LA-UR 94-3656

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Authors: T. R. Jervis, J. P. Hirvonen, T. G. Zocco, and J. R. Tesmer

Submitted To: Materials Research Society Symposium Proceedings, Materials Research Society, Pittsburgh, PA

Los Alamos

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

TRIBOLOGY AND SURFACE MECHANICAL PROPERTIES OF EXCIMEP LASER NITRIDED TITANIUM

T. R. Jervis*, J. P. Hirvonen**, T. G. Zocco*, and J. R. Tesmer*
*Materials Science and Technology Division
Los Alamos National Laboratory, Los Alamos, NM 87545
**Metallurgy Laboratory, Technical Research Institute of Finland, SF-02150 Espoo, Finland.

ABSTRACT

We have nitrided Ti-6Al-4V alloys using excimer laser pulses at 1.2 J-cm^{-2} in high purity N_2 at approximately one atmosphere. Substantial nitrogen and some oxygen incorporation resulted from multiple pulse processing. Formation of a TiN surface film was not observed. We have examined the tribological and mechanical properties of these surfaces using pin-on-disk and nanoindenter techniques respectively. Nitrogen alloying results in reduced friction and torque noise in the pin-on-disk measurements. At higher N concentrations, very little wear is observed, even after the friction behavior suggests surface deterioration. This is consistent with the formation of a transfer film at the sliding interface. Nanoindenter measurements of the surfaces show increasing hardness proportional to nitrogen incorporation. The tribological improvements can therefore be ascribed to a combination of increased surface hardness and tribochemical effects.

INTRODUCTION

Titanium alloys are widely used in applications which require a high strength to weight ratio at relatively high temperatures (up to 300 C), as well as in surgical prostheses on account of their biocompatibility[1]. However, Ti alloys are also known for their poor tribomechanical properties and as a result, numerous surface modification techniques have been applied in order to increase wear resistance of the alloy's surface. In particular, laser techniques have focused on treatment of Ti alloys in a nitrogen or ammonia atmosphere[2, 3, 4, 5, 6]. These have relied on infrared (IR) laser energy, generally from either CO_2 or Nd-YAG lasers, as these are standard industrial lasers used for a number of surface modification processes[7]. These methods produce a thick TiN surface layer, which is indeed quite hard. However, much of the incident energy of these lasers is wasted as Ti is a good reflector at these wavelengths. Excimer lasers, using an ultraviolet wavelength at which coupling between the laser light and the metal surface is quite strong, have also been used to create a TiN surface layer, but under processing conditions in which the Ti surface remains molten between laser pulses[8]. Nitrogen ion implantation of Ti alloys has also increased hardness and improved wear behavior through precipitation of TiN particles in the α-Ti matrix[9, 10, 11, 12, 13, 14] and formation of a TiN surface layer[15].

We have studied the alteration of surface properties of Ti alloys using excimer laser radiation at low repetition rates. At these rates, the surface cools fully between pulses and each pulse can be considered independent. Thus phase formation is determined in large part by the rapid solidification and cooling (~10^{10} K-s^{-1}) experienced by the sample[16]. In previous work we processed the surface in air and found extensive oxygen incorporation into the surface and precipitation of TiO (γ phase) particles[17]. We observed substantial surface hardening of Ti-6Al-4V from solution and precipitation mechanisms. This paper will report on the effect of excimer laser melting and solidification in nitrogen on the tribology, microstructure, and surface hardness of Ti-6Al-4V.

