J. Condensed Matter Nucl. Sci. 15 (2015) 268–278

Research Article

Surface Preparation of Materials for LENR: Femtosecond Laser Processing

Scott A. Mathews*

The Catholic University of America, 620 Michigan Ave NE, Washington, DC 20064, USA

David J. Nagel and Brandon Minor

The George Washington University, 2121 I St NW, Washington, DC 20052, USA

Alberto Pique

Naval Research Laboratory, 4555 Overlook Ave SW, Washington, DC 20375, USA

Abstract

Because surfaces have been shown to be important for Low Energy Nuclear Reactions (LENR), their preparation for experiments or energy generators is naturally of interest. We demonstrate that irradiation of Pd with pulses from a femtosecond laser produces surface topography with features on both micro- and nano-meter size scales. Micrographs of these features were analyzed to obtain the spatial frequencies for later correlation with production of excess heat.

Keywords: Femtosecond lasers, LENR, Low energy nuclear reactions, Surface modification

1. Introduction

The experimentally proven ability to produce nuclear reactions with chemical energies is a vexing scientific problem with great practical promise. Because of data from many past experiments, it appears possible to produce clean power using small and cost-effective distributed generators. Much data, and some theories, indicate that LENR occur on or very near the surfaces of materials. Hence, the willful preparation of surfaces of materials for LENR experiments and power generators is an important topic. Oddly, it has received relatively little attention. Many techniques can be employed to modify the composition and structure of surfaces of materials for use as LENR substrates. We report here on the first use of laser structuring prior to experiments as a means to promote the functionality of cathodes for LENR electrochemical experiments. This work is not to be confused with studies in which laser light was shined onto LENR materials during experimental runs to trigger or increase production of excess power [1–3].

*E-mail: mathewss@cua.edu

Section 2 gives a brief summary of LENR, and reviews some past work on surfaces of cathodes for electrochemical loading and foils for gas permeation experiments. Then, we survey some of the methods that might prove beneficial for making the surfaces of diverse materials active for the occurrence of LENR. The effects of lasers of widely different pulse lengths on materials surfaces are summarized. In particular, femtosecond lasers have been found to produce surface structures with widely varied spatial frequencies. Next, we describe the laser and experimental setup employed for the work reported here. Samples of Pd were exposed to varying numbers of femtosecond pulses, with the energy per pulse being another variable. Scanning electron micrography was used to examine the samples after laser processing. The observed structures were generally in the micrometer range, but some features as small as 20 nm were seen. The micrographs were analyzed using MatLab to obtain the distribution of spatial frequencies. We will use the laser irradiated foils as cathodes in future calorimetric electrochemical experiments. We note possible additional physical and chemical processes than might be used to modify the structures and composition of laser-induced features.

2. LENR and Surface Studies

LENR, initially called "cold fusion", are now well established experimentally [4]. These reactions were and remain contentious, mainly because there is no accepted theoretical explanation of how it is possible to employ chemical energies on the scale of an eV to trigger nuclear reactions with energies in the range of MeV.

The field of scientific research on LENR involves many ways to bring together isotopes of hydrogen with materials, and numerous techniques for measurements of the results of such interactions. Currently, there are two main approaches to producing LENR, electrochemical loading of deuterons into Pd and gas loading of protons onto Ni. The first of these is widely used in scientific studies. The second is expected to be the basis for practical energy generators. In both of these cases, the measurement of energy amplification (from electrical to thermal) is of great interest.

There is experimental evidence that, at least in several cases, LENR occur on the surfaces of materials. This is not to exclude the possibility that such reactions also occur within the bulk of materials. If LENR occur exclusively or preferentially on surfaces, practical energy generators based on them should be simpler in both construction and operation.

A significant database exists for the likelihood that LENR occur upon surfaces in electrochemical loading experiments. One of the clearer indications is an experiment done by Storms in which he reversed the electrode materials from the normal configuration of a Pd cathode and Pt anode. During the course of the run, Pd atoms dissolved from the Pd anode and were deposited on the Pt cathode. Only a thin film was produced, but excess heat was still measured [5]. It was found early in the field that the production of excess power in electrochemical experiments scaled linearly with the flux of deuterons through the surface of a Pd cathode. This is significant circumstantial evidence for the importance of surfaces for production of LENR.

