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ELECTROCHEMICAL PASSIVITY OF TITANIUM IMPLANTED WITH 1 MeV GOLD IONS

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Abstract—Titanium samples implanted with 1 MeV gold ions at doses of 8.8×10^{14} ions/cm² to 1.5×10^{16} ions/cm² were allowed to corrode freely in 20 wt% sulfuric acid solution at 40°C while continuously measuring the open circuit potential (OCP). Inductively Coupled Plasma (ICP), was used to calculate the corrosion rates from the corrosive solutions. The time required for the OCP to drop to a value characteristic of pure titanium in this solution (-718 mV_{SCE}), was related to the implant dose. Implantation of gold produced a passivating effect but the observed trend towards passivity persisted beyond the depth of implanted gold. Rutherford Backscattering (RBS) and Nuclear Resonance Scattering (NRS) spectra revealed the presence of oxygen atoms recoil-implanted slightly deeper than the gold. Scanning Tunneling Microscopy (STM) was used to study the differences in surface roughness before and after ion implantation. © 1998 Elsevier Science Ltd. All rights reserved

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INTRODUCTION

Titanium is a technologically important metal that resists corrosion due to a protective oxide layer that spontaneously forms on its surface (TiO₂). The thickness of this oxide layer¹ is generally less than 10 nm. Enhancement of the corrosion resistance has been studied using noble metal alloying,² thermal oxidation (to increase the thickness of the oxide film)³ and ion implantation.⁴⁻⁶

Stern and Wissenberg applied the mixed potential theory to explain the corrosion dynamics of titanium alloyed with noble metals.² It was shown that titanium alloyed with gold (0.48 wt%) has a corrosion rate of 3 mpy in 1 wt% sulfuric acid compared to 460 mpy for unalloyed titanium. However, with only 0.11 wt% gold the corrosion rate increased to 1050 mpy. It was deduced that the addition of the noble metal caused a shift in the exchange

current density of the hydrogen reduction reaction resulting in an increase (more noble or less negative with respect to a saturated calomel electrode) in the mixed potential. The increase in corrosion potential, caused by the low concentration of noble metal, increased the corrosion rate since it was still in the active region, but the higher concentration caused the titanium to become passive resulting in a lower corrosion rate.

Noble metals like palladium have also been implanted into titanium at low energies (<600 keV) by Munn and Wolf.⁵ These samples exhibited passive behavior in 20 wt% sulfuric acid for 100 days compared with pure titanium samples which became active between 6 and 10 hours, suggesting that the implantation process had a significant effect on the properties of the oxide layer. In another study,⁶ performed at Oak Ridge National Laboratory, different doses of platinum ranging from 2×10^{12} ions/cm² to 2.8×10^{16} ions/cm² at energies of 100 to 260 keV were implanted in titanium. The open circuit potential measured versus time was monitored while the samples were immersed in a 1 N sulfuric acid solution. Once the surface oxide was removed, as indicated by the drop from the initial OCP to -0.745 V (SCE), the potential rose again as the titanium dissolved and the implanted platinum became exposed. The magnitude of this rise in potential was greater for higher doses and the sample with the highest dose remained in the passive state for 30 days. The time required to dissolve the surface oxide layer varied from sample to sample which was attributed to variations in oxide layer thickness.

In this study, five titanium samples were polished, implanted with increasing doses of 1 MeV Au⁺ ions and tested in 20 wt% sulfuric acid at 40°C to determine a qualitative relationship between implanted ion dose and the time required to dissolve the oxide layer. The titanium concentration was measured in the sulfuric acid solution using Inductively Coupled Plasma (ICP) Spectrometry at various time intervals for one of the implanted samples. The results were used to determine if the observed rise in potential occurred at a depth in the titanium corresponding to the maximum concentration of gold ions.

