LASER ANNEALING EXPERIMENTS WITH NIOBIUM

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Abstract

We describe our recent pulsed laser annealing studies on small samples of bulk niobium. We compare the effects of annealing over a range of single pulse energy density, and in three gas environments: air, nitrogen, and argon. Our Nd:YAG laser allows annealing studies with 266 nm UV light, and with 532 nm green light. We examine the sample surface for structural changes by SEM (Scanning Electron Microscope) and by MicroXAM (a surface mapping microscope).

INTRODUCTION

We investigate the possible benefits of fast-pulsed laser annealing the inner surface of niobium SRF cavities. We report here results of small sample tests based on achieving a local, short-lived surface melt condition on bulk niobium, with no significant global heating. In an SRF cavity, surface smoothing will tend to reduce high field emission, and impurity reduction will tend to reduce residual surface resistance. The ultimate goal of this program is cavity operation with higher Q at higher accelerating field.

The same sort of procedure might benefit both bulk niobium cavities and niobium film cavities, and the program will soon turn to the study of niobium films on copper and other substrates. However, ten years ago a CERN group [1] used a XeCl Excimer UV laser at 308 nm to anneal sample niobium films on copper substrates. They found that eruptive events confined them to a very narrow operating range in single pulse energy density. Since this limiting behaviour might be an artifact of the nature of the film and/or of the Nb/Cu interface, we begin our program on bulk niobium.

The absorption/penetration profile of UV may differ from than that for visible light, so we compare annealing with both UV and with green laser light.

The momentarily hot spot on the niobium surface will eject atoms of surface contaminants, but it will also tend to reabsorb any light element atom that strikes it during its rapid cool-down. To investigate any recontamination tendency, we annealed in three different ambient gas environments, air, nitrogen, and argon.

EXPERIMENTAL PROCEDURE

This is a collaborative study involving 3 institutions. Laser annealing is done at Simon Fraser University, SEM surface studies are done at York University, and profilometry studies are done at Cornell University. Three samples of bulk niobium were tested. Samples 1 and 2 were 0.25 mm 99.9% pure rolled Nb foil supplied by Goodfellow Corp. (UK), while sample 3 was a three millimeter thick high purity sample. It was our last remaining fragment from a batch annealed by DESY at 1400C, and initially had very high RRR [2]. This fragment had experienced further experimental treatment at Cornell. All 3 samples were rather rough. The first 2 were cut from rolled 0.25 mm niobium foil, and had a sharp "nap" which could be felt by the hand. The roughness of the third was associated with a large-grained crystal structure from its treatment history.

The laser annealing setup at SFU uses a Coherent Infinity Nd:YAG laser, modified to selectively switch between the fundamental 1064 nm (Near IR), second harmonic (532 nm, Green), fourth harmonic (266 nm, Deep UV), fifth harmonic (213 nm) using non-linear optical crystals. The laser pulses are 4 nsec long, and maximum power ranges from 600 mJ/pulse (for 1064 nm) to 40 mJ/pulse at 216 nm. The laser table system directs the laser beam using dielectric mirrors to an objective lens system for focus on the Nb sample surface. The sample is held on a X,Y,Z table system that can position the laser spot within 0.05 microns. A camera system observes the sample through the same objective lens. The lenses used were 50 to 100 mm quartz simple lenses, depending on the experiments. Initial tests on Nb sample 1 were done with a 532 nm (second harmonic) beam focused by an f=50 mm lens, and a 266 nm (fourth harmonic) UV beam focused by an f=100 mm lens. The beams were defocused on the surface to give a 100 micron diameter spot. Better results were obtained on samples 2 and 3 with 532 nm using a defocused spot from a 50 mm lens. The surface was located 5 mm above the focus to yield a 260 micron spot with much higher uniformity across the annealed areas. Samples were annealed in air, nitrogen and argon atmospheres. For nitrogen and argon a 37 mm diameter tube ran from the lens to the mounting block with gas flowing in the system. With the sample located near the center of this tube end, and the end nearly flush with the mounting block, gas flow was such that very little backflow occurred. Little of that reached the sample, which was always at least 15 mm from the edge of the tube. This is a typical set-up for laser annealing in selected atmospheres where high purity is not required and flexibility of movement is needed.

The laser was run typically at a 10 hz pulse repetition rate. The surface melt condition lasts more than an order of magnitude longer than the pulse length of 4 ns, but global heating is negligible. The temperature rise of a sample during its entire annealing exposure is typically a fraction of one degree C.

On each sample, many 1 mm square "lands" were

annealed in a rectangular array, each row with a particular laser wavelength and ambient gas environment, each column with a particular incident energy per pulse. Each 1 mm square land was raster scanned in several passes with these parameters fixed. A land-to-land separation prevented one land's annealing exposure impacting that of its neighbours. Sample 3 was scanned in the pattern shown in Fig. 1, while samples 1 and 2 were scanned with all passes in the same direction.