There is relatively little published data on the locations where LENR occur in gas loading experiments. Possibly the best example is from experiments by Iwamura and his colleagues [6]. The experiments involved permeation of deuterons, which originated in the gas phase, through Pd foils containing multiple thin layers of CaO. A thin layer of Cs was deposited on the surface of the Pd foils prior to the runs. Sensitive surface analytical measurements during the course of the experiments indicated that Pr appeared in place of the Cs. Depth profiling of the foils showed that the Pr was confined within 10 nm of the surface [7].

3. Surface Modification and Characterization

We emphasize that two steps, (a) surface modification and (b) subsequent determination of the makeup and structures of surfaces, are mandatory for LENR as they are for numerous other processes in physics, chemistry, biology and engineering.

Techniques for tailoring the composition and structure of surfaces are numerous. Many of them are well developed commercially in the microelectronics and other industries. The three major types of processes for production of integrated circuits, MEMS and other microdevices are patterning, etching and deposition. The primary processes for production of nano-scale structures are the same three top-down techniques, and also the bottom-up physical or chemical growth of nanomaterials. All of the techniques in these categories, individually and in combinations, are available for modification of surfaces of materials that will go into LENR experiments and generators.

Many experimental tools are used to characterize commercial micro- and nano-materials and devices, that is, to determine their composition and structure. They involve irradiating the items of interest with photons, electrons or ions, and simultaneously measuring the photons, electron or ions that result from the bombardment. Optical and electron methods, and atomic force microscopes, are widely used for imaging of structures. We employed a Scanning Electron Microscope (SEM) in this work. Figure 1 is a flow diagram for our program. This paper deals with the first three aspects, the procurement, modification and characterization of the Pd cathodes for later LENR experiments.

It must be noted that our characterization work to date is informative, but well short of what is possible. There are many methods for obtaining the surface composition and structure of materials beyond scanning electron microscopy and analysis. They include a wide variety of means to measure the distribution of elements on a surface, notably Auger electron analysis and secondary ion mass spectroscopy. And, there are other methods for obtaining structure on atomic levels, notably x-ray diffraction and atomic force microscopy. Castagna and his colleagues [8] employed the last two tools to obtain the surface crystalline orientation and the scale of roughness of Pd cathodes they produced. Then, they ran those cathodes in electrochemical cells and measured the amount of excess heat produced. It was found that (100) surface crystal orientations and atomic-scale roughness in the range of 1–4 inverse microns gave the best excess heat production.

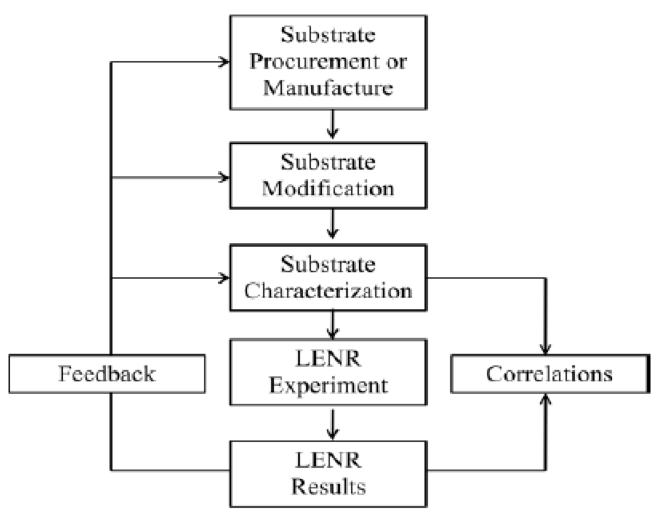

Figure 1. Sequences of steps in the current program.

