Dynamic mixing deposition/implantation in a plasma immersion configuration

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A surface layer consisting of titanium, nitrogen, and oxygen is implanted/deposited onto SS304 stainless steel using dynamic mixing and plasma immersion ion implantation. Titanium is introduced into a nitrogen glow discharge plasma from a metal arc plasma source. Dynamic mixing is achieved via the co-implantation of Ti ions with high charge states as well as nitrogen and oxygen ions in the plasma. The resulting surface layer possesses superior tribological properties and corrosion resistance. The observed improvement in the wear resistance is more than a factor of 10. The enhancement in the surface properties is believed to be due to the synergistic effects of the coexistence and dynamic mixing of titanium, nitrogen, and oxygen at the interface. © *1999 American Vacuum Society.* [S0734-2101(99)06006-6]

I. INTRODUCTION

Austenitic stainless steel is frequently used in the industry due to its good corrosion resistance. However, its relatively low surface hardness and inferior wear resistance lead to a short working lifetime, especially for abrasively stressed components made of the material. Several techniques such as plasma nitriding, elevated temperature ion implantation, and special coatings have been introduced to increase its surface hardness and wear resistance. Unfortunately, the modified surface layer is frequently not thick enough to be useful in many real engineering applications and in the field. The deficiency is due to the slow diffusion of nitrogen in stainless steel with a high chromium content and the impeding effects of the chromium nitride or oxide surface barrier layer. Recently, a process combining the benefits of plasma nitriding and a titanium nitride coating has attracted attention.[1,2] The nitrided layer acts as a mechanical support for the TiN layer, and the characteristics of components treated by this hybrid process become improved. However, there is high internal stress at the interface, and surface, crystallographic, chemical, and physical mismatches tend to worsen the adhesion of the coating to the base metal. Hence, the performance of the treated materials can be further enhanced by improving the adhesion between the nitrided zone and the TiN coating, and it has thus become a topic of intensive research. A transition layer between the TiN coating and the plasma nitrided base metal has been suggested.[3–5]

In this work, we introduce a dynamic ion mixing technique utilizing simultaneous gaseous and metal ion plasma immersion ion implantation (PIII).[6] This process offers good adhesion as a result of the smooth interfacial transition, low porosity, as well as the enhanced wear and corrosion resistant properties. Because PIII is intrinsically a nonline-of-sight technique,[7–10] the methodology offers the additional capability of treating industrial components that are large or that have an irregular shape.

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II. EXPERIMENT

A schematic of the plasma immersion ion implanter is displayed in Fig. 1 and described elsewhere.[11] A nitrogen plasma was sustained by hot filament glow discharge in the main vacuum chamber, and a titanium plasma generated in the metal vacuum arc (MEVVA) plasma sources diffused into the vacuum chamber. The plasma in the vacuum chamber thus contained both titanium and nitrogen. The SS304 stainless steel samples were laid on the sample platen that was biased by a high power modulator. During the negative high voltage pulses, titanium and nitrogen ions were implanted into the exposed surface at the biased voltage (the pressure inside the vacuum chamber was low enough so that collisionless conditions were met). During the ''off cycles'' of the power modulator, titanium and nitrogen condensed onto the sample surface. Therefore, sequential deposition and implantation took place, and the energetic (implanted) ions induced a significant amount of ion mixing at the interface between the deposited/implanted thin film and the SS304 base metal (that is, the original surface of the SS304 samples) and throughout the film. The instrument conditions are displayed in Table I.

