



POTENTIAL EFFECT ON THE LEACHING OF ALLOYING ELEMENTS OF THE LASER TREATED AND UNTREATED Ti-6Al-4V

Mazen M. Khaled¹

1: Department of Chemistry, KFUPM, Dhahran 31261

mkhaled@kfupm.edu.sa

ABSTRACT

Potentiodynamic scans performed on Ti-6Al-4V and laser treated Ti-6Al-4V showed that laser treatment enhanced the corrosion protection of the laser treated specimen below 0.5V. However, the current profile of the laser treated specimen was noisy, indicating an unstable surface and continuous dissolution and re-passivating. Controlled potential electrolysis at selected active/passive regions were performed. ICP analysis of metals in solution after electrolysis showed that aluminum leached out at a highest percentage. The percentage of titanium and vanadium were the lowest. After two hours of electrolysis the percentage of aluminum reached a maximum of 94% indicating selective leaching of aluminum. Laser treatment increased the leaching of titanium in the passive region.

Keywords: *corrosion, laser, surface, treatment, Ti-6Al-4V, coatings.*

Ti-6Al-4V

ICP

.%

1. INTRODUCTION

Ti-6Al-4V alloy is an important alloy for engineering applications and has excellent resistance to corrosion, particularly oxidizing and chloride-containing process streams. [Budinski,1991] The alloy resistance to corrosion is mainly due to the formation of a very stable, continuous, highly adherent, and protective oxide films. The oxide film consists mainly of TiO₂, but may also contain a mixture of other oxides such as Ti₂O₃ and TiO. [Feng et. al 2002]

Many techniques were developed to improve the tribological properties of the alloy surface to make it more resistive to wear and corrosion. One of the promising techniques relies on the use of lasers to modify the surface structures and composition; thereby, improving the tribological properties [Akgun and Inal, 1994]. Recently there have been many studies that show the importance of laser surface melting to improve the surface properties. [Zum and Schneider, 2000], [Wang, 2000], [Ghanamotheu, 1979], [Kumar and Banerjee, 2001] and [Bordji et.al, 1996b]. Byproducts of wear are a serious problem in the implants industry. It was found, for instance, that metallic ions released in vitro are cytotoxic, in titanium-base [Nakashima et.al, 1999] and cobalt-chromium alloys. [Howie et. al, 1996] Another study found that patients on chronic renal hemodialysis may develop systematic aluminum toxicity manifested as aluminum-associated osteomalacia. [Martyn et. al, 1986] Aluminium produces toxic effects at the cell membrane by altering the physical properties of the membrane, by interfering with the function of voltage-activated ionic channels, and by altering the secretion of transmitters. Ti-6Al-4V alloy clearly contains 6% aluminum and is used in hip replacement, facial implants and dentistry.

Recently we have shown that the Laser treatment of Ti-6Al-4V improved the corrosion resistance of the alloy as deduced from electrochemical measurements. [Khaled et. al, 2001] Controlled current experiments showed that upon electrolysis in acid/chloride solution the aluminum metal leaches selectively into the solution with approximately 90% compared to titanium and vanadium. The goal of this paper is to investigate the potential dependent leaching of the alloys constituents in different regions of the potentiodynamic scans.

2. EXPERIMENTAL

A commercial Ti-6Al-4V alloy consisting of α and β phases, was used as the workpiece material. The workpieces were prepared from rectangular dimensions of 40 x 12 x 2 mm. They were polished with a diamond paste of grade 0.1 μm to produce the maximum Ra value of 0.5 μm . A CO₂ laser with nominal output power of 1.6kW was used to irradiate the workpiece. The Ti-6Al-4V workpieces were polished gently and washed with deionized water prior to conducting the electrochemical tests. The electrolytic solution used all the electrochemical tests is made of 0.1N H₂SO₄ + 0.05M NaCl. The cell used was composed of three electrodes. The Ti-6Al-4V workpiece was used as working electrode, a platinum wire was used as a counter electrode, and a Ag/AgCl electrode was used as a reference electrode. The electrochemical experiments were performed using a EG&G PARC model 273 A potentiostat-galvanostat.

3. RESULTS AND DISCUSSION

Figure 1 shows the potentiodynamic scans of the untreated Ti-6Al-4V and laser treated alloy. Table 1 shows that the corrosion potential of the laser treated alloy was 0.087 V as compared to -0.323 V for the untreated specimen.