EXPERIMENTAL METHOD

The composition of the cylindrical titanium rod, (obtained from Goodfellow, Co.), 9.5 mm in diameter, which was used in this study is listed in Table I. The rod was cut into 12.5 mm lengths, a hole was drilled in one of the faces of each piece and screws were inserted into the holes. The undrilled face of each sample was sequentially sanded on 320 (34.3 μm) and 600 (14.5 μm) grit sandpaper. The resulting samples were polished to a mirror finish by using aluminum oxide (300 nm diameter abrasive) and water. The initial mean surface roughness, R_r , of an 88×88 μm coupon portion measured with STM was 292 nm and the pooled, R_q , was 46.3 nm. A solution containing 40 ml of 52 wt% hydrofluoric acid, 20 ml of concentrated hydrochloric acid and 40 ml of deionized water was used to etch one of the

Table 1. Manufacturer supplied elemental Analysis of Titanium Samples Supplied by Goodfellow Corporation.

Elemental analysis for titanium (99.6%) in ppm														
Al	Co	Cr	Cu	Fe	Mg	Mn	Ni	Si	Sn	Ta	V	C	H	N
500	2	500	200	300	20	500	500	200	10	500	200	30	20	80

samples. Microscopic analysis at $200\times$ confirmed that the samples were not cold worked.⁷ The sample average grain size was visually classified as ASTM No. 3 ($157\ \mu\text{m}/\text{grain}$).

A 1.7 MeV SSDH-2 Tandem Pelletron[®] ion accelerator system was used to implant the gold into the titanium samples and to conduct ion beam analyses. Sample #1 was left unimplanted and five subsequent samples were implanted with 1 MeV Au^+ at doses of 8.82×10^{14} ions/cm² (#2), 1.77×10^{15} ions/cm² (#3), 3.57×10^{15} ions/cm² (#4), 7.25×10^{15} ions/cm² (#5) and 1.5×10^{16} ions/cm² (#6). Rutherford Backscattering Spectrometry (RBS) spectra using 2 MeV He^+ were obtained for samples #5 and #6 to determine the depth profile of the implanted gold. RBS and Nuclear Resonance Scattering (NRS) were used to study oxygen in sample #6.

The corrosive solution was prepared by diluting 96.1 wt% sulfuric acid with deionized water to a 20 wt% solution. A saturated calomel reference electrode (SCE), counter electrode (graphite rod) and test electrode (titanium sample) were placed in 375 ml of the acidic solution in a three electrode cell immersed in a constant temperature water bath at 40°C, while nitrogen was bubbled in the sample solution. The open circuit potential of the titanium sample was recorded as a function of time using an EG&G Model 273 potentiostat. During the test of sample #5, 5 ml portions of the acid solution were withdrawn at various time intervals, dependent upon the observed potential and ICP spectrometry was used to determine the titanium concentration in each solution; it was possible to calculate the corrosion rate from this information.

EXPERIMENTAL RESULTS AND DISCUSSION

The results of the acid tests are shown in Fig. 1. In all cases, the OCP of the titanium was initially high (noble) due to a protective oxide layer. The potential slowly decreased to approximately $-300\ \text{mV}_{\text{SCE}}$. At that point the potential rapidly decreased to approximately

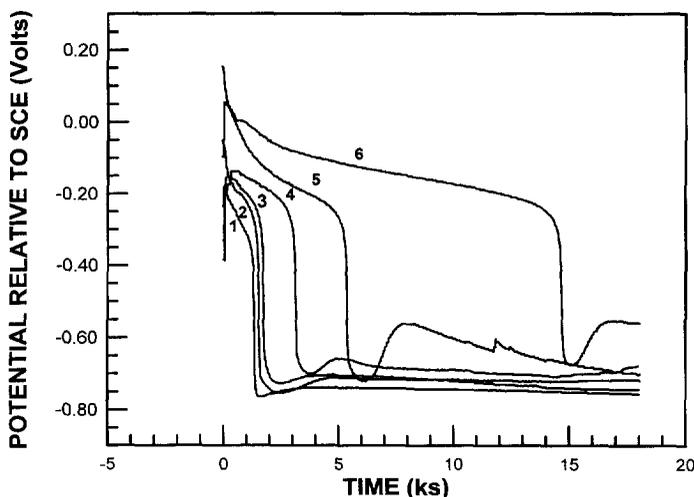


Fig. 1. OCP (in Volts *vs* SCE) versus time for titanium in 20% sulfuric acid at 40°C implanted with 1 MeV gold ions. (1) Unimplanted, (2) 8.82×10^{14} ions/cm², (3) 1.77×10^{15} ions/cm², (4) 3.57×10^{15} ions/cm², (5) 7.25×10^{15} ions/cm² and (6) 1.5×10^{16} ions/cm².

