DEC 13 1990

TITLE: STRUCTURE-PROCESS-PROPERTY RELATIONS
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SUBMITTED TO: Materials Research Society Symposium
Proceedings, ~~Pittsburgh, PA~~
Boston, MA, Dec 79

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STRUCTURE-PROCESS-PROPERTY RELATIONS IN EXCIMER LASER SURFACE PROCESSED Ti-6Al-4V ALLOY

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Abstract

Excimer laser processing results in very rapid solidification of metal surfaces. In addition to mixing or segregation processes, rapid heat treatment can result in phase transformations which yield beneficial surface properties. We have investigated the effect of pulsed excimer laser radiation on the microstructure and surface hardness of Ti-6Al-4V alloy. This material undergoes a well defined martensite transformation during rapid quenching from temperatures in the β phase field. The depth of the transformed layer is thus a marker for the temperature profile during processing. We find that the depth of the transformed layer agrees well with a simple 1-D calculation of heat flow following the laser pulse. As measured by the nanoindenter, we find that the surface martensite is softer than the as-rolled alloy. Multiple pulse processing at high fluences results in an increase in surface hardness, but at a depth much less than that of the martensite, suggesting an independent mechanism.

Introduction

Titanium alloys, in particular Ti-6Al-4V, are useful engineering alloys in a number of applications. However, their wear and corrosion properties restrict their use in extreme environments such as those encountered in space or surgical implant applications. Surface processing by ion implantation and mixing has been successful in improving the mechanical properties of the alloy. Laser surface processing also has the potential for improving the properties of the alloy through microstructural changes or surface alloying. Previous work has concentrated on laser nitriding [1], production of dispersoids [2], and surface finish [3] using lasers operating in the infra red (IR) portion of the spectrum. Excimer laser processing, using light in the ultra-violet (248 nm wavelength), offers a rapid and efficient alternative to IR techniques for surface processing. We have demonstrated the formation of an amorphous B-Ti alloy layer by excimer alloying[4]. In order to more fully understand the effect of excimer laser processing we have begun to study the effects of processing parameters on the properties and microstructure of Ti-6Al-4V alloy. In this paper we will report preliminary results of this study.

Thermal Calculations

Excimer laser radiation is absorbed within a very short distance in virtually all materials. Typical absorption depths in Ti alloys are of the order of 3 nm. Absorption, typically in electron shells, is rapidly thermalized to a heat pulse which is conducted away from the surface. There is radiation from the hot surface and convection at the free surface, but these effects are relatively minor at the time scales which 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 melt process. The melt front then stops and a resolidification front moves back toward the 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. If we assume that the laser pulse has a square temporal profile, so that power incident is either a constant P_0 or zero, the temperature, T , of the material at any depth z and time t is given by[5].

$$T(z,t) = (1 - R) \frac{2P_0\sqrt{\kappa t}}{K} \operatorname{ierfc}\left(\frac{z}{2\sqrt{\kappa t}}\right) \quad \text{for } t \leq t_0$$

and

$$T(z,t) = (1 - R) \frac{2P_0\sqrt{\kappa}}{K} \left(\sqrt{t} \operatorname{ierfc}\left(\frac{z}{2\sqrt{\kappa t}}\right) - \sqrt{t - t_0} \operatorname{ierfc}\left(\frac{z}{2\sqrt{\kappa(t - t_0)}}\right) \right) \quad \text{for } t > t_0$$

where:

R = reflectivity

κ = thermal diffusivity

K = thermal conductivity

t_0 = pulse length

Melting is accommodated by a heat of fusion term in $T(t)$ and appropriate conditional statements. Although this calculation ignores many significant aspects of the melt 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[6,7]. The same calculation is applicable to heat treatment below the melt threshold. The result reported here use no adjustable parameters and the room temperature values of all material properties.

Experiment

Samples of commercially obtained Ti-6Al-4V alloy were polished with successively finer grits to a mirror finish (0.3 μm final grit). The samples were then laser processed using excimer laser radiation at 248 nm wavelength and per pulse fluences of 0.5, 1.0, and 2.5 $\text{J}\cdot\text{cm}^{-2}$. Samples were processed with one, two, and five overlapping pulses/position. A further sample was treated with 10 pulses/position at 2.5 $\text{J}\cdot\text{cm}^{-2}$. In addition to the homogenization due to the overlapping pulses, a multi-element refractive beam homogenizer was used to create uniform illumination of the sample.

The surface hardness of the samples was measured using a commercially available nanoindenter[8]. This instrument directly measures the load on a triangular pyramid type diamond indenter tip as a function of displacement, h , from the surface. Hardness is determined from the load data using the relation:

$$H = \frac{L(h)}{A(h)},$$

where L is the measured load, and A the projected area of the indent. Measurements were made under constant load rate of 75 $\mu\text{N}\cdot\text{sec}^{-1}$ to a nominal depth of 400 nm. Nine indents were made on each sample and the data averaged in 4 nm increments. As discussed by Doerner and Nix [9], the actual depth of the indent must take into account the elastic recovery of the material as the indenter is removed. As we are interested primarily in comparative measurements, this was not a concern, and in any case, elastic recovery was of the order of 10% of the depth of the indent. Nevertheless, the hardness and displacements indicated in the data are subject to this error.