4. Laser Effects on Surfaces

The ability to produce short pulses of laser light was demonstrated soon after the development of the laser in 1960 [9]. That technology enabled generation of pulses approaching gigawatts in optical power. When focused to spots 10 μm, and even smaller in diameter, irradiances on the order of or greater than 10^{15} W/cm^2 were achievable. It was found that such power densities produced plasmas on the surfaces of targets with extreme temperature gradients in space and time, sometimes on the order of a million degrees over distances of less than tens of micrometers and faster than tens of nanoseconds. The high temperatures and pressures in the plasmas caused significant, albeit localized effects on the targets beyond melting, vaporization and plasma formation. The field of laser processing of solid surfaces emerged from these observations [10], including a specialization to femtosecond laser processing [11].

When laser pulses on the order of picoseconds and shorter strike a solid, they interact with electrons at solid state densities, because there is insufficient time for establishment of a laser-photon-absorbent surface plasma. Such interactions can produce features on targets that are termed Laser Induced Periodic Surface Structures (LIPSS). They have been observed for decades [12]. But, they are not yet thoroughly predictable in behavior. For instance, in some transparent materials, periodic structures will form inside the material, rather than on the surface. As LIPSS have become a more popular topic of research, ways have been found to create structures with periodicities somewhat larger than, similar to and even smaller than the wavelength λ of the laser. These observations have prompted investigations into the origins of such vastly different spatial frequencies.

Structures with two different frequencies commonly appear on LIPSS: High Spatial Frequency LIPSS (HSFL) and Low Spatial Frequency LIPSS (LSFL). Their spatial frequencies are typically about 10 and 100% of the laser wavelength, respectively [13]. HSFL can be produced using the shorter wavelength second harmonic light from a particular laser. They normally appear at a lower fluence than LSFL. Increasing the number of pulses put on a given spot both makes the laser-affected area on the target larger and produces more LSFL.

We are investigating whether or not the LIPSS produced on a Pd target by a femtosecond laser might promote LENR. The following sections describe the laser and focal setup, the foils used, the features found on them and our analyses of the spatial frequency distributions of those features.

5. Experimental Setup and Parameters

Fifty-micron thick Palladium foils about 7 $\times$ 40 mm were purchased from Sigma-Aldrich. The foils were 99.9% pure on a trace metal basis. A Pharos SP laser (Light Conversion, Ltd., Vilnius Lithuania) operating at λ = 1.03 μm was used to irradiate the foils. The laser output was linearly polarized and orthogonal to the long dimension of the Pd foil. The laser pulse duration was measured at the laser output, using an optical correlator, and found to be between 190 and 210 fs. The delivered pulses were approximately 210–230 fs, due to dispersion in the optical system. The laser pulses were focused onto the Pd foils using a 10$\times$ microscope objective, model LMH-10X-YAG (OFR-Thorlabs, Newton NJ), with a numeric aperture of 0.25 and an effective focal length of 20 mm. The focused laser beam had a Gaussian profile with an estimated spot size of 10–15 μm (FWHM). The laser delivered individual pulses at a rate of 200 kHz. Hence, the maximum number of shots on a given spot was delivered in a time of only 0.5 ms. All laser exposures were performed in ambient air.

The Pd foils were translated using a precision XY translation stage (Aerotech Inc., Pittsburgh PA). In addition to translating the sample in a raster pattern, the program that drove the *XY* motion also controlled an electro-optic modulator in the laser. Hence, a preprogrammed number of shots could be fired on each location with a chosen laser power. A burst of laser pulses was fired every 25 μm. Five square regions were laser irradiated with 1, 3, 10, 30, and an unknown number exceeding 100 shots/spot. Within each square region, the laser power was adjusted to one of five power settings, ranging from 0.35 to 1.1 W. These laser powers corresponded to laser fluences varying from 0.96 to 3.1 J/cm^2. In this way, a single Pd foil was created that allowed us to investigate the laser induced surface texturing as