III. RESULTS AND DISCUSSION

Elemental depth profiles of the two samples, treated for 50 and 90 min, were acquired by Auger electron spectroscopy and are exhibited in Figs. 2(a) and 2(b), respectively. An average sputtering rate of 1 Å/s based on 3 kV, 3 μA Ar^+ bombardment was used to calibrate the depth scale. However, since the surface film and stainless steel substrate sputter at different rates, the sputtering rate throughout the interface is likely to vary as well. Therefore, the depths are only approximations, even though the comparison between the two profiles is valid. The concentrations are derived using archival sensitivity factors, but again, they vary as a function of the composition. The concentrations shown in these two profiles are thus approximate as well. A surface layer containing titanium, nitrogen, and oxygen is observed

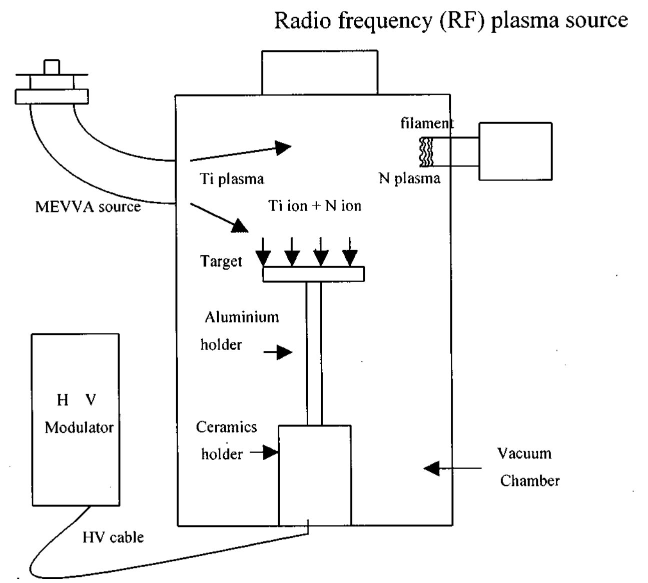

FIG. 1. Schematic of the plasma immersion ion implanter. Four sets of electron emitting filaments and four sets of MEVVA sources are positioned symmetrically around the vacuum chamber.

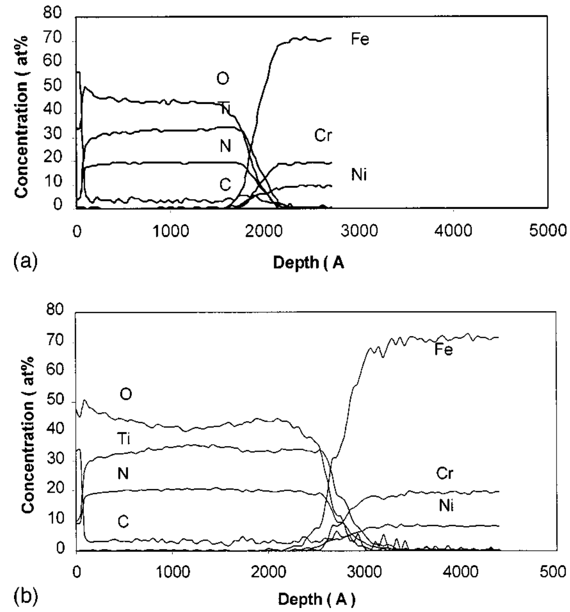

FIG. 2. Elemental depth profiles acquired by Auger electron spectroscopy: samples processed for (a) 50 and (b) 90 min.

on both samples. Since the oxygen concentrations are high throughout the film, oxygen is incorporated during the deposition process and is not a result of posttreatment oxidation. There are four possible sources of oxygen. First, the vacuum chamber was pumped down to a pressure of only 2×10^{-3} Pa before the experiments, and there is oxygen in the residual vacuum. Second, there is oxygen outgassing due to radiation heating in a filament glow discharge. In fact, during our experiments, the pressure went up when the filaments were turned on and we had to decrease the nitrogen flow rate to keep the pressure constant. Third, after the experiments, the vacuum chamber was brought to atmospheric pressure using room air. It has been reported that a high oxygen content (15%) can be introduced into the sample during air venting.[12] Last, but not least, a plasma activated surface consisting of Ti has a strong affinity for oxygen. The carbon in the films probably comes from similar sources as well as from pump oil.[13]

The direct absorption/implantation of titanium, nitrogen, and oxygen in concert with the dynamic mixing effects gives rise to a fairly uniform layer and an ion-mixed interface that is over 350 Å thick based on our high depth resolution Auger data. This broad mixing zone which is believed to be one of the reasons for the enhanced characteristics discussed later in this article is similar for the two treatment times, indicating that very little thermal diffusion has taken place. The low implantation/deposition temperature also prevents the formation of chromium nitride which tends to lower the corrosion resistance. The elemental in-depth distributions are quite uniform and, as shown in Fig. 3, the Ti to N ratio is about 1.65 to a depth of more than 2250 Å. More Ni diffusion into the TiN layer is observed compared to chromium (Fig. 4), and at the interface the Ni to Cr concentration ratio is much greater than that in the base metal.