Samples were analyzed by cross sectional scanning electron microscopy (SEM) to determine the depth of the transformed layer. Ninety degree cross sections were cut, the surfaces polished and Ar ion etched to reveal the microstructure. Samples for analysis by transmission electron microscopy (TEM) were prepared by thinning from the back of the samples.

Figure 1 shows the SEM cross-section of the sample treated at 2.5 J-cm^{-2} . On the left, the $\alpha + \beta$ alloy (b) structure is clearly seen below the transformed layer. On the right, at larger magnification, the lath structure (a) of the transformed layer can be more clearly seen. The thickness of this layer varies between about $1.5\text{--}2.0 \mu\text{m}$ across the treated surface. Figure 2 shows the peak temperature profile calculated for an incident fluence of 2.5 J-cm^{-2} . The β transus (at approximately 1000 C) is shown by the dashed line. Based on this calculation, one would expect the transformed region to be about $1.1 \mu\text{m}$ thick.

Based on this calculation, layers treated at 0.5 and 1.0 J-cm^{-2} would be expected to transform to martensite with thicknesses of 0.3 and $0.8 \mu\text{m}$, respectively. Cross section SEM images of the surface treated at 1.0 J-cm^{-2} showed a thinner martensite layer ($\sim 1.3\text{--}1.5 \mu\text{m}$) and the martensite was unobservable in SEM images of the 0.5 J-cm^{-2} treated sample. However, the presence of martensite even at the lowest fluence was confirmed by TEM. In both the 1.0 and 2.5

$\text{J}\cdot\text{cm}^{-2}$ cases, the calculated depth of transformation is systematically less than that observed. In the lowest fluence case, the time at temperature is short ($\sim 10^{-8}$ sec), and the calculation is less reliable. This calculation assumes that the reflectivity of the alloy surface is 0.50. This parameter is not well established and a slight adjustment could easily improve agreement with the measured thickness.

We found no significant difference in the transformed layer thickness of any of the samples treated with multiple pulses. That is, the transformation that occurred after a single pulse did not deepen after multiple pulses. This is consistent with the cooling calculation which indicates that the surface has returned to room temperature in a time shorter than the repeat time of the laser pulses (0.5 sec).

Figure 3 shows hardness data for single pulse processing at the three fluences used. In each case, the surface is softer than that of the as-rolled alloy. The sample treated at $0.5 \text{ J}\cdot\text{cm}^{-2}$ is slightly harder than those treated at the higher fluences. This could be the result of the fact that the transformed layer is much thinner than in the higher fluence cases, comparable to the depth of the indents. Martensite in Ti alloys reportedly does not contribute to hardening[1] and in any case we do not know the stress state of the as-rolled material. Surfaces melted (and transformed) to much greater depth using infra-red lasers show substantial tension in the surface layer, sufficient to cause cracking[3]. It is clear that whatever the mechanism, martensite in Ti-6Al-4V is softer than the as-rolled $\alpha + \beta$ alloy.

At 0.5 or $1.0 \text{ J}\cdot\text{cm}^{-2}$, there was likewise no difference in the hardness of surfaces treated with 1, 2, or 5 pulses/position. At $2.5 \text{ J}\cdot\text{cm}^{-2}$, however, there was a strong dependence of the

surface hardness on number of pulses. Figure 4 shows this effect at a depth of 100 nm, with the data normalized to the hardness of the as-rolled material at the same depth. The effect was more pronounced at shallower depths and decreased with depth through the range of the indentation measurements.

Because we found no essential difference in the transformed layer thickness due to multiple pulse processing and because in any case, the thickness of the transformed layer is much greater than that suggested by the increase in surface hardening, we feel that the hardening mechanism is independent of the martensitic transformation. As the samples were laser treated in air, and since the surface becomes fully molten at this fluence, it is possible that oxygen or nitrogen has been dissolved in the surface. Oxygen in particular is rapidly dissolved interstitially in Ti and has a strong effect on hardness[10]. We have not directly observed the formation of oxide or nitride phases in the laser processed surfaces but studies are continuing.

Conclusions

We have examined the transformation of $\alpha + \beta$ Ti-6Al-4V alloy to martensite under the influence of excimer laser processing. We find good agreement between the observed thickness of the transformed layer and a simple model of the process based on 1-D heat flow. Nanoindenter measurements indicate that the transformed martensite surface is softer than the as-rolled material. Hardness increases in the surface after multiple pulse processing at 2.5 J-cm^{-2} are due to a different mechanism than the martensitic transformation, and may be related to interstitial solute hardening.

Acknowledgements

We would like to acknowledge the assistance of Jim Gray, Darryl Garcia, and Jose Archuleta in sample preparation and microscopy. This research was supported by the United States Department of Energy under contract W-7405-ENG-36 through the Los Alamos Center for Materials Science

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