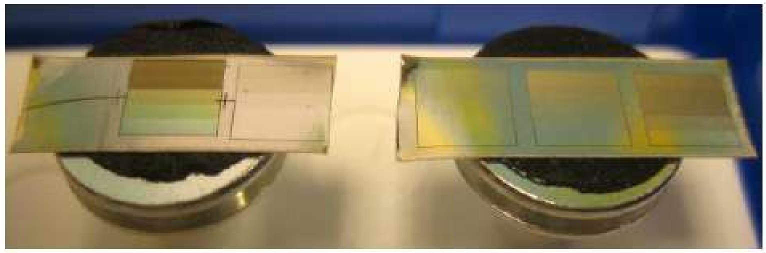

Figure 2. Visible light mages of the laser irradiated Pd foil cut into two pieces and mounted on 1 cm diameter SEM stubs. The squares are 5 mm on a side. The six regions are (left to right) not irradiated, heavy irradiation, and these numbers of shots per spot: 1, 3, 10 and 30. The total numbers of shots on the heavily irradiated square are not known, but exceeded 100. The focal spot laser fluences varied within each band inside of each square (bottom to top): 0.96, 1.1, 1.4, 2.4 and 3.1 in J/cm^2.

a function of both laser power and number of laser shots.

6. Optical Appearance

Visual examination of the irradiated Pd foils revealed colors that depended on the angle of observation. This indicated that those colors were due to diffraction. That observation immediately implied that there were structures on the surfaces of the foils with spatial wavelengths near the wavelengths of visible light, that is, fractions of a micrometer. Fig. 2 shows a photograph (taken under an ordinary fluorescent light) of the Pd foil, cut into two pieces and mounted on the stubs for the scanning electron microscope.

7. SEM Images

A Zeiss Sigma VP scanning electron microscope was employed to obtain micrographs of the laser processed Pd. A secondary electron signal was measured with an in-lens detector. We recorded SEM images of the unirradiated part and many of the irradiated areas on the Pd foil. Several of them are presented in this section to show the effects of the laser pulses on the target under various conditions.

Figure 3 is an image taken from the unirradiated part of the Pd foil. It contains significant structures. However, it will be seen that the features observed on the laser-processed parts of the foil are very different from those present in this figure. That is, the pre-shot structures seen in Fig. 3 seem to be irrelevant. We note that irradiation of a target with short pulse laser effectively cleans it, in addition to altering the surface topography.

One of the basic concerns in this study was the completeness of the coverage of the target surface with laser-effected regions. That coverage is determined by the spacing of the individual laser focal spots, the fluence per pulse and the number of shots placed onto the same spot. Figure 4 shows the coverage for fluence values between 0.96 and 2.4 J/cm^2 and for 3 and 30 shots on a given spot. It can be seen that a low fluence and smaller number of shots yields sparse coverage of the Pd surface. At the other extreme illustrated, the larger fluences and number of shots gives patterns over most of the surface. At this time, we do not know which, if any, of the achievable coverages is best for production of excess energy. The optimum structures for production of LENR are similarly unknown.

The next concern is the shapes of the structures within the focal spots, again as a function of the fluence and number of shots. Visual inspection of the images showed that there were two primary types of structures, roughly parallel lines and sponge-like regions, plus some small spherical features. Figure 5 shows three spots each subjected to over 100 laser shots at two magnifications. It is seen that the edges of these spots, which were subjected to lower fluencies, exhibit the

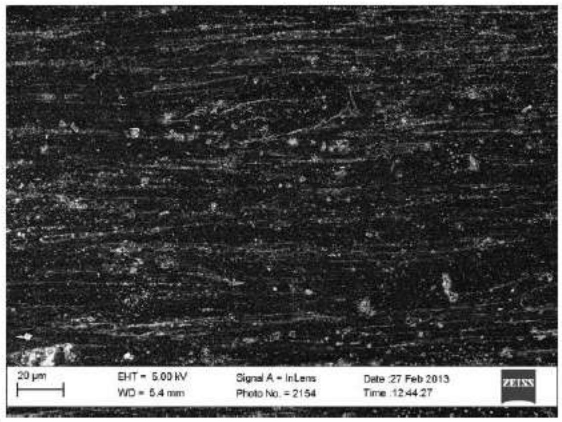

Figure 3. SEM image of a region of the Pd foil not subjected to the femtosecond laser pulses.

parallel structures, while their centers have the disordered and more equiaxed sponge-like features. The approximate periodicity of the parallel structures is evident, even though they are somewhat curved.

The pseudo-linear structures we produced vary in detail, depending on the number of shots. Figure 6 shows examples for two low-fluence (0.96 J/cm^2) cases, one with 30 shots and the other with over 100 shots. The first shows rows of singular features, while the latter has paired structures, both roughly periodic.