–718 mV_{SCE} which corresponds to the active corrosion potential of titanium in this solution as indicated by the curve for sample #1. These results suggest an initial slow dissolution of the protective oxide layer. Figure 2 indicates that increasing doses of gold resulted in increasing times required to dissolve the oxide layer. Possible explanations for these results are:

- (1) the implantation process changed the surface morphology (roughness) which increased the surface area onto which oxide could adhere,
- (2) the presence of gold atoms near the surface helped maintain the potential high for an extended time,
- (3) some of the oxygen present in the oxide was recoil-implanted into the sample by collisions with gold ions, or
- (4) oxygen diffused into the surface.

Pre-implant and post-implant STM images were obtained for sample #6 (Fig. 3(a) and Fig. 3(b)). The surface roughness, R_t , was increased from 292 nm to 1230 nm due to the implanted gold. This increase in roughness supports the premise that the surface area of the samples was increased by ion bombardment.

As seen in Fig. 1, after the titanium became active, the potential increased and reached a maximum and then decreased again. The time for the sample to reach secondary passivity does not appear to depend on the ion dose (see Fig. 4). In retrospect, this result should be expected since all gold ions were implanted at the same energy, thereby producing the maximum concentration of gold at the same depth in all five samples. As shown in Fig. 5 the height of the maximum in the difference in potential between the onset of activity and the subsequent return to secondary passivity increased with higher doses of gold up through

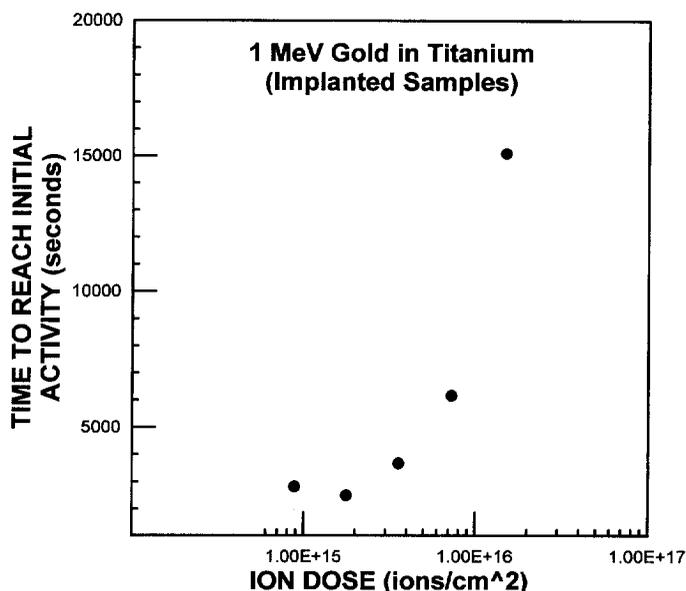


Fig. 2. Time required for implanted titanium surfaces to reach initial activity after immersion in test solution. This time is related to the oxide layer formation on the surface subsequent to ion implantation.