EXPERIMENT

Samples of commercially obtained Ti-6Al-4V were mounted in standard metallurgical mounts and mechanically polished with 1 μm grit prior to electropolishing. Samples were then laser processed in dry, ultra-high purity nitrogen at a fluence of 1.0 J-cm^{-2} using 248 nm light from a KrF excimer laser. The samples were mounted in a vacuum chamber which was repeatedly evacuated to a pressure of the order of 10^{-7} T and backfilled with ultra-high-purity nitrogen before being filled to one local atmosphere (~600 T) for the processing. The beam was homogenized using a multi-element refractive homogenizer which produces a square spot of uniform illumination intensity on the sample[18]. Because the sample returns essentially to room temperature within 0.1 sec, repetition rates of up to 10 Hz can be used without significant bulk heating of the sample. One region of each sample was unprocessed for comparison in the analysis.

Analysis of the nitrogen content of the material was performed using non-Rutherford resonant backscattering of α particles at 8.81 MeV in Ti alloy samples[19]. This technique provides relative nitrogen concentration (N:Ti ratio) as a function of depth from the surface. The measured density of N was normalized to at % concentration using the density of Ti. This analysis was used to calibrate the nitrogen concentration–processing relationship.

Transmission electron microscopy (TEM) samples were obtained from the various areas and jet-thinned from the back. The laser processed side of the TEM disk was protected during the thinning operation. The thinned samples were examined in a JEOL 2000EX TEM-STEM operating at 200 KeV.

Tribological measurements were made using a standard pin-on-disk tribometer with a AISI 52100 steel pin. Pin diameter was 6 mm, the diameter of the track 4 mm and the speed 1 revolution per second. The load on the pin produced a Hertzian contact stress of 0.44 GPa and a Hertzian contact diameter of approximately 50 μm. All tests were terminated after 1000 revolutions.

The surface hardness of the samples was measured using a commercially available nanoindenter[20]. This instrument directly measures the load on a triangular pyramid diamond indenter tip as a function of displacement, h, from the surface. Hardness is determined from the load data using the projected area of the indent, obtained from previous calibrations[21]. Measurements were made under constant loading rate of 80 $\mu N\text{-}s^{-1}$ to a nominal depth of 100 nm. At least nine indents were made on each sample and the data for each sample averaged.

RESULTS AND DISCUSSION

As in excimer laser surface processing in air, incorporation of N scales with the total melt duration. However, incorporation of N is not so efficient as that of O. Figure 1, based on the nuclear reaction analysis profiling of O and N in separate experiments, demonstrates this clearly. Diffusion scales with the square root of melt duration (number of pulses x approximate per pulse melt duration of 100 ns) as expected for a diffusion process. Further, the diffusivities calculated from these measurements are of approximately the correct order of magnitude for liquid state diffusivities. However, although the experiments reported here were done in high purity N_2, the purity of which was checked using a residual gas analyzer, we find substantial incorporation of O in the material along with the N. The source of this O is unknown, as analysis of the samples in untreated regions shows no anomalous O. The possibility exists that very small quantities of O in the lattice diffuse rapidly to the surface during the heating cycle. However, although the effect is seen both in the Ti-6Al-4V samples used in these experiments and in ultra high purity Ti samples, it is not seen in some other Ti alloys[19].

The evolution of the microstructure of laser nitrided Ti is also quite similar to that reported for Ti processed in air. The initial α grains transform immediately to martensite and then gradually form smaller and smaller grained dispersions of Ti and TiN/TiO. The microstructure found in Ti processed in pure N_2 is consistent with either TiO or TiN as these two FCC phases are indistinguishable by selected area electron diffraction. The concentrations of N and O found in the nuclear reaction analysis suggests that both TiO and TiN precipitates are present.

Figure 2 shows the friction behavior of the untreated and treated (160 and 320 pulses) surfaces. Measurements were terminated after 1000 revolutions, at which point the friction and torque noise for the three cases were similar. The untreated surface shows a rapid deterioration of friction coefficient due to adhesion of the Ti surface to the sliding pin. In the 160 pulse treated case, an initial period of low friction and low torque noise is followed by a gradual increase in friction and torque noise to a similar to that of the untreated material. In the 320 pulse treated case, a comparable period of relatively low friction is followed by an increase to levels well above that of the untreated material. After 1000 revolutions the friction is the same for all three cases.