Table 1: Electrochemical corrosion parameters

	E _{corr} (mV)	I _{corr} $\mu\text{A}/\text{cm}^2$	Corrosion Rate $\mu\text{m}/\text{y}$
Untreated	-0.323	0.371	12.7
Laser Treated	0.085	0.168	5.74

Hence, laser surface melting has improved the corrosion potential by 410mV. The corrosion current density for the laser treated specimen was 0.168 $\mu\text{A}/\text{cm}^2$ where as the untreated corrosion current density was 0.371 $\mu\text{A}/\text{cm}^2$. The corrosion rate of the laser surface melted specimen was 5.74 $\mu\text{m}/\text{y}$ compared to 12.7 $\mu\text{m}/\text{y}$ for the bare Ti-6Al-4V specimen. Hence, corrosion parameters show an improvement of corrosion resistance by approximately a factor of two. However, analysis of the full potentiodynamic scans reveals a real-time resistance behavior as compared to the theoretically extracted corrosion parameters in the Tafel region. The figure shows oscillation in the potentiodynamic scans of the LASER treated specimen. Transient currents are very apparent around the corrosion potential. These transients are very frequent up to 0.5V, after which the curve becomes less noisy. Current transients indicate that the surface film is not stable and is subject to fast repetitive pitting and refilming. Moreover, this is an indication that the LASER treatment does not yield a very homogenous surface and although it improves the corrosion rate and corrosion potential but still it can sustain severe film break even in the vicinity of the open circuit potential. The untreated Ti-6Al-4V exhibits a constant passive current of $10^{-5.7}$ A that is not observed for the laser treated specimen. The laser treated specimen exhibits a continuously increasing current with current densities values lower than the untreated specimen at very small overpotentials. Moreover, the laser treated specimen shows a very interesting feature, an abrupt change

in the slope at 251mV showed a sudden transformation into a more passive region. Hence, the laser surface passivate quicker than the untreated sample but shows a continuous variation of current with potential and does not exhibit a constant current vs potential feature. This feature is required by the implants industry, since the faster an inherent metal passivation results in less ions released in vitro and hence results in less toxicity. [Zitter and Plenk, 1987], [Zum and Schneider, 2000].

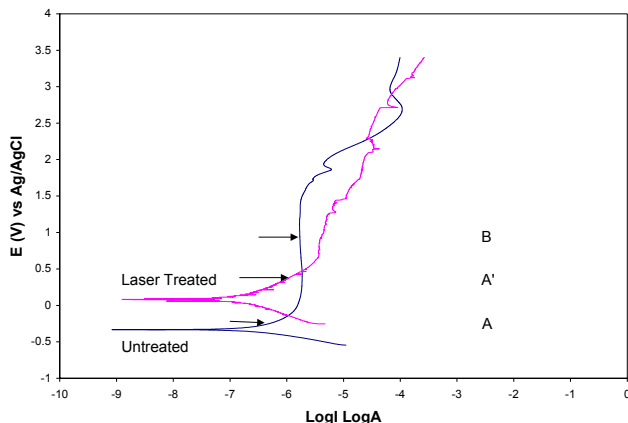


Figure 1: Potentiodynamic scans of untreated and laser treated Ti-6Al-4V alloy. Scan rate 0.166mV/s in 0.1N H₂SO₄ + 0.05M NaCl.

At potentials higher than 0.5V the current densities of the laser treated samples is significantly higher than the untreated one up to 2.3 V where the untreated specimen suddenly shows severe breakdown and refilming and peak at 2.7 V. Above 2.9V the laser specimen current densities become higher again showing more susceptibility to corrosion.

Electrolysis of the untreated and laser treated specimen were carried out at the potentials corresponding to the arrows in figure 1, regions A, A' and B (table 2).

Table 2: Selected potentials for electrolysis in Volts vs Ag/AgCl reference electrode

Untreated	-0.24(A)	1.01(B)
Laser Treated	0.4(A')	1.01(B)

Regions A and A' correspond to the active region of the untreated and the laser treated specimen respectively. These regions were selected to compare the dissolution of metals in the active or kinetically controlled region and the passive region. Table 3 shows the ICP results of solution metal composition after 2 hours of electrolysis.

Table 3: ICP analysis for Ti, Al, V after 2 hours of electrolysis in each region

	%Ti	%Al	%V
Untreated	8.68 (A)	88.3 (A)	3.02 (A)
	2.64 (B)	95.26 (B)	2.10 (B)
Laser Treated	4.7 (A')	94.44 (A')	0.855 (A')
	23.8 (B)	75.23 (B)	0.906 (B)

Vanadium solution composition remains in the range of 1 % to 3%. Vanadium reaches a minimum of 0.855% at 1.01V of the laser treated specimen. The titanium solution composition for the untreated specimen is 8.68% in region A while it dropped to 2.64% in region B. This is accompanied by an increase in aluminum percentage from 88% to 95%. Hence, in the untreated alloy case, the titanium leaching decreases upon going from the active to the passive region, while aluminum increases. The opposite is observed in the laser treated sample. The titanium concentration increased sharply from 4.7% in the active region to 23.8% in the passive region, while aluminum decreased from 94% to 75%. Hence, laser treatment increases the leaching of aluminum in the active region and decreases the leaching in the passive region probably due to the melting of the surface and the formation of more homogeneous composition. On the other hand, laser treatment increased the leaching of titanium in the passive region resulting in less titanium on the surface and decreasing its corrosion resistance properties that is reflected in the observation of transient currents.

4. CONCLUSION

Generally, laser treatment decreases the corrosion rate of Ti-6AL-4V but it exhibits an unstable current indicating continuous dissolution and passivation. Aluminum is selectively leached out in solution at all selected potentials with its maximum of 94% after two hours of electrolysis at 1.01V in the passive region of the potentiodynamic curve. Titanium dissolution increases with laser treatment resulting in transient currents.

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