The measured microhardness data depicted in Fig. 5 show that the treated samples are more superior. They were acquired using a Vickers HX-1000 microhardness tester. The measurements were performed at a load of 10, 25, 50, 100, 200, or 500 G for 20 s. Each microhardness value was obtained by averaging six measurements (for small loads) or three (for large loads). Based on the Auger data, the im-

TABLE I. Instrumental parameters of the dynamic ion mixing PIII process.

	Arc/ implantation voltage (V)	Arc/ implantation current (A)	Pulse frequency (Hz)	Pulse duration (μs)	Remarks
MEVVA source	50	100	100	300	Ti plasma generation
Filament glow discharge	90	0.5	dc		N plasma generation
Implantation/ ion mixing	20 000	5	100	30	Implantation and dynamic ion mixing

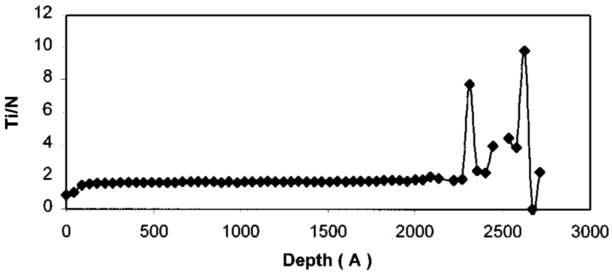

FIG. 3. Titanium to nitrogen concentration ratios vs depth for the 50 min treated sample in Fig. 2(a).

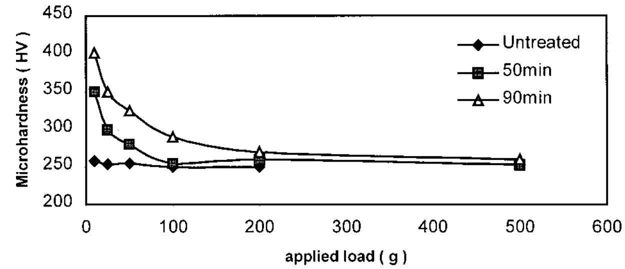

FIG. 5. Microhardness vs applied load for the three samples: untreated and treated 50 and 90 min.

provement is believed to be due to the formation of a fine TiN_xO_{2-x} phase in the layer. Degradation of the surface hardness with an applied load is observed to be more gradual for the 90 min treated sample because the layer is thicker.

The tribological behavior of the untreated and treated samples was assessed using a pin-on-disk test. The wear tracks were further investigated by alpha-step stylus profilometry and scanning electron microscopy (SEM). In the pin-on-disk test, a 25 G load was applied to a 6 mm diam silicon nitride ball. The coefficients of friction as a function of the number of turns are plotted in Fig. 6. The improvement is quite apparent for the treated samples and similar to that achieved by elevated temperature PIII at 350–450 °C.[14] However, the monotonic trend is unlike that of conventional PIII of titanium alloys[15,16] when a rapid transition from low friction to high friction is usually observed. The rate of wear can be determined by stylus profilometric measurements of the wear tracks, and the results are exhibited in Fig. 7. Each data point is an average of four measurements. After 500 turns, the cross-sectional area of the wear track on the untreated sample is as high as 25 μm^2. In contrast, sample 2 (treated 50 min) shows an area of only 2 μm^2. The improvement is more than a factor of ten. The SEM micrographs displayed in Fig. 8 corroborate the wear track measurements. As shown in Fig. 8(a), the untreated sample shows severe wear as well as adhesion, abrasion and plastic deformation in and around the wear track. The track is wide and deep, and consists of grooves up to 2000–3000 Å in depth, demonstrating severe metal sticking and tearing. The edges of the wear track are ragged and deformation slip bands have formed, indicating plastic deformation of the materials close to the tracks. On the other hand, the wear track of the treated sample [Fig. 8(b)] is manifested by fine, shallow grooves with no severe smearing. The wear on this latter sample is much less severe and is consistent with a higher surface microhardness and lower coefficient of friction.