Figure 3 shows both the wear track and the pin surface for the untreated and 320 pulse treated cases shown in figure 1. Although the friction at the end of the test is similar, the appearance of the sliding surfaces is quite different. In the untreated case, there is substantial adhesion of the Ti to the pin with resulting damage to the wear track in the Ti. In the treated case, by contrast, there is much less damage in the wear track, and the pin appears to be abraded by the treated Ti surface. In the 160 pulse treated case, the appearance of the pin is comparable to that in the untreated case and the wear track is damaged but less severely as in the untreated case.

Figure 4 shows the relative hardness of the surface film as a function of the number of pulses of laser radiation. No particular significance is inferred by the linear behavior. We would expect that hardness would increase as the interparticle distance between the TiN and TiO precipitates became smaller until it saturated. Of significance in this case, at 320 pulses, the hardness of the composite surface is comparable to that of the steel pin, while at 160 pulses, it is well below that of the pin.

The picture of the wear process that emerges from these observations is that the initial period of low friction and also low torque noise is associated with a transfer film of unknown composition that develops on the surface of the Ti. As this film is worn away, a differentiation occurs between the 160 pulse and the 320 pulse conditions. In the 160 pulse case, the depth and degree of N incorporation is not so great. The interaction of the pin and the sample is dominated by the same adhesive interactions that control friction and wear in the untreated case. The friction and torque noise are essentially the same. In the 320 pulse case, the composite surface is comparable in hardness to the pin and further has embedded within it precipitates of TiN which are very hard and abrasive. In this case, abrasive wear of the pin dominates the interaction, resulting in high friction, but relatively less wear on the Ti surface. The result is that changes in the tribochemistry of the surface have a short range effect on the friction and wear through the formation of a transfer film while in the intermediate range, the mechanical properties and complex composition of the treated surface determine the behavior.

CONCLUSIONS

Excimer laser processing of Ti-6Al-4V in N_2 results in the formation of a composite surface of TiN and TiO precipitates in a matrix of Ti. The hardness of this surface approaches a value several times that of the unprocessed material. Sliding friction of a steel pin against the treated surface shows an initial period of quite low friction due to the presence of a transfer film. After this film is worn away, a modified adhesive wear regime for 160 pulse treated samples and an abrasive wear regime for 320 pulse treated samples dominates. This behavior is consistent with the observed hardness of the treated surface. The abrasive wear regime being found as the hardness of the composite surface approaches that of the pin.

ACKNOWLEDGMENTS

We would like to thank Darryl Garcia and the personnel of the Los Alamos Ion Beam Materials Laboratory for technical assistance. This research was supported by the United States Department of Energy under contract W-7405-ENG-36.

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Figure Captions

Figure 1. Diffusion of N and O in Ti-6Al-4V. Half width of distribution as determined by nuclear reaction analysis vs. the square root of the total melt duration. Linear dependence is expected for diffusion processes.

Figure 2. Friction measured in pin on disk geometry as a function of number of revolutions for untreated Ti-6Al-4V surface and surface treated with 160 and 320 pulses of excimer laser radiation in N_2.

Figure 3. Wear tracks (top) and pin surface (bottom) for a) untreated Ti-6Al-4V surface and b) surface treated with 320 pulses of excimer laser radiation in N_2. Adhesive wear in the untreated surface becomes abrasive wear in the 320 pulse treated case.

Figure 4. Relative hardness measured using a nanoindenter as a function of the number of pulses of excimer laser radiation in N_2. No significance is inferred from the linear behavior.