The final comparison of SEM images in Fig. 7 shows two high-magnification regions of the sponge-like structures on targets subjected to 3 shots at 1.1 J/cm^2 and greater than 100 shots at 2.4 J/cm^2. This mixture of fluences does not mask the trend for the disordered structures to grow somewhat with increasing shot number.

Small spherical objects appear in the bottom part of Fig. 6 and both parts of Fig. 7. These provide evidence that, at some point during the train of multiple pulses striking the target, the temperature of at least small parts of the Pd exceeded the melting point of 1554°C. It seems likely that the fine structures produced by the earlier shots were heated past the melting point by the later shots in a series of multiple shots.

Examination of higher magnification images than presented in Figs. 5–7 showed both irregular and spherical features on the scale of 20 nm, near the resolution limit of the microscope.

We emphasize that the images presented here and analyzed in the following section are only small samples for the large number of combinations of the parameters, namely the laser fluence and number of shots on each spot, plus all the potential laser and geometrical variables.

8. Image Analysis

Simple inspection of the SEM images shows the existence of LIPSS in some regions of the irradiated spots on the Pd foil. But, it was necessary to analyze the images to obtain quantitative information on spatial frequencies of the Pd structures. Such data might be of use for later correlations of surface structures with the performance of the laser-processed foils in LENR experiments. Those analyses and a sample result from them are described in this section.

Two steps were employed in order to obtain the spectrum of spatial frequencies. First, the varying brightness in the images was determined as a function of position along lines across the images. That brightness is dependent on the number of secondary electrons generated and intercepted by the detector when the SEM beam strikes a fine spot on the target being imaged. The geometry of the surface and the instrument both influence the electron signal and,

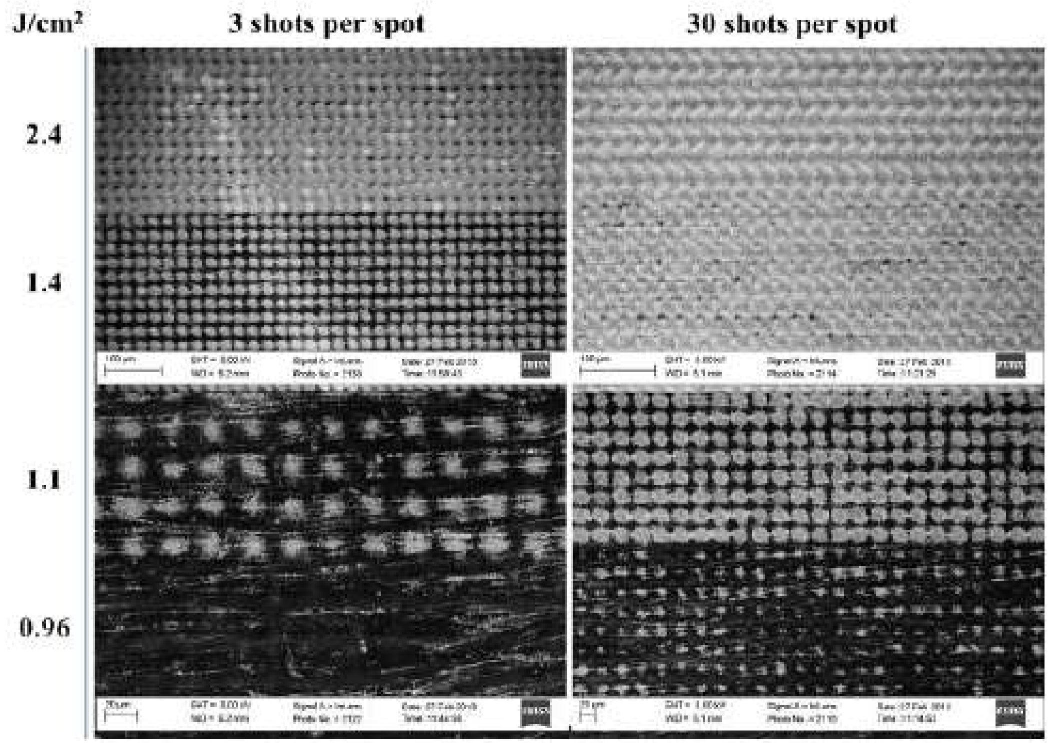

Figure 4. Micrographs for the noted fluences per shot and numbers of shots on individual locations on the Pd foil. The magnifications are indicated by the labeled bars in the lower left hand corner of each micrograph.