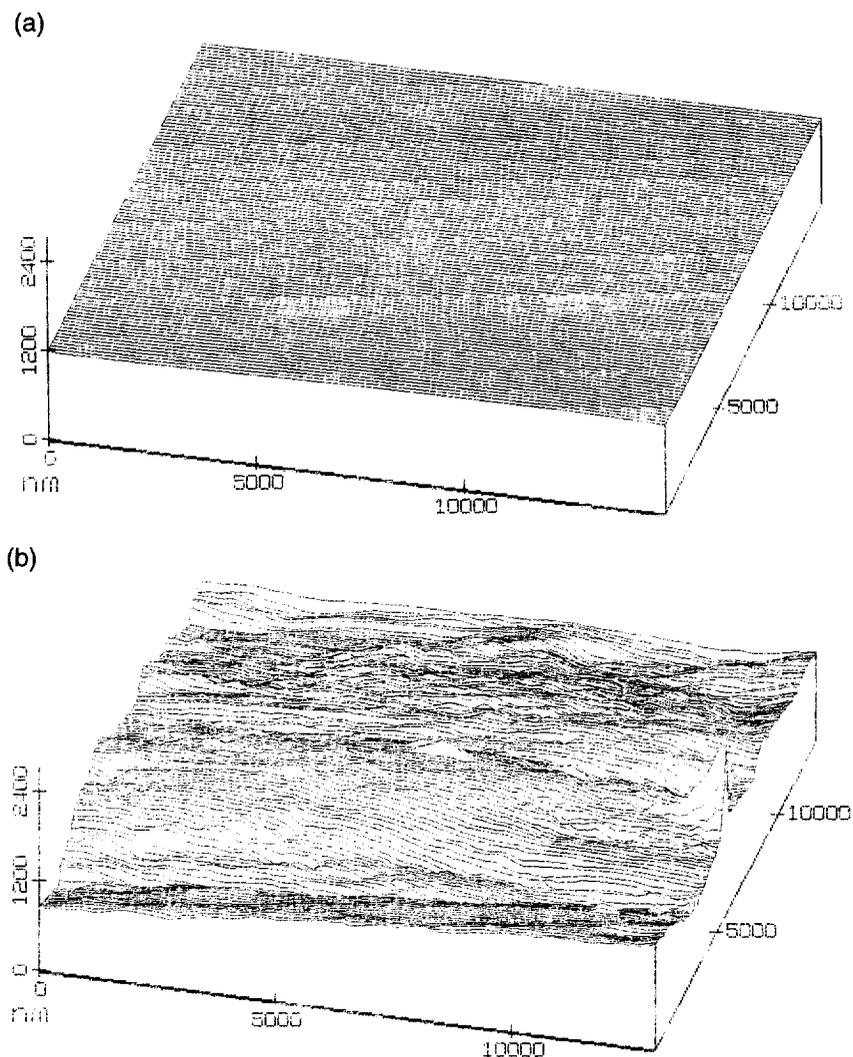


Fig. 3. Scanning Tunneling Micrographs of: (a) unimplanted titanium surface, and (b) titanium implanted with $1.5 \times 10^{16} \text{ Au}^+$ ions/cm² at 1 MeV. The titanium surface was polished with $0.3 \mu\text{m}$ aluminum oxide prior to implantation.

sample #5 and then decreased for sample #6. When the OCP became constant in the active region, a Tafel extrapolation test was performed on sample #1. The result of this test is shown in Fig. 6. This figure also shows that at higher potentials (above $-200 \text{ mV}_{\text{SCE}}$), the titanium is passive. The partial cathodic branch associated with sample #5 is superimposed on this figure. The intersection of these branches with the anodic scan relates to the corrosion current which can be converted to the corrosion rate. Notice that only the hydrogen current density is changing due to the implanted gold (point A in Fig. 6). This sample had a corrosion current density of $3.98 \times 10^{-4} \text{ A/cm}^2$ compared to the corrosion

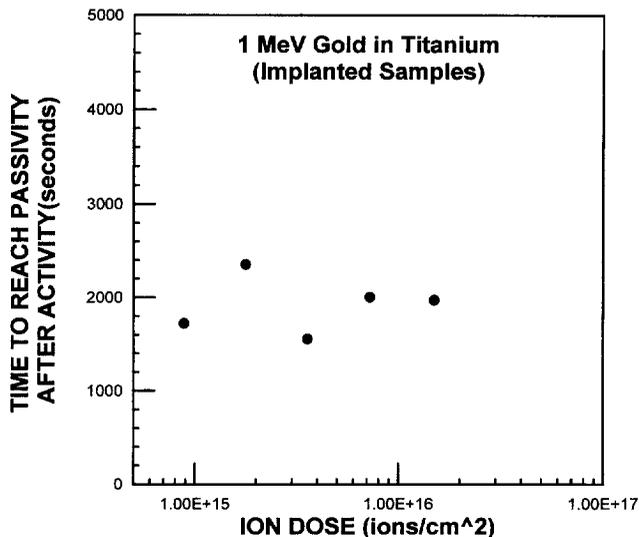


Fig. 4. Time required to reach secondary passivity after initial activity. Notice that the effect of ion dose is not significant.