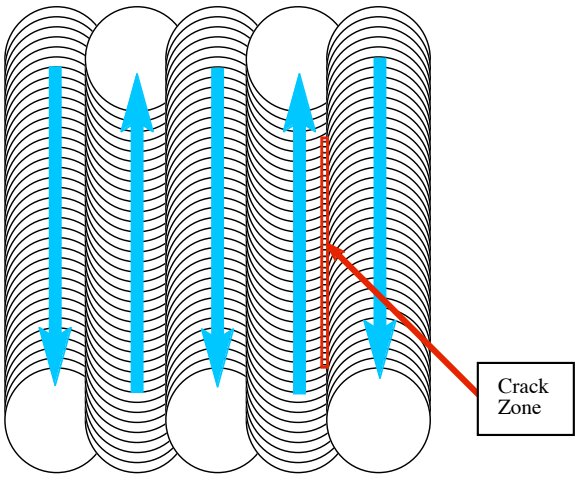

Figure 1. Annealing a "land" on sample 3.

To ensure that there were no unannealed gaps within each 1 mm square land, the table movement was programmed to provide a generous overlap, both pulse-to-pulse and pass-to-pass. For example, for the 260 micron defocused spot used in annealing samples 2 and 3, the pulse-to-pulse advancement was 25 microns, and the pass-to-pass offset was 200 microns.

Niobium expands when it melts. With our present technique a single pulse produces a slight rim as the melt overflows onto the cooler surrounding metal, giving a characteristic rimmed footprint. As the table moves, each subsequent laser pulse melts down the forward part of the footprint of the previous pulse, leaving a pattern of stern-wave ripples spaced by 25 microns. This pattern gives a very heavy overlap at the side of each pass, which tended to produce hairline cracking in the narrow regions near the overlap from the subsequent pass, indicated by Fig. 1's inclined arrow. These cracks show in many SEM pictures for samples 2 and 3, where the large 260 micron spot was used, simply because they provided a tempting object for focusing the SEM at X5000 in a field without other sharp features. Their actual occurrence is limited to the region indicated in Fig. 1.

The SEM work at York U used a Hitachi S520 Scanning Electron Microscope with output on Kodak 125PX-220 photographic film. After development, the film was scanned into a computer for comparative studies. The profilometry studies at Cornell used MicroXAM, a surface mapping microscope made by ADE Phase Shift, Inc.

RESULTS

The impact of annealing is explored in Fig. 2 using SEM images from samples 1 and 2 at X5000. Each image is 18 microns wide. The annealing atmosphere was air.

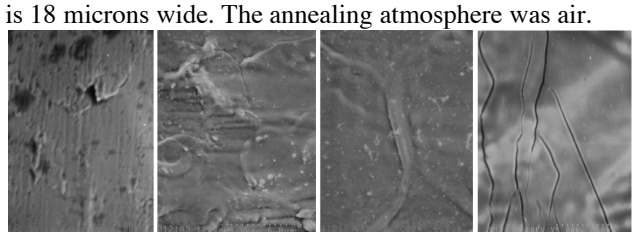

Figure 2a-d: Niobium surfaces laser-annealed in air.

The surface shown in Fig. 2a is unannealed; in Fig. 2b, annealed with UV (266 nm); in Figs. 2c and 2d, annealed with green light (532 nm). The annealing beam spot was smaller and more focused for Figs. 2b and 2c, larger and defocused for Fig. 2d. Note the sharp rough "nap" on the unannealed surface shown in Fig. 2a. The annealed surfaces appear smoother on the submicron scale, and much of the sharp nap has been melted down. However, they reveal the footprint of the laser beam. Fig. 2c shows the rim that tends to be produced at the spot perimeter, while Fig. 2d shows the very fine hairline cracks mentioned above. These do not in general follow grain boundaries, but are predominantly aligned with the laser scan direction. Our best SEM images often contain these cracks, because they provide a good target on which to focus at X5000.

All our further studies were done with the larger defocused 260 micron diameter beam spot, and with the wavelength at 532 nm (green). Possible advantages of UV annealing will be investigated in the future, but visible light requires less single-pulse energy than UV to produce a surface melt condition, and is much easier and cheaper to handle in the lab (and in industry).

We looked for effects of ambient gas environment during annealing. In Fig. 3 we use Sample 2 SEM photos from regions with thermal cracks for this comparison because the surface here is otherwise typical, and the cracks facilitate good focus at X5000 on our film-output SEM. Single pulse energy density was 8.4 J/cm^2.

