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**Title** FEMTO-SECOND LASER SURFACE PROCESSING OF TITANIUM

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# **Excimer Laser Surface Processing of Titanium**

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## **ABSTRACT**

We have examined the effect of laser surface processing of Ti alloys using pulsed excimer laser light at 248 nm. Thermal transformations of the surface are accomplished by heating the surface and rapid cooling. Alloying and formation of compounds can be obtained by melting and mixing surface layers into the material and by gas alloying. Multiple melting-resolidification cycles result in the inter-diffusion of surface layers in the liquid state and the diffusion of gas species into the material. The effect of alloying from both solid and gas sources and the effects of thermal transformations on the microstructure and surface hardness properties of these alloys will be examined.

## **INTRODUCTION**

Titanium alloys are used in many 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<sup>1</sup>. 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 surface. These have generally relied on forming a hard N rich surface layer by ion<sup>2, 3, 4, 5, 6, 7, 8, 9</sup> or laser<sup>10, 11, 12, 13</sup> techniques, although some work on C<sup>+</sup> and B<sup>+</sup> implantation has also been carried out<sup>7, 14, 15, 16</sup>. All of the laser techniques mentioned above have relied on infrared (IR) laser energy, generally from either CO<sub>2</sub> lasers operating at 10.6  $\mu\text{m}$  or Nd-YAG lasers operating at 1.06  $\mu\text{m}$ , as these are standard industrial lasers used for a number of surface modification processes<sup>17</sup>. Excimer laser radiation at ultraviolet wavelengths, where coupling between the laser light and the metal surface is quite strong, is increasingly being used for surface modification<sup>18, 19, 20</sup>. A second feature of excimer laser processing is the high cooling rate ( $\sim 10^{10}$  K/s), which favors the formation of non equilibrium phases.

We have observed transformation of  $\alpha + \beta$  material to martensite as a result of rapid cooling. We have also formed amorphous Ti-B surface alloys by mixing an evaporated B layer into the surface, N alloyed surface layers by processing in N<sub>2</sub>, and solution and dispersion strengthened surfaces by oxygen alloying in air. In this paper we will describe the essential physics of excimer laser surface processing and examine the effects of these transformation and alloying experiments on the microstructure and surface hardness of the alloys.

## **EXCIMER LASER MATERIAL INTERACTIONS**

Although the energy per photon of excimer laser radiation is high ( $\sim 5$  eV for 248 nm), the effect of laser radiation on the surface of metals is essentially purely thermal below the threshold for ablation. Thus, at the

fluences used in these experiments ( $\sim 1 \text{ J}\cdot\text{cm}^{-2}$ ), processing can be thought of in terms of a short duration ( $\sim 25 \text{ nsec}$ ) energy pulse which is thermalized essentially instantaneously. Further, the short absorption depth of ultraviolet light in metals ( $\sim 3 \text{ nm}$  in Ti) means that this energy is deposited at the surface of the material with no appreciable distribution. The interaction can therefore be modeled in terms of one-dimensional heat flow into the bulk of the sample from a surface source<sup>21</sup>. There is also radiation from the hot surface and some convection at the free liquid surface, but these effects are relatively minor at the very short time scales of concern here. With sufficient energy deposition the surface of the material melts, and the melt front propagates inward until the energy of the pulse is dissipated in the melting process. The melt front then stops and a resolidification front moves back toward the free surface. The time history of the temperature of the melted surface layer of metals can be calculated directly from the fundamental optical and thermal constants of the material<sup>22</sup>. Although this type of calculation ignores many significant aspects of the solidification process, such as the temperature dependence of many of the variables, we have found it useful in predicting the effect of excimer laser processing on a number of materials<sup>23, 24</sup>. The same calculation is applicable to heat treatment below the melt threshold.

