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MECHANICAL PROPERTIES OF EXCIMER LASER MODIFIED TITANIUM SURFACES

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ABSTRACT

Excimer laser processing enables both thermally-driven transformations and the incorporation of solutes into the surface of materials through melting and diffusional mixing. We have examined the effect of excimer laser processing on the microstructure and surface mechanical properties of titanium alloys. Changes in the surface hardness due to laser processing were studied using a Nanoindenter™. Alloying experiments using both mixing of evaporated surface layers of boron and laser gas alloying in air and in nitrogen all result in changes in the surface hardness of the material. Alloying with boron results in an amorphous surface which is somewhat harder than the as polished surface. Laser processing in air and pure nitrogen results in incorporation of oxygen and nitrogen and the development of fine (~ 50 nm) precipitates of TiO and TiN respectively. Substantial increases in surface hardness result due to solution and precipitation mechanisms. The effects of alloying on the surface hardness of the materials will be discussed in terms of the concentration of the solute and microstructures observed.

INTRODUCTION

The use of depth sensing indentation load measurements for materials property determinations with appropriate calibrations of indenter tip shape can provide useful information on hardness vs depth for surface modified materials[1, 2]. We have used nanoindenter™ techniques extensively in the evaluation of surface modified materials and find that the results of these measurements can be correlated well with depth sensitive determinations of microstructure and composition. This paper will present data on hardness determinations of excimer laser surface modified Ti alloys. Specifically, we will examine thermal transformations, the formation of amorphous B-Ti alloys, and solution and precipitation hardening of Ti-6Al-4V by laser gas alloying. Excimer laser surface processing has been described at length in these proceedings[3, 4, 5]. Briefly for Ti alloys, laser light at 248 nm wavelength is used to melt the surface at fluences of approximately 1.0 J-cm⁻². Mixing with a previously evaporated surface layer of some other material or with the gas ambient results in alloying with the depth of processing on the order of a few tenths of microns. Melt durations per pulse are of the order of 100 ns. Cooling and solidification are very rapid, with cooling rates of the order of 10¹⁰ K-s⁻¹.

Indentation measurements were made using the commercially available Nanoindenter™ with calibrations of tip shape following the prescription of Pharr and Oliver[2]. In some cases where the tip shape was not adequately calibrated, we have normalized the data from modified surfaces by that from the unprocessed surface. If this is done using the plastic depth of the indent, which is determined by subtracting the elastic portion of the displacement from the surface, the tip shape calibration, or lack thereof, is removed from the result and only differences in hardness remain. Multiple indents, at least nine and often more, were made in

each sample and the data from multiple indents averaged to obtain the final result. Error bars shown in the data are the standard deviations of these averages, thereby representing only data scatter and not systematic errors.

RESULTS

Surface preparation can have a significant effect on surface hardness measurements. Figure 1 shows the relative hardness as a function of depth for mechanically polished and as rolled surfaces normalized to the hardness of an electropolished surface. Clearly, mechanical polishing, in this case to a mirror finish, results in measureable work hardening to a depth greater than that of surface processing techniques.

Figure 1. Hardness as a function of depth, normalized to the hardness of the electropolished surface, of mechanically polished, as rolled, and single pulse laser treated Ti-6Al-4V.

The thermal transformation of α -Ti to α' from heating above the transformation temperature (925 C for Ti-6Al-4V) and cooling at rates greater than 30 K-s^{-1} is well documented[6]. Figure 1 also shows the hardness measured for a surface treated with a single pulse of excimer laser energy at 1.0 J-cm^{-2} . In this case the surface is actually melted, but the transformation occurs regardless. The surface hardness is about 80% that of the electropolished surface. Thus any processing designed to harden the surface starts from this slight deficit. This transformation also softens the mechanically polished surface by a comparable amount, however laser processing does not completely relieve the work hardening of the surface.

Boron implantation of Ti alloys has been suggested as a means to improve the tribological properties of these alloys. We have alloyed B into Ti-6Al-4V by excimer laser mixing of a 60 nm B surface layer into Ti alloy substrates[7] using 5 pulses of radiation at 2.5 J-cm^{-2} . Despite the large negative heat of formation of TiB_2 , rapid solidification apparently suppresses the formation of this compound and the resulting alloy is amorphous. Figure 2 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. Note that at greater depths, the hardness is less than that of the mechanically polished starting material, consistent with the thermal transformation discussed above.

Figure 2. Hardness as a function of depth, relative to that of a mechanically polished surface, of a laser produced amorphous B-Ti alloy. The depth of the hard surface is commensurate with that of the measured B concentration.

Because of the high affinity of Ti for oxygen and nitrogen, excimer laser alloying of the surface from gas sources is feasible. Because of the reduced density of the source, compared with the mixing of solid surface layers, many more laser pulses are required to obtain significant alloying concentrations.

Laser treatment of Ti in air produces oxygen incorporation[8, 9]. Oxygen is dissolved in the lattice until the equilibrium solid solubility of oxygen in Ti is exceeded, at which point γ -TiO precipitates from the solid solution. Analysis of the oxygen concentration as a function of depth for samples which do not exhibit TiO precipitation can be directly correlated with hardness vs depth information. For hardening by this dislocation-solute interaction, one expects the hardness to follow a square root dependence on the oxygen concentration. This is shown in figure 3, where the relative hardness measured at a depth of 100 nm is plotted vs the square root of the oxygen concentration as measured by resonant elastic scattering of α particles at 3.05 MeV[10]. These samples received between 1 and 16 pulses of laser radiation in air.

Figure 3. Relative hardness at a depth of 100 nm as a function of the square root of the oxygen concentration in Ti 6Al 4V laser treated in air. The linear dependence is that expected for solution strengthening.

In samples treated with a sufficient number of pulses to initiate TiO precipitation, transmission electron microscopy, which gives the TiO precipitate size as a function of processing, can be joined with the oxygen concentration measurements to provide precipitate density and size as a function of depth. Observed hardness as a function of depth can then be related to the precipitate density through the Orowan strengthening mechanism[11]. Figure 4 shows the dependence of the hardness on the inverse mean free path between precipitates which calculated from our data and the analysis of Corti et. al.[12]. The expected linear dependence is found. It should be noted that these data include values from more than one depth in the material, correlated to the oxygen and precipitate distributions. The agreement emphasizes the validity of hardness vs depth information as obtained from the nanoindenterTM. We have performed experiments with nitrogen alloying and find similar dependence of the relative hardness on the precipitation of TiN particles.

Figure 4. Relative hardness as a function of inverse mean-free-path between TiO precipitates in laser processed Ti-6Al-4V. The data, from several depths per sample, follow the behaviour expected for dispersion strengthening.

CONCLUSIONS

We have demonstrated that hardness-depth information obtained from nanoindenterTM measurements of laser surface processed Ti alloys can be used in conjunction with the processing and microstructural information obtained by other techniques to further illuminate the effects of these processes on the modified surfaces. The depth sensitive information is sufficiently self consistent to enable comparison with theories of strengthening mechanisms and hence the determination of those mechanisms.

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