hence, the apparent brightness from each location on the target. Despite such limitations, the brightness vs distance plots do depend on the structures present on the Pd foil. All images contained 1024×768 pixels after digitization using MatLab. Hence, the brightness vs distance plots contained numbers of points depending on whether the lines were oriented horizontally or vertically relative to the images (and the long dimension of the Pd foil). We used the highest magnification available images. These typically had 100 pixels per micron on the Pd sample. The brightness values were normalized to the 0–1 range.

The second step in the analyses was to subject the brightness vs distance plots to a Fast Fourier Transform (FFT), again using MatLab. Because the plots were relatively noisy, the brightness vs distance curves were subjected to a smoothing function prior to use of the FFT. The resulting spectra contained peaks that quantified the spatial frequencies in the samples.

We focused on the images shown in the top of Fig. 6 and the bottom of Fig. 7 because they were good examples of both the linear and sponge-like features produced by the femtosecond laser. Fig. 8 is one example of the brightness variation taken along a vertical line in the image on the top of Fig. 7, about one third of the way from the left edge to the right edge. As indicated, the brightness vs distance plot was smoothed. The results of the FFT are shown in the bottom of Fig. 8. It is seen that there is one dominant spatial frequency at about 0.25 inverse micrometers. Analyses such as this will be made for many more lines in regions of targets irradiated with different fluences and numbers of

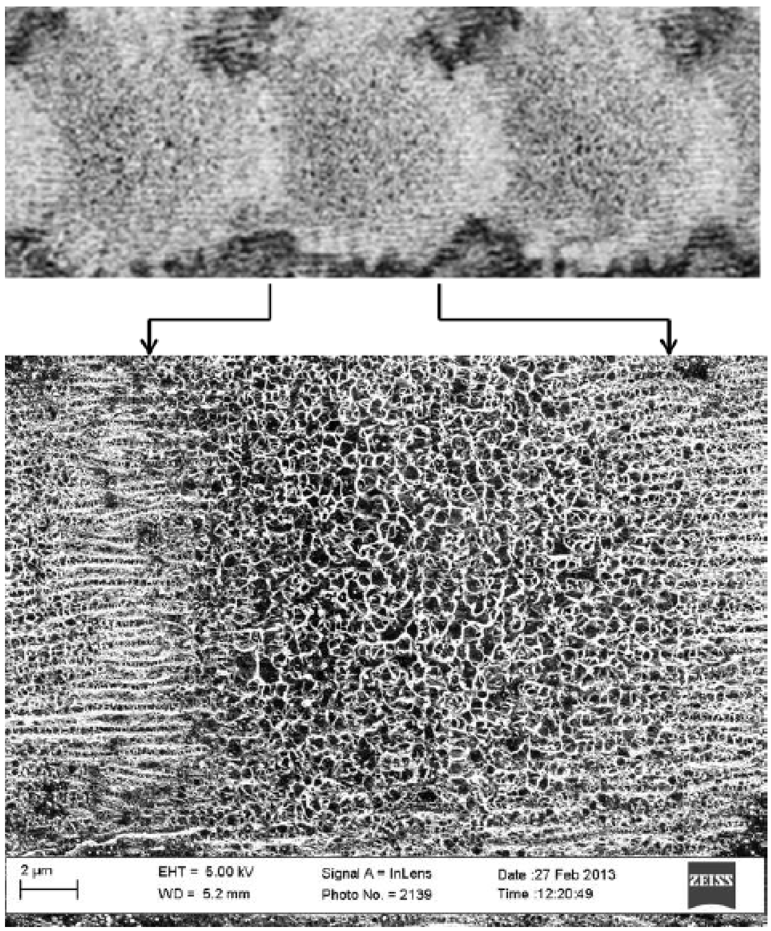

Figure 5. Top. Images of three spots irradiated with ovwe 100 shots at 3.1 J/cm^2. Bottom. Higher magnification of the central spot showing the two major types of structures observed in this work.

shots.