As an example of this type of calculation, Figure 1 shows the temperature as a function of depth in the materials for an incident fluence of  $1.0 \text{ J}\cdot\text{cm}^{-2}$  on Ti-6Al-4V at two times; shortly after the pulse terminates at 30 ns and just at final solidification at 80 ns. Based on the depth at which the  $\beta$  transition temperature is exceeded, we expect a region about  $0.6 \mu\text{m}$  thick to be transformed to martensite. This correlates well with measured

transformation depths<sup>24</sup>. At this fluence, the surface layer is molten for a period of approximately 50 ns. During this time, diffusion in the liquid state ( $D \sim 10^{-5} \text{ cm}^2\text{-sec}$ ) can occur on a distance scale of the order of 10 nm. Multiple pulse processing can increase this distance substantially in direct proportion to the number of pulses. Liquid flow (convection) over comparable distances would require velocities of the order of  $0.1 \text{ m}\cdot\text{s}^{-1}$ , substantially higher than the  $\sim 0.01 \text{ m}\cdot\text{s}^{-1}$  velocities observed in IR laser processing<sup>13</sup>. Direct measurements of diffusion of  $^{13}\text{C}$  in Fe support the assumption that effectively all mass transport occurs by diffusion in the liquid state and not by convection<sup>25</sup>.

In comparison with IR laser processing, the high coupling efficiency, short pulse duration, and shallow absorption depth result in two significant advantages. The first is the rapidity of the solidification which follows melting. Calculations give a cooling rate after solidification in excess of  $10^9 \text{ K}\cdot\text{s}^{-1}$ <sup>18</sup>. This cooling rate is sufficient to suppress the formation of equilibrium phases, a feature we have noted in other systems<sup>26</sup>. The second advantage is the overall efficiency of the process. For processing with 100 pulses per position at  $1.0 \text{ J}\cdot\text{cm}^{-2}$ , a laboratory scale laser with an output of 15 W (average) can treat material at approximately  $0.15 \text{ cm}^2\cdot\text{s}^{-1}$ . Industrial excimer lasers with average outputs of 150 W exist and can process material at rates of approximately  $1.5 \text{ cm}^2\cdot\text{s}^{-1}$ . Comparable processing rates with IR lasers (either  $10.6 \mu\text{m}$  or  $1.06 \mu\text{m}$ ) require tens of kilowatts<sup>10,12,13</sup>. Since excimer lasers are comparable to IR lasers in output efficiency, excimer laser processing provides an increase in processing energy efficiency of the order of  $10^3$  over IR laser processing.

## EXPERIMENT

Samples of commercially obtained Ti alloys were mounted in standard metallurgical epoxy mounts and electropolished using an electrolyte of 84% methanol, 10% butanol, and 6% perchloric acid. Polishing conditions for a 1 cm<sup>2</sup> sample were 30 Vdc for 1.5 min at a temperature below -50 C. Samples were mechanically polished with 1 μm grit prior to electropolishing. A comparison was made of the mechanical properties of electropolished, mechanically polished, and as received specimens and the effect of laser processing on these differing surfaces.

Samples were laser processed at varying fluences using 248 nm light from a KrF excimer laser. The beam was homogenized using a multi-element refractive homogenizer which produces a square spot of uniform illumination intensity. Pulses were overlapped at various repetition rates to alter the number of pulses/ position on the sample. Because the sample returns essentially to room temperature within 0.1 sec, repetition rates of up to 10-20 Hz can be used without significant bulk heating of the sample. Samples were processed in air for the B and O alloying experiments. For the N alloying experiments, the samples were mounted in a vacuum chamber which was repeatedly evacuated to a pressure of the order of 10<sup>-7</sup> Torr and backfilled with ultra-high purity nitrogen before being filled to one local atmosphere (~600 Torr) for the processing.

Analysis of the oxygen content of the material was performed using resonant elastic scattering of α particles at 3.05 MeV<sup>27</sup>. This technique provides relative oxygen concentration (O/Ti ratio) as a function of depth from the surface. Analysis of the nitrogen content of the material was performed using non-Rutherford resonant backscattering of α particles at 8.81 MeV<sup>28</sup> in Ti alloy samples. This technique provides relative nitrogen concentration

(N:Ti ratio) as a function of depth from the surface. The measured densities of O and of N were normalized to at% concentration using the density of Ti. This analysis was used to calibrate the oxygen and nitrogen concentration-processing relationship.

The extent of boron mixing was determined by Rutherford Backscattering spectroscopy (RBS) using 2.0 MeV alpha particles with the substrate held at a 60° angle to the beam to maximize the depth resolution. Boron concentration was determined from the RBS data using RUMP<sup>29</sup>.

Transmission electron microscopy (TEM) samples were obtained from the various areas and jet-thinned from the back side using the electrolyte described above and a high-speed jet. The laser processed side of the TEM disk was protected using microstop, which was removed with acetone upon completion of the thinning operation. The thinned samples were examined in a JEOL 2000EX TEM-STEM operating at 200 KeV. Phase identification was made on the basis of selected area diffraction (SAD) patterns.