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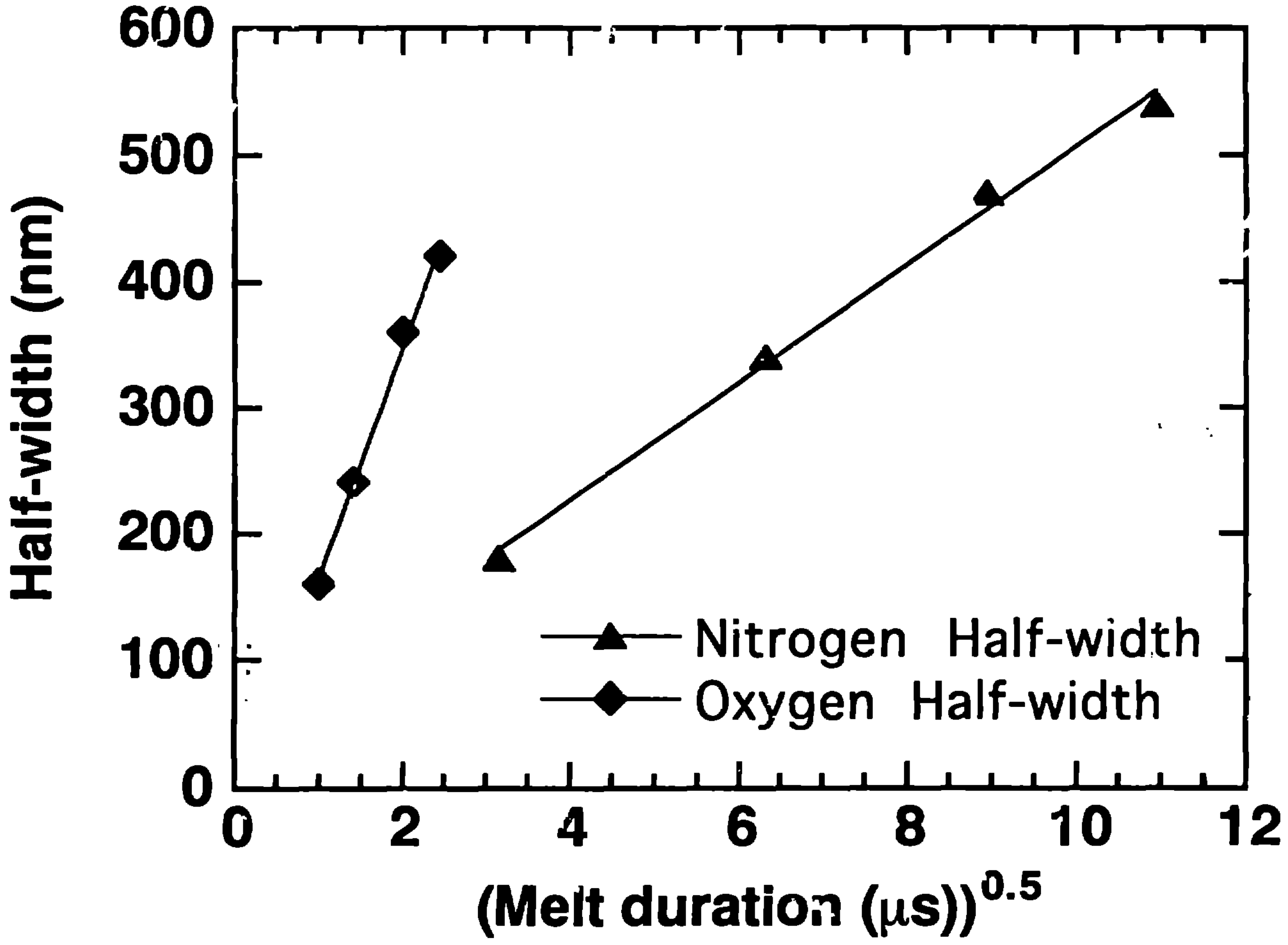
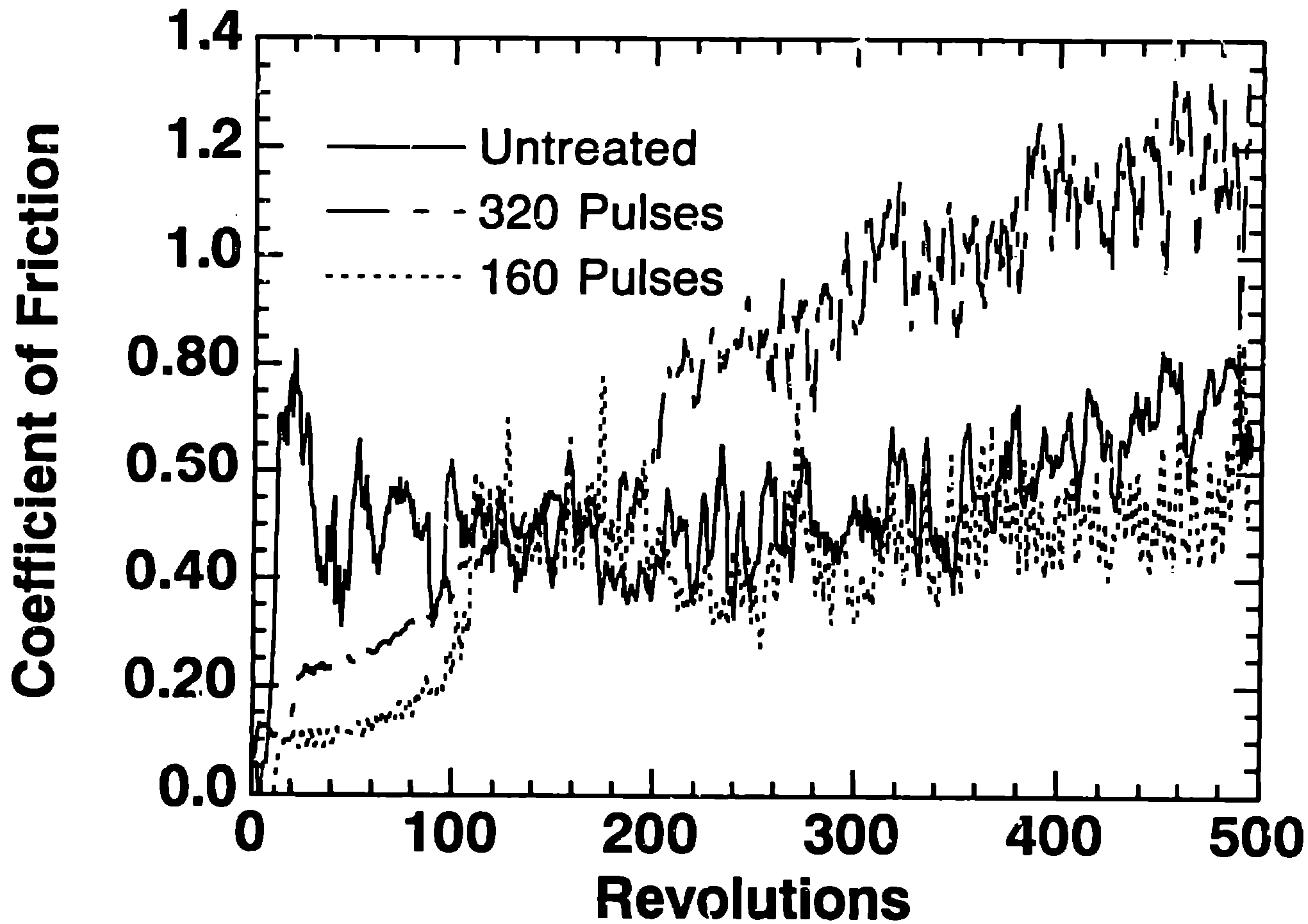