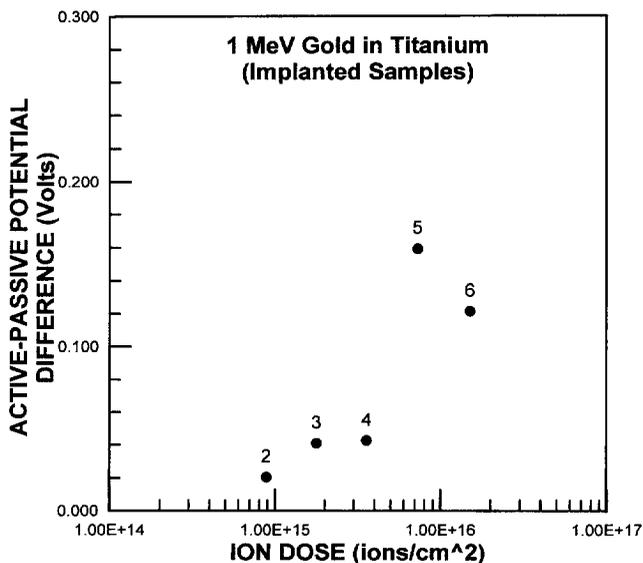


Fig. 5. Potential difference (in Volts *vs* SCE) between active and secondary passive regions (see Figure 1) as a function of ion dose.

current density of 2.32×10^{-4} A/cm² for the unimplanted sample as shown by point B in Fig. 6. The corrosion rate calculated from these values were 4.64 mm/yr (183 mpy) and 2.71 mm/yr (107 mpy), respectively. The experimental curves indicated an increase in the corrosion rates. These increases were experimentally confirmed by ICP analysis of titanium in the corrosive solution, as shown in Table 2. Figure 7 shows the relationship between the

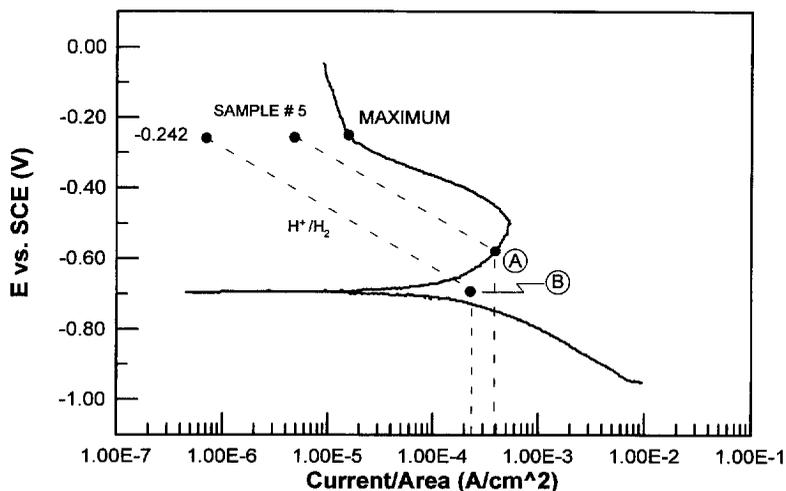


Fig. 6. Tafel plot for pure titanium in 20% sulfuric acid at 40°C with a calculated corrosion rate of 107 mpy. The partial cathodic branch associated with the unimplanted titanium and titanium implanted with 7.25×10^{15} Au ions/cm² (sample #5) are also superimposed on the figure.

Table 2. Concentrations, Corrosion Rates, and Depths Removed for Titanium Implanted with 7.25×10^{15} Au⁺ ions/cm² (Sample #5)

Time (seconds)	Potential (V vs SCE) (Volts)	Concentration (mg/l)	Corrosion rates from last potential mm/yr (mpy)	Total depth removed (nm)
6120	-0.718	<0.01	0.0	0
8208*	-0.560	0.20	3.47 (137)	230
11808	-0.636	0.585	3.99 (157)	455
18000	-0.699	1.055	2.72 (107)	988
21600	-0.712	1.325	2.64 (104)	1289

* Time in the active potential region of the curve when maximum occurs.

depth of material removed from the surface and the time in solution to achieve the dissolution when of that amount of material from sample #5. The corrosion rate was measured as a function of depth of material removed from sample #5 using ICP and is shown in Fig. 8.

