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TITLE FORMATION OF TITANIUM-BORON SURFACE ALLOYS
BY EXCIMER LASER MIXING

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FORMATION OF TI-B SURFACE ALLOYS BY EXCIMER LASER MIXING

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ABSTRACT

We have formed a surface Ti-B alloy by excimer laser mixing of a single B layer on a Ti-6Al-4V alloy substrate. Rutherford backscattering spectroscopy indicates a uniform B:Ti ratio of approximately 0.7 in the surface layer. A Boron layer 60 nm thick resulted in an alloy layer approximately 200 nm thick. There is little indication, by either Auger electron spectroscopy or nuclear reaction analysis, of substantial oxygen incorporation in the surface alloy despite the fact that the processing was done in air. Transmission electron microscopy of the surface alloy shows a completely amorphous surface layer underlain by a martensitic structure.

INTRODUCTION

The use of Ti alloys in tribological applications is limited by the poor coefficient of friction exhibited by these materials in sliding tests. Values of 0.7 to 0.8 for the unalloyed material are typical¹, due in part to the reactivity of Ti with the sliding counterpiece. Nitrogen ion implantation has been used to increase the hardness and reduce the coefficient of friction of Ti-6Al-4V alloys in sliding against ruby². A dramatic reduction in wear in the Ti alloy polyethylene couple typically used in orthopedic implants was found after N implantation³. Although effective, ion implantation is a relatively slow process, the concentration of an alloying element is limited by sputtering, and the process requires a substantial vacuum system. We have previously shown that excimer laser processing can rapidly form surface alloys in a number of metal and ceramic systems⁴. Because Ti and B can react to form a stable, hard, ceramic, TiB₂, we have begun experiments in the excimer laser mixing of B on Ti alloys. In the following, we will report on the formation of a Ti-B surface alloy by excimer laser mixing

EXPERIMENT

Coupons of commercially obtained Ti-6Al-4V alloy were polished with conventional techniques to a mirror finish. The resulting samples were then coated with a 60 nm layer of B evaporated in an e-beam system with a base pressure of 10⁻⁹ Torr. Promptly after evaporation the samples were laser treated at different fluences with light from an excimer laser operating on KrF at 248 nm wavelength. Multiple overlapping

pulses were used to mix the surface layer with the substrate. The beam was homogenized so that each pulse was spatially uniform in intensity. Samples were exposed to several different fluences based on expectations of the optical and thermal properties of the B/Ti alloy surface. Mixing experiments were done with one pulse at 0.7 J-cm^{-2} , one and five pulses at 1.25 J-cm^{-2} , and one and five pulses at 2.5 J-cm^{-2} .

The extent of mixing was initially 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. Samples were also analyzed by Auger electron spectroscopy combined with sputter depth profiling but the differential sputtering rates of B and the Ti alloy were such that meaningful information on the B:Ti ratio could not be obtained.

Transmission electron microscopy (TEM) of the samples was used to determine the microstructure of the mixed surface. Samples which were thinned in a conventional Ti electropolishing solution did not provide uniformly thin areas which isolated the surface layer so subsequent samples were thinned using a combination of electropolishing and Ar ion milling.

RESULTS

Mixing experiments at the two lower fluences resulted in no mixing. It was apparent from the appearance of the surface that the boron melted, but apparently the fluence was not sufficient to melt the Ti alloy

Figure 1. Rutherford Backscattering spectra from as deposited B on Ti-6Al-4V alloy and B surface alloy formed by excimer laser mixing with 5 pulses at 2.5 J-cm^{-2} .

and mix the surface layer. Figure 1 shows the RBS spectra of the as deposited B/Ti surface and that mixed with 5 pulses at 2.5 J-cm^{-2} . The spectrum after a single pulse at this fluence showed some mixing at the interface but no Ti at the surface. After 5 pulses, the mixing is more complete; Ti has moved to the surface and the faint B "peak" at about 0.4 MeV has vanished. A fit to the spectrum of the mixed layer using RUMP⁵ gives a B:Ti ratio of 0.7 ± 0.2 in a layer approximately 200 nm thick. The fit also shows that the interface between the mixed film and the substrate is graded over a distance of about 60 nm.

Figure 2 is a TEM image of the surface film. There is no apparent structure in the film itself (upper left hand corner). The associated selected area diffraction pattern taken from the center of the image (inset) confirms the amorphous structure of the mixed layer. The spots visible in the diffraction pattern are from the residual Ti alloy substrate. Images of material from material near the surface below the mixed layer shows clear acicular martensite⁶ consistent with the rapid solidification of the alloy.

Figure 2. Transmission electron micrograph and associated selected area diffraction pattern of amorphous B-Ti alloy and substrate.

CONCLUSIONS

We have demonstrated that excimer laser mixing of B on Ti alloy surfaces produces an amorphous alloy with a B:Ti ratio of about 0.7. This mixed layer is underlain by a layer of fine grained acicular martensite formed by rapid solidification from molten Ti-6Al-4V⁷. The high rate of solidification⁴, of the order of 10^9 K-sec⁻¹, seems to have suppressed the reaction of Ti and B, implying the existence of a kinetic barrier to the formation of TiB₂. Further experiments in this system are continuing.

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