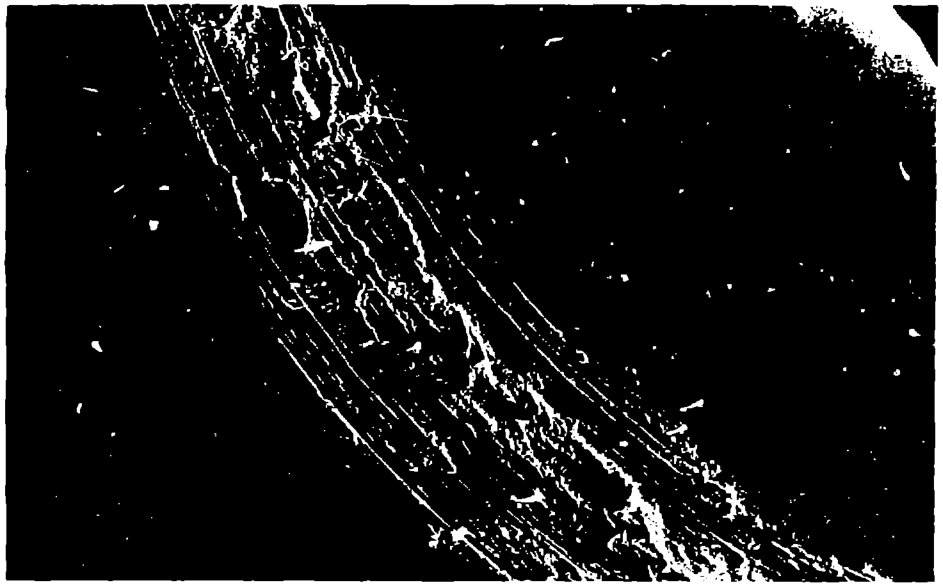
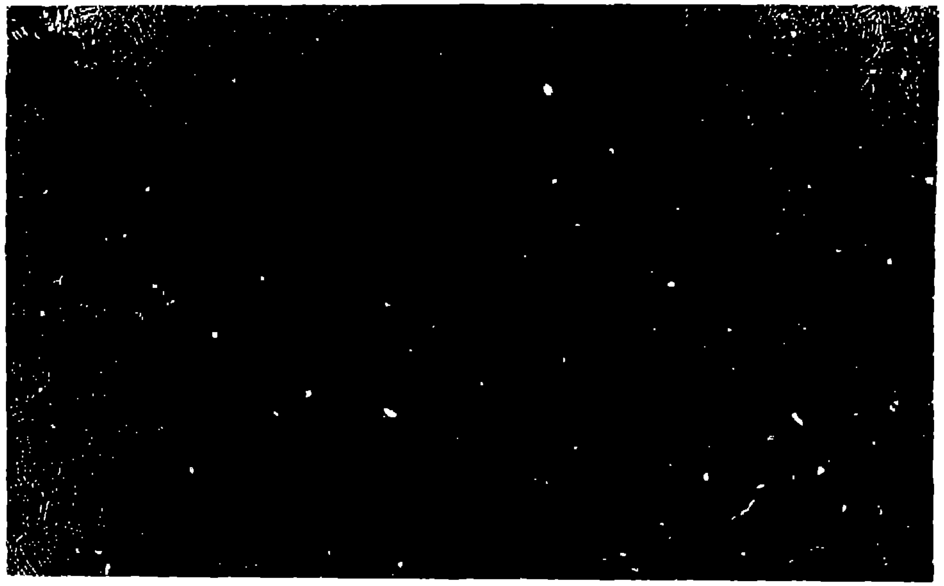