9. Discussion

The aim of this paper was to exploit LIPSS, but not necessarily advance their understanding. There are several possibilities for the influence of the produced and analyzed laser-induced structures on the ability to produce LENR. One is that the structures reported here will have no beneficial influence on generation of excess power. Another is that they will assist in the production of power, but the variety of structures will not matter. That is, LIPSS of different characters and scales will help with the production of LENR. And, it might be that those variations will prove significant, with some producing no or little excess power and others causing significant increases in the rate of LENR.

It might happen that laser processing of surfaces of materials for LENR, followed by a second and separate physical

Figure 6. Images showing roughly parallel and periodic structures for 30 shots (top) and over 100 shots.

or chemical process, will be beneficial. Deposition of thin films of other materials onto the laser targets is one option. Etching of the features seen above in order to remove the finest structures or sharpen the larger structures is also possible. The problem, of course, is the very large number and range of parameters, even with one step of surface preparation. Only some of them were exercised in this study. An additional step in surface preparation adds many possibilities. However, it might turn out that doubly processed cathode surfaces will prove to be the best for production of LENR.

10. Planned Work

The next phase of our program is to repeat the laser exposures shown in this paper in order to insure that they are reproducible, at least statistically. In the process, we will continue to perform parametric studies in order to insure that we can willfully produce structures with desired shapes and sizes within the limits of surface processing with a femtosecond laser.

Having a wide variety of structures on the surfaces of a single Pd foil enables combinatorial experiments. If cathodes with diverse structures in different locations of the cathode produce excess heat, then we will make new cathodes with

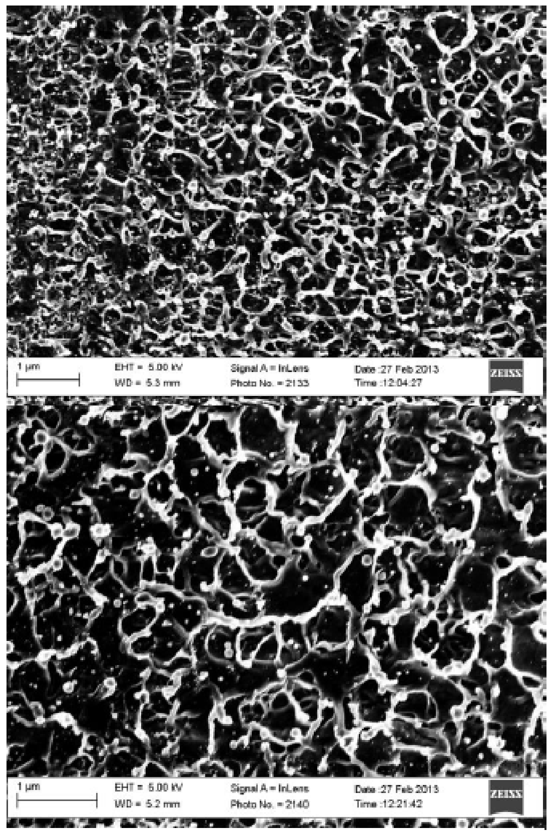

Figure 7. Comparison of central focal regions for spots with 3 shots (top) and over 100 shots.

larger areas of the surface topographies that were present on the initial sample. Sequential experiments will permit us to identify the structures, and the associated laser processing parameters, with the ability to produce the most excess power.

As noted earlier, the work reported here deals with the first three steps in a research program to produce excess power electrochemically and to correlate performance with the structures on the surfaces of Pd cathodes. Figure 1 shows all parts of the program. A Seebeck calorimeter has been constructed and calibrated, and will be used in the near future to run laser-processed cathodes.

References

[1] D.J. Cravens and D.G. Letts, Practical techniques in CF research: triggering methods, *Proc. ICCF-10, Condensed Matter Nuclear Science*, P.L. Hagelstein and S.R. Chubb (Eds.), World Scientific, Singapore, 2006, pp. 171–181.

