyramids formed during ion beam bombarded copper [16], as well as through nanosecond laser machining of polymers [17–19] and graphite [20]. As reported in this previous work, the onset of formation occurs when a small portion of the surface has a higher ablation threshold than the surrounding regions, and thus results in preferential ablation along with the subsequent formation of a precursor cone. The existence of regions with increased ablation thresholds is attributed to impurities that are either originally present in the material or deposited during the ablation process. A unique aspect of the pyramidal structures formed using FLSP that is not present through other methods is a thick layer of nanoparticles that builds up on the surface. As a result, the NC-pyramids discussed here appear to be formed as a hybrid structure type that lies between the pyramids formed during nanosecond ablation and the nanoparticle aggregates discussed in one of our earlier publications [21]. One advantage of using FLSP for the formation of NC-pyramidal structures is the minimized heat affected zone [22]. Thus, using FLSP to produce NC-pyramids is an improvement over the use of longer pulsed lasers for applications where the bulk material needs to remain unaltered. This is the first demonstration, to our knowledge, of the formation of NC-pyramidal structures formed on a metal surface using FLSP.

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2. Experiment

NC-pyramids were produced through two techniques: stationary ablation of the sample using pulses with a square flat-top beam profile and by rastering pulses with a Gaussian-shaped beam profile across the sample surface. The multipulse growth mechanisms of NC-pyramids on nickel using stationary ablation were studied using a stop-motion scanning electron microscopy (SEM) technique similar to that described in our previous publication [15]. Using this technique, a single area on the sample was alternately irradiated and imaged in order to produce a series of high-resolution SEM images that depict the formation processes of individual NC-pyramids with increasing pulse count. These still frame images were sequenced to form high resolution stop-motion SEM videos. The NC-pyramid formation processes occur gradually over 1,000–20,000 pulses. Therefore, the number of pulses between SEM imaging was varied to balance the time commitment and the step size over which interesting results could be observed. The redeposition of ablated nanoparticles on the surface of the pyramids was investigated using both stationary flat-top pulses and rastered Gaussian-shaped pulses in order to isolate the impact of sample motion during processing. The stop-motion imaging work presented here was performed on nickel, which was chosen because of its potential use as electrodes in pseudocapacitor and electrolysis systems, its purity, and the volume of published work on femtosecond pulse interactions with nickel. Similar NC-pyramids have been fabricated via FLSP on stainless steel (SS) (type 316, 304, and 430) in our laboratory. Results on 316 SS are also included.

The laser used for carrying out this research was a Spectra Physics Spitfire, Ti:Sapphire femtosecond laser system capable of producing 1 mJ, 50 fs pulses. In combination with a computer-controlled shutter, the repetition rate of the laser was adjustable from single pulses up to the maximum of 1 kHz. The pulse length and chirp were monitored using a Frequency Resolved Optical Gating (FROG) instrument from Positive Light (Model 8-02). The position of the sample with respect to the laser focal volume was controlled using computer-guided Melles Griot nanomotion translation stages with 3 axes of motion. The laser power was controlled using a half waveplate and a polarizer. All of the work was completed in open atmosphere.

In our previous publication, we demonstrated that the growth of self-organized surface structures is critically dependent on the laser fluence [15]. For this reason, a square-shaped flat-top beam was used for the stop-motion SEM experiments in order to generate a uniform laser fluence on the material surface. The experimental setup and beam profile can be seen in our previous publication [15]. This beam profile was created using a refractive beam shaper from Eksma Optics (GTH-4-2.2FA). The laser fluence varied by less than 20% across the central portion of the beam, and any fluence fluctuations in the flat-top distribution are attributed to the asymmetries and inhomogeneity of the input beam. The flat-top profile is constant over the 50 μm ablation depths studied in this work. The spot size on the sample was determined using the same techniques as described in our previous publication [15]. The impact of sample motion during processing, which is necessary for the fabrication of large structured areas, was investigated by translating the sample through the path of the laser in a rastering pattern. For this portion of the research, the laser had a Gaussian beam profile with an ablation diameter of 600 μm, which was achieved by removing the Gauss-to-top hat beam shaper, 500 mm focal length lens, and beam expander/collimator from the setup described in our previous publication [15].

3. Results

3.1. Shot by shot growth

NC-pyramids form on nickel at laser fluence values in the range of 0.09–0.17 J/cm^2, which is near the 0.05 J/cm^2 ablation threshold for nickel when measured with 300 fs pulses centered at 527 nm [23]. Utilizing stop-motion SEM techniques, the shot-by-shot formation process of the NC-pyramids was analyzed and broken into two growth phases. The first phase is the formation of precursor cones. The second phase is described in two parts occurring concurrently: continued growth of the pyramidal structure on the surface, and the development of the nanoparticle layer. The shot-by-shot growth experiments were completed using a constant laser fluence of 0.12 J/cm^2, and are demonstrated in the stop-motion video (multimedia online: media 1) and a sequence of images from this video in Fig. 1. It is highly recommended to view the stop-motion video (multimedia online: media 1) in addition to viewing the images in Fig. 1 in order to be in a position to most readily understand the intricacies of the formation dynamics. These SEM videos provide a powerful shot-by-shot visualization of the growth of single structures in the ablation region and greatly contribute to the understanding of the dynamics involved in the formation of these structures in time and space.

3.1.1. Phase I: Development of precursor cones

The first phase of NC-pyramid development is the formation of precursor cones over a large number of laser pulses, which occurs at the same time that laser induced periodic surface structures (LIPSS) are produced on the surface. LIPSS from FLSP is well published in the literature, including work on metals [24–26]. These LIPSS lines do not contribute to the formation of the NC-pyramids being reported in this paper. However, LIPSS are present over the entire ablation region before NC-pyramids begin to form, in the flat regions between NC-pyramids throughout the formation process, and even on the surface of the pyramids before the nanoparticle layer fully develops and covers the pyramids (see Fig. 1a and b). With increasing pulse counts, small cones begin to form on the LIPSS covered surface (the first cone appears around 1000 pulses in this sample). Fig. 1a is a SEM image of a cone that has developed by the end of the first phase. As has been previously discussed, these conical structures develop from localized regions with an increased ablation threshold relative to the bulk material. Since NC-pyramids form with laser fluence values near the ablation threshold, any variation in the ablation threshold has a direct impact on the ablation rate. Over many thousands of pulses, the cumulative effect of a variation in the ablation rate is the formation of features tens of microns in size. The source of the initial inhomogeneity that causes the formation of the precursor cone has been previously attributed to impurities on the sample when fabricated with nanosecond pulses. For example, Krajnovich and Vazquez conclude in their work on nanosecond ablation of polymers that the higher ablation threshold is from carbon enrichment [18]. Species are preferentially ejected from the material, leaving behind a carbon rich surface, which has a higher ablation threshold. As a different example, Krajnovich et al. conclude in their work on nanosecond ablation of highly oriented pyrolytic graphite (HOPG), cone formation is initiated by micrometer-sized impurities of Ti, V and Fe. It is suggested that the impurities act as heat sinks, shunting heat away and leading to lower sputtering rates in the localized area [20]. In the case of FLSP, it is believed that sources for localized variations in the ablation threshold include: a localized crystalline structure difference (e.g. grain boundaries), impurities in the sample, or modifications in the material from previous pulses (e.g. redeposition of material ejected during the ablation process, which leads to an