600
500
400
300
200
100
0
Half-width (nm)
0
2
4
6
8
10
12
(Melt duration (μs))0.5
Nitrogen Half-width
Oxygen Half-width


Untreated
320 Pulses
160 Pulses
Coefficient of Friction
1.4
1.2
1.0
0.80
0.60
0.40
0.20
0.0
0
100
200
300
400
500
Revolutions



◄400 μm►



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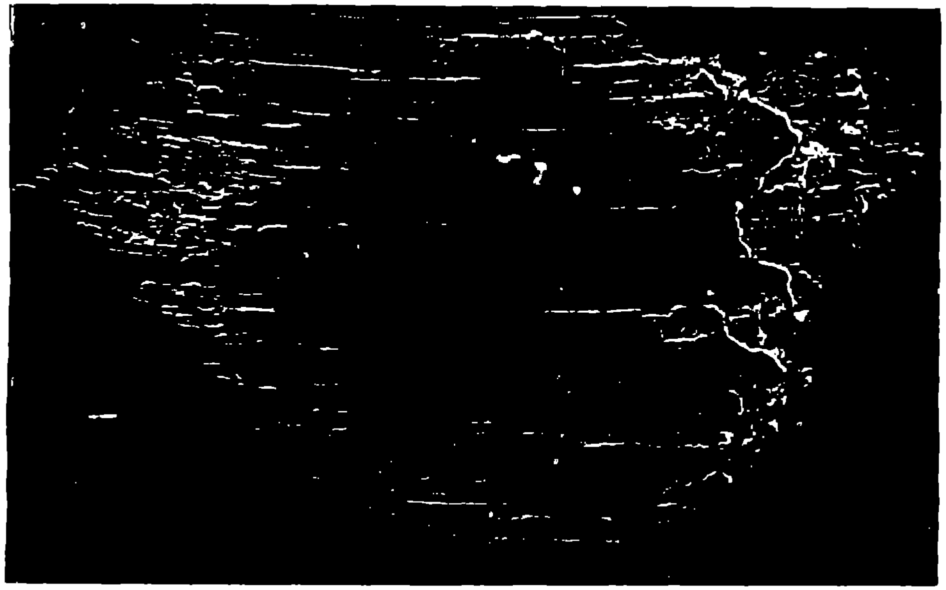
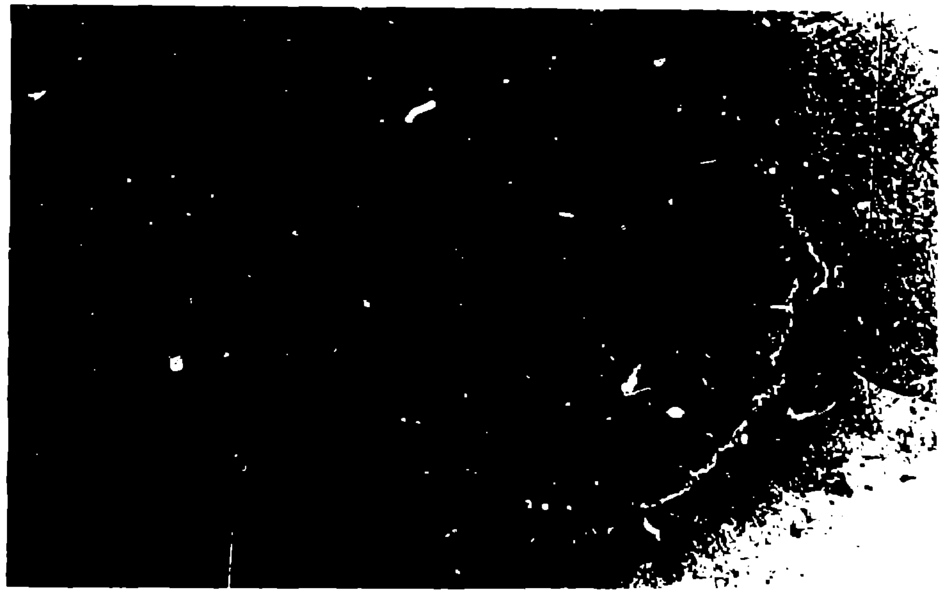
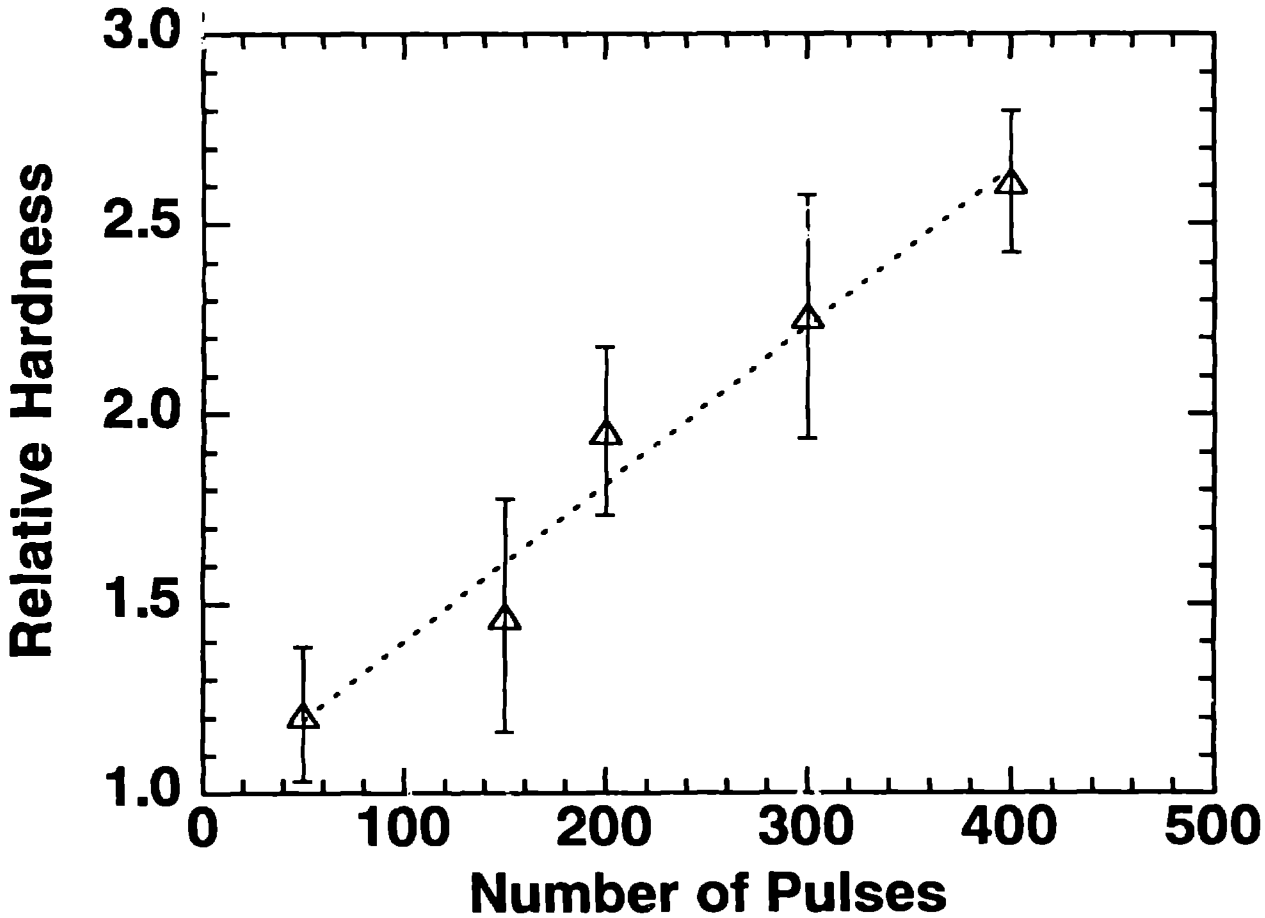


◄200 μm►



◄200 μm►



3.0
2.5
2.0
1.5
1.0
0
100
200
300
400
500
Relative Hardness
Number of Pulses

Fig 4