The surface hardness of the samples was measured using a commercially available nanoindenter<sup>18,30</sup>. This instrument directly measures the load on a triangular pyramid diamond indenter tip as a function of displacement from the surface. Hardness is determined from the load data using the projected area of the indent, obtained from previous calibrations<sup>31</sup>. Measurements were made under constant loading rate. At least nine indents were made on each sample and the data for each sample averaged.

## **RESULTS AND DISCUSSION**

Figure 2 shows the effect of different polishing treatments on the surface hardness of the samples. The change in hardness with depth is a

feature common to nanoindenter measurements and is primarily due to lack of precision in the tip shape function used to calculate the hardness. At small displacements, the effect of a native oxide on the surface may also play a role. From this data it is apparent that the mechanically polished material is more highly strained than the as-received or electropolished materials, resulting in a surface hardness about 1.4 times higher than the electropolished material. The as-received material is about 1.1 times as hard as the electropolished surface.

Differences in the surface hardness of the starting material may be due to differences in the initial surface composition and strain state in the starting material. Strains from mechanical polishing, not present in electropolished material, will serve to harden the material. Differences in composition, particularly at the  $\alpha$ - $\beta$  boundaries, due to segregation during the fabrication of the plate, may play a role in the hardness of unpolished material. Laser processing of any of these surfaces results in the formation of martensite, and the martensite in every case is less hard than the starting material. The relative effect of laser processing is similar for the different starting surfaces, but the final hardness values depend as much on the starting surface hardness as on the laser processing.

Figure 3 shows the oxygen concentration as a function of depth for the four samples analyzed. Intermediate oxygen concentrations and depth dependence consistent with increasing diffusion of oxygen with increased laser processing (numbers of pulses) are apparent. Beyond a certain point, increased processing does not result in greater oxygen incorporation relative to Ti, only in greater depth of oxygen incorporation.

Figure 4 shows the development of the microstructure of the alloy as oxygen is incorporated. In 4a, the unprocessed material shows the diffraction of the unprocessed material, typical of  $\alpha + \beta$  Ti alloys. In 4b, the SADP for the sample exposed to 15 pulses is shown. The transformation to  $\alpha'$  martensite is apparent and some grain refinement is observed. Rings in the SADP indicate the formation of a new phase, TiO. The darkfield image based on these rings, shows the presence of very small particles with a diameter of approximately 10 nm. For samples processed with 10 pulses, no TiO rings are observed, suggesting that the solid solubility of O in the alloy is exceeded between 10 and 15 pulses. In figure 4c taken after 30 pulses, further  $\beta$  grain refinement is apparent, the particles are somewhat larger ( $\sim 17$  nm), and the rings that correspond to TiO are prominent in the SADP. Finally, after 60 pulses, figure 4d, the martensite rings have effectively disappeared, and the TiO rings in the SADP are very well defined. The final structure is of very fine TiO particles.

By distorting the lattice, oxygen atoms in interstitial sites in Ti increase the resistance of the lattice to deformation. This hardening by dislocation-solute interaction is characterized by a square-root dependence on the solute concentration<sup>32</sup>. Figure 5 shows the normalized hardness at a depth of 100 nm Vs the square root of the oxygen concentration for samples treated with 1, 2, 5, & 10 pulses of laser radiation at  $1.0 \text{ J-cm}^{-2}$  incident on a mechanically polished surface. The hardness data is normalized to the untreated surface hardness and the oxygen concentration is estimated from the data in figure 3. As expected for a solution hardening situation, the dependence is linear. The slope of this line, as normalized to the one pulse position value, is  $0.4 (\text{wt}\%)^{-0.5}$ . Typical values for solution hardening in

this alloy with the same normalization are between 0.6 and 1.2 (wt%)<sup>-0.5</sup> as reported by Liu and Welsch<sup>33</sup>. Liu and Welsch report on material with 0.1-1.0 wt% oxygen, while the data reported here is for 0.7-6.0 wt% oxygen. The difference in slope is probably due to the fact that the mechanism is operating in  $\alpha'$  martensite in this case but the difference in oxygen concentration may also play a role.

After 15 pulses of laser radiation, TEM observations demonstrate that TiO precipitates from the solid solution. After 15 pulses, or above an oxygen concentration of approximately 25 at%, we therefore would expect that a precipitation strengthening mechanism would be observed. The Orowan strengthening mechanism<sup>34</sup> predicts that the normalized hardness would scale as the inverse of this mean-free-path between particles (MFP).