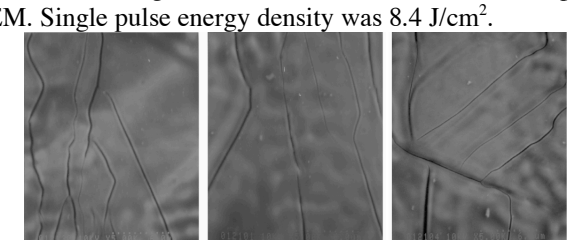

Figure 3a-c: Niobium surfaces laser-annealed in air, nitrogen, and argon. Each image is 18 microns wide.

The surfaces seen by SEM at X5000 in Fig.3 are very similar to each other, but quite different from the unannealed surface of the same sample shown in Fig. 2a.

The higher the single pulse energy density, the more the melt process modifies the surface. The effect is seen in SEM images of sample 3 shown in Fig. 4. Starting from the left, these 90 micron wide images show the

progression of roughness with single pulse energy density from 0 (unannealed), to 6, 9, 12, and 15 J/cm^2/pulse.

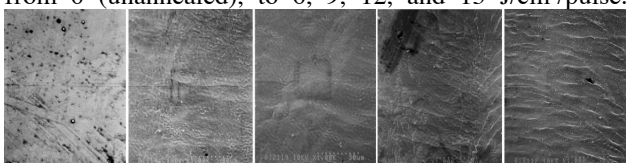

Figure 4: Roughness increasing with energy density.

Our rough surfaces prevent detailed interpretation of our profilometry measurements. However, they do show the roughness to be large and variable, with rms values ranging from 300 to over 1000 nanometers. They also show the expected tendency to increasing roughness of the laser footprint with increasing single pulse energy density. The dominant contribution to roughness is from large excursions (see Fig. 4d) associated with the overlap ridges between successive overlapping annealing passes.

Optical photographs of all three samples show a brownish coloration of the annealed lands, which increases with increasing single pulse energy density. An optical photograph (by a Canon S70 in macro mode) of Sample 2 is shown in Figure 5, where each of the 18 annealed lands is 1 mm square.

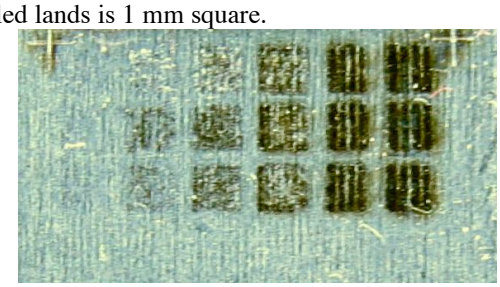

Figure 5: Increased coloration with energy density.

Row 1 was annealed in air, row 2 in nitrogen, and row 3 in argon. Energy density varies from 0.6 J/cm^2/pulse on the left to 15.0 J/cm^2/pulse on the right. The effect appears independent of ambient atmosphere used for annealing.

CONCLUSIONS

Our aim was to use a laser to produce a momentary surface melt condition on samples of niobium, and to test its ability to smooth the surface and/or improve the subsurface chemistry. We find that a Nd:YAG laser can melt down substantial surface roughness features on a niobium surface, using either its 266 nm or 532nm beam.

Our present annealing beam melts down existing surface roughness features, but it leaves its own rough footprint. This footprint of ripples and waves gives too much roughness for an operating SRF surface, and it prevents the study of profiles of subsurface light element contaminants in the first 200 nanometers. Our future developments must first reduce the roughness of the laser beam's footprint to a few tens of nanometers. This may take us in the direction of a much lighter overlap and/or lower single pulse energy density. The overlap-associated problem of hairline cracks may solve itself at the same time. Lower energy density will be more useful for annealing Nb films on Cu and other substrates.

The SEM images of our laser-annealed surfaces show no dependence of the annealed surface on our annealing gas environment, over a wide range of single pulse energy density. However, visible light photos show a brownish coloration for all 3 annealing gas environments, whose intensity increases with single pulse energy. The short duration of the surface melt condition may not allow significant gas absorption at the liquid surface, but our newly annealed niobium surface will remain a strong getter during subsequent cool-down, and may have found enough residual air in our argon environment to saturate itself with nitride, for example. Further, light elements can diffuse to the new surface from the interior of the sample during cool-down from the melt condition. Finally, at least oxygen and hydrogen will be absorbed by the newly annealed surface from moist lab air [3] at room temperature on a longer time scale, i.e. after removal from the argon environment.

Surface chemistry studies will have to wait for the roughness improvement. We may find a UV beam to be a more effective tool for changing the subsurface interstitial chemistry; but unless UV is shown to be necessary, visible light is a better choice. Second harmonic 532 nm beams from Nd:YAG lasers give us higher power ranges at lower cost, and they are easier to focus with regular optics.

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