To evaluate the corrosion resistance of the samples, a potentiodynamic polarization test was conducted using a model 342 Softcorrv™ corrosion measurement system. A 3.5 wt % NaCl solution was prepared from analytical grade reagents and distillated water. The scanning rate was 0.5 mV/s. The results measured for the three samples are displayed in Fig. 9. The plasma treatment has caused no appreciable change in the corrosion potential, namely −0.326, −0.382, and −0.379 V for the untreated, and 50 and 90 min treated samples, respectively. In fact, the polarization curves of the treated samples shift to the left, implying slightly better corrosion resistance. It can be attributed to the TiN_xO_{2-x} surface film and the absence of chromium nitride precipitates (deduced from the Auger results) as a result of the low temperature processing.

Dynamic ion mixing by plasma immersion ion implantation gives rise to a thicker interface for better adhesion between the surface layer and the SS304 base metal. The implanted Ti ions introduce more mixing at the interface and throughout the film, much more than nitrogen ion implantation alone. Not only is Ti heavy, the high average charge state of the incident Ti ions generated from the metal arc plasma source (between +2 and +3)[17] yields deeper penetration and a broader mixing zone. The resulting surface film possesses lower friction, higher microhardness, and resists wear and corrosion better. We believe that the enhanced properties are the consequence of the synergistic effects of the coexistence of titanium, oxygen, and nitrogen as well as

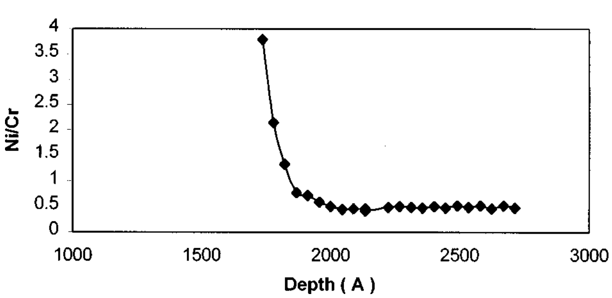

FIG. 4. Nickel to chromium concentration ratios vs depth for the 50 min treated sample in Fig. 2(a).

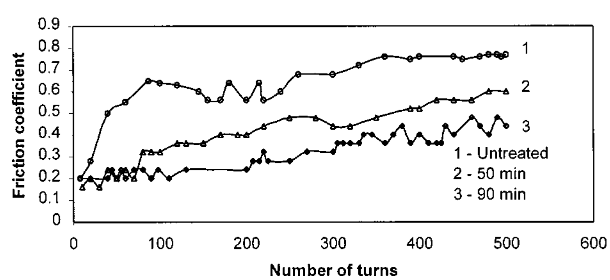

FIG. 6. Coefficients of friction vs the number of turns (pin-on-disk test) for the three samples.

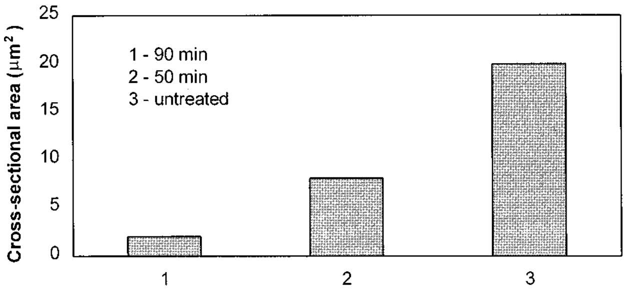

FIG. 7. Wear track cross-sectional areas obtained after 500 turns at a load of 25 G for the three samples.