Using the specific densities of TiO and Ti-6Al-4V ( $7.72 \times 10^{-2}$  and  $9.40 \times 10^{-2}$  respectively) we can calculate the volume fraction of TiO in the material as a function of the oxygen concentration. Adding the particle size information from TEM observations, the mean-free-path (MFP) between these particles can be estimated<sup>35</sup>. The data for the multiple pulse samples is plotted in figure 6. Because of evidence for accelerated TiO particle growth above 45 pulses, data from the 60 pulse sample is not included in this figure. The dependence of the normalized hardness on inverse MFP is as expected for a precipitation hardening mechanism.

Figure 7 gives the concentration of nitrogen as a function of depth for different numbers of pulses. In contrast to oxygen incorporation, many more melt solidification cycles are needed to incorporate significant amounts of nitrogen into the material. This is consistent with the relative diffusivities of

O and N in Ti. However, a similar pattern appears, that is that the nitrogen concentration appears to saturate at 50 at% N. Extensive processing results in both more nitrogen incorporation and a deeper alloyed layer. TEM observations of samples processed with 200 pulses of laser radiation at  $1.0 \text{ J cm}^{-2}$  shows the development of TiN precipitates.

In figure 8 we show the surface hardness of Ti alloyed with N as a function of the number of pulses. Analysis of the mechanism for this surface hardening is in process. Preliminary analysis similar to that performed in the TiO case suggests that the process is entirely a precipitation mechanism.

Boron alloying experiments were performed by laser mixing of a 60 nm B surface layer into Ti alloy substrates<sup>36</sup> using 5 pulses of radiation at  $2.5 \text{ J cm}^{-2}$ . Despite the large negative heat of formation of  $\text{TiB}_2$ , rapid solidification apparently suppresses the formation of this compound and the resulting alloy is amorphous. Figure 9 shows the hardness-depth relationship for the amorphous B-Ti alloy. Measurement of the B concentration gives a half-width of approximately 75 nm and a peak B concentration of 35 at%. The increased hardness of the B containing alloy is seen in the top 100 nm of the material, consistent with the B distribution.

## CONCLUSIONS

The data presented here demonstrates that excimer lasers provide a fast and efficient method of surface modification of Ti alloys. We have demonstrated alloying from both gas and solid sources at industrially significant rates despite the laboratory scale laser used in these experiments. Controllable changes in both alloy composition and microstructure lead to predictable changes in the surface properties of the alloyed materials. The

excimer laser process therefore enables effective surface engineering of these materials.

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## **FIGURE CAPTIONS**

- 1. Temperature as a function of depth into the material for 1.0 J-cm<sup>-2</sup> excimer laser pulse on Ti-6Al-4V. Curves represent approximate peak temperatures (30 ns) and temperature at solidification (80 ns).**
- 2. Hardness as a function of depth, relative to that of electropolished material, for mechanically polished, as rolled, and single-pulse laser processed material.**
- 3. Oxygen incorporation due to excimer laser processing. As number of pulses is increased, both peak concentration and depth of incorporation increase.**
- 4. Selected area diffraction patterns for showing oxygen incorporation in Ti-6Al-4V a). As received material showing typical a + b structure. b). Pattern after 15 pulses showing beginning of TiO formation. c). Pattern after 45 pulses; further grain refinement and formation of TiO is evident. d). Pattern after 60 pulses; only TiO rings are seen.**
- 5. Hardness at a depth of 100 nm, normalized to that of mechanically polished surface as a function of the square root of the O concentration for low concentration samples. The data follows the behavior expected for solution strengthening.**
- 6. Hardness normalized to that of electropolished surface as a function of the inverse of the mean free path between precipitate particles. The data follows the behavior expected for dispersion strengthening.**

7. Nitrogen incorporation due to excimer laser processing. As number of pulses is increased, both peak concentration and depth of incorporation increase.
8. Hardness as a function of the number of pulses for N alloyed Ti-6Al-4V. Depth of the measurement is approximately 70 nm.
9. Hardness as a function of depth for amorphous B alloyed Ti-6Al-4V. The depth of the hard layer is commensurate with that of the B incorporation.

# T(z) for Ti

25 ns pulse at  $1.0 \text{ J-cm}^{-2}$

