From time 0 to 6120 sec. the corrosion rate was 0 and no titanium was found in solution. From 6120 sec. to 8280 sec. the titanium concentration was measured to be 0.20 mg/l which gives an average corrosion rate of 3.47 mm/yr (137 mpy). The cumulative amount of titanium removed at this time corresponded to a depth of 230 nm (see Table 2). Since the potential in the active region at 8280 sec. was maximum and, assuming that the Mixed Potential theory is valid here, this suggests that the maximum concentration of gold in the titanium is found at a depth of 230 nm. According to our computer simulation using the program Trim-95 (Transport of Ions in Matter), which utilizes Lindhard, Scharff and Schiot's (LSS) theory,⁸ the maximum concentration of gold was calculated to occur at a

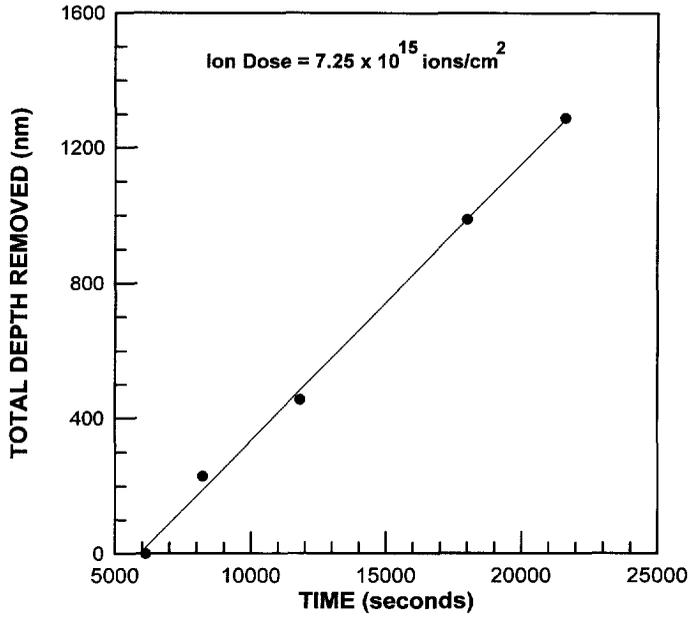


Fig. 7. Relationship between total depth removed from surface and exposure time in the solution.

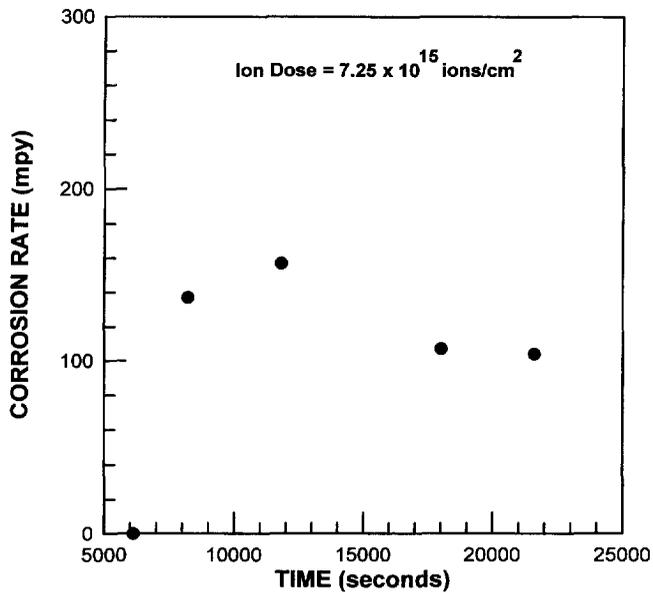


Fig. 8. Calculated corrosion rate (mpy) for sample #5 versus exposure time in the solution.

depth of 161 nm, which closely corresponds to the 170 nm depth of the implanted gold determined by RBS analysis.