[2] V. Violante et al., Material science on Pd–D system to study the occurrence of excess power, *Proc. ICCF-12, Condensed Matter Nuclear Science*, A. Takahashi et al. (Eds.), World Scientific, Singapore, 2006, pp. 55–64.

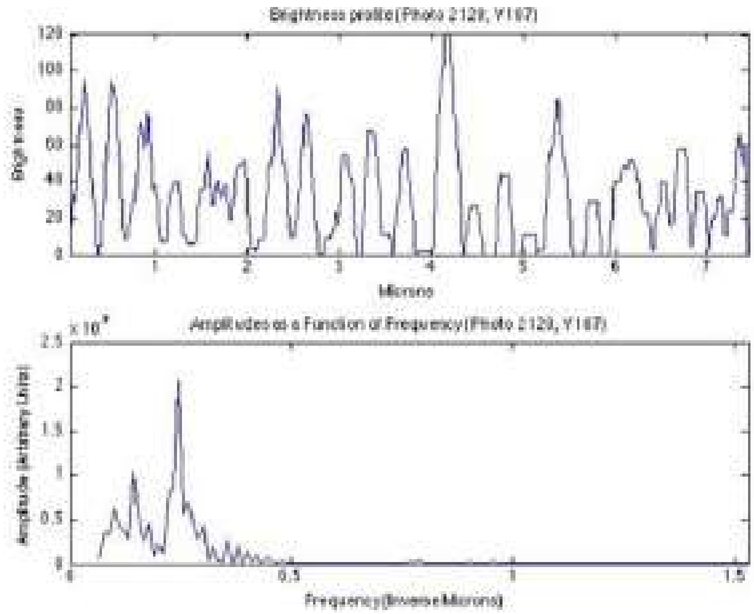

Figure 8. Top: brightness vs distance from Photo Number 2120 in Fig. 6. Bottom: the spectrum of spatial frequencies, where the horizontal scale is in inverse micrometers.

[3] V. Nassisi et al., Modification of PH_2 and Pd–D_2 thin films processed by a He–Ne laser, *J. Cond. Matter Nucl. Sci.* **5** (2011) 1–6.

[4] E. Storms, *The Science of Low Energy Nuclear Reactions*, World Scientific, New Jersey, 2007.

[5] E. Storms, Excess power production from platinum cathodes using the Pons–Fleischmann effect, *Proc. 8th Int. Conf. on Cold Fusion,* F. Scarammuzzi (Ed.), Italian Physical Society, 2000, pp. 55–61.

[6] Y. Iwamura, T. Itoh and S. Sakai, Observations of low energy nuclear reactions induced by D_2 gas permeation through Pd complexes, *Proc. of ICCF-9*, X. Z. Li (Ed.), Singhua Univ. Press, 2002, pp. 1412—146.

[7] Y. Iwamura et al., Low energy nuclear transmutation in condensed matter induced by D_2 gas permeation through Pd complexes: correlation between deuterium flux and nuclear products, *Proc. ICCF-10, Condensed Matter Nuclear Science*, P.L. Hagelstein and S.R. Chubb (Eds.), World Scientific, Singapore, 2006, pp. 435–446.

[8] E. Castagna et al., Metallurgical characterization of Pd electrodes employed in calorimetric experiments under electrochemical deuterium loading, *Proc. ICCF-14*, D. J Nagel et al. (Eds.), 2008, pp. 44450.

[9] http://en.wikipedia.org/wiki/Laser#History

[10] W.M. Steen and J. Mazumder, *Laser Material Processing*, Springer, London, 2010.

[11] Md. S. Ahasn and M.S. Lee, *Femtosecond Laser Processing of Materials: Fundamentals, Technologies, and Applications*, Lago Academic, Saarbaiicken (Germany) 2014.

[12] A.Y. Vorobyev, V.S. Makin and C. Guo, Periodic ordering of random surface nanostructures induced by femtosecond laser pulses on metals, *J. Appl. Phys.* **101** (2007) 34903.

[13] J. Bonse et al., Femtosecond laser-induced periodic surface structures, *J. Laser Applications* **24** (2012) 42006.