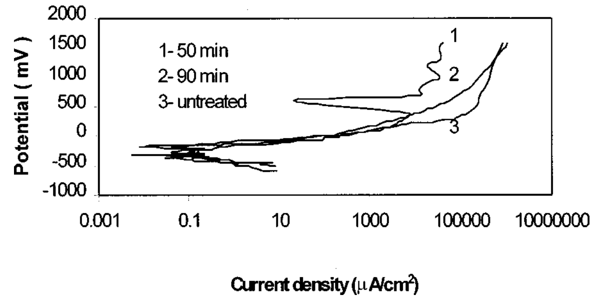

FIG. 9. Potentiodynamic polarization curves acquired in 3.5 wt % NaCl solution.

the ion-mixed interface. It has been reported that nitrogen ion implantation into titanium alloys not only produces nitride in the near surface region, but also promotes the formation of a smooth oxide film on the surface.[18,19] The oxide layer is stabilized by nitrogen.[18,20] Hence, the dominant mode of wear is changed to that of a mild, oxidative nature involving the loss of fine oxide particles from the alloy surface. It is not surprising that our dynamic PIII mixing process encompassing titanium deposition, titanium, oxygen, and nitrogen ion implantation, as well as oxygen adsorption, yields superior tribological properties. The conflicting wear results from previous studies on nitrogen implantation into titanium alloys are primarily a result of the lower hardness as a result of the small thickness of the modified layer.[18,19]

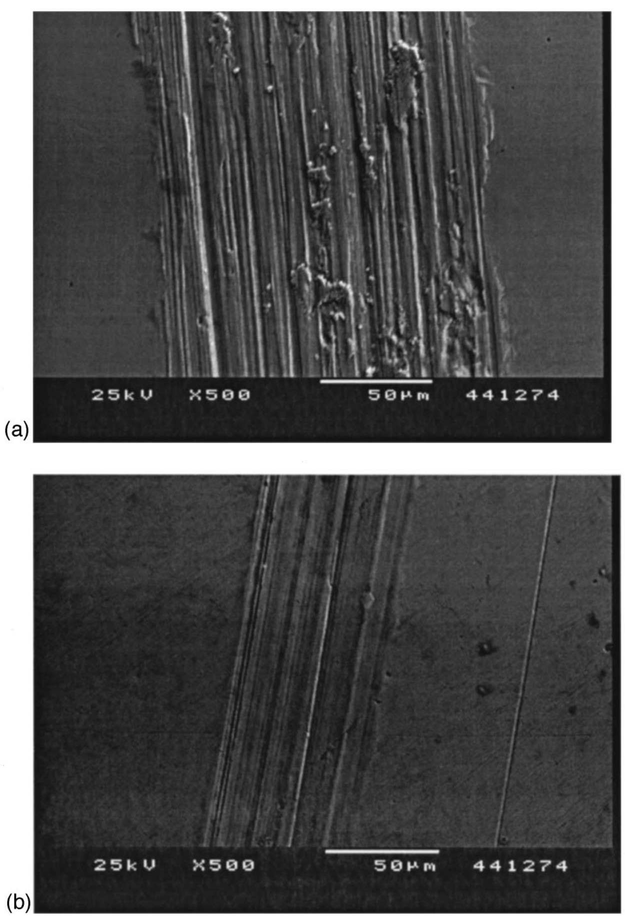

FIG. 8. SEM micrographs of the wear tracks of the (a) untreated and (b) 90 min treated samples.

IV. CONCLUSION

The tribological properties of SS304 stainless steel can be improved significantly by dynamic mixing and plasma immersion ion implantation. The synergistic effects of ion mixing and the coexistence of titanium, oxygen, and nitrogen lead to improved tribological properties and a factor of 10 improvement in the wear resistance. The potentiodynamic polarization test shows a small improvement in the corrosion resistance. The technique is also very flexible and versatile. For example, by synchronizing the metal plasma and sample bias pulses, the process can be used to achieve 100% deposition, 100% implantation, or something in between. Other adjustable parameters include the ion energy[21] and plasma density of each individual species. The nonline-of-sight advantage of PIII is also attractive for the treatment of industrial components that possess a complex geometry such as industrial ball bearings.[22]

ACKNOWLEDGMENTS

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