It is difficult to detect and quantify small amounts of low mass impurities, such as oxygen, in higher atomic mass substrates using standard RBS. However, by using NRS and taking advantage of a nuclear elastic resonance scattering of He^+ on oxygen⁹ having a relatively high cross section, more accurate results can be obtained. The use of this technique (NRS) indicated that oxygen was present beneath the surface of the titanium.¹⁰ In that study, titanium samples were prepared in the same manner as previously described here. A NRS spectra was used to characterize the oxide layer; the sample was then implanted with gold and post-implant with NRS was performed. Comparison of the pre- and post-implanted spectra suggested that oxygen was spread into the substrate resulted in a thicker layer. The profiles of gold and oxygen from sample #5, generated by RUMP6 (RBS computer analysis program) and smoothed with a seventh order polynomial fit, are shown in Fig. 9. This suggest that although the gold may have contributed to the increase in passivity, it was not the only factor. Further analysis of the RBS spectrum revealed relatively high concentration of oxygen at the surface and at a depth of approximately 280 nm (see Fig. 9) with a lower concentration between the surface and the 280 nm depth. Since the titanium oxide layer is generally less than 10 nm thick at the surface, and RBS shows this layer to be about 10 times that amount, this high concentration of oxygen at both regions was probably a result of the ion implantation process. This phenomenon could be explained either by recoil-implantation of the surface oxide layer into the titanium as a result of collisions with the gold ions or by the diffusion of oxygen inward through ion-damaged pathways. Recoil-implantation of the oxygen from the surface oxide layer would have resulted in a lower concentration of oxygen at the surface; however, upon exposure to air,

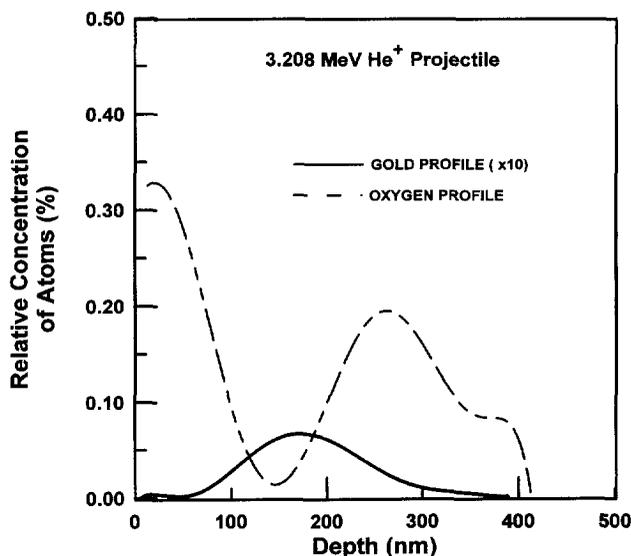


Fig. 9. Gold ($\times 10$) and oxygen concentration profiles calculated from backscattering spectrum of titanium implanted with gold. These profiles, which are smoothed by a polynomial fit, revealed the presence of recoil-implanted oxygen slightly deeper than the gold and may have contributed to the return-towards-passivity during the OCP measurements.

additional oxygen could have reacted with titanium to replenish the oxygen diffusing inward from the surface (as shown in Fig. 9). Therefore, the increased passivity (see Fig. 1) at the surface could be due to an increased oxide thickness. Once this oxide layer was dissolved by the corrosive solution the secondary passivity in the active region could be attributed to both the gold and the oxide layer detected below the gold (see Fig. 9).

CONCLUSIONS

The results of the OCP tests indicate that titanium remains in passive state for a longer period of time when implanted with increasing doses of gold. Once the surface oxide and the first layers of titanium are removed, the open circuit potential and the corrosion rate of the samples apparently increase as the implanted ions are encountered. Since noble metal alloying has been shown to cause spontaneously passivation in titanium, it is reasonable to deduce that the observed shift in potential was due (at least) in part to the implanted gold. However, the presence of oxygen in the region that coincides with noble potentials indicates that the oxygen is partially responsible for the passivating effect.

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