

Anodic Behavior of Ti6Al4V in Citric Acid/Phosphate Solutions containing Fluoride

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Introduction

Recent works have showed that Ti based alloys are very resistant in aggressive media due to a TiO_2 thin passive film formed even at open circuit conditions. Sibert¹ has shown that phosphate based solutions allow the films on Ti to grow with the best protective performance. On the other hand, Raetzer² has verified that fluoride ion attacks the primary oxide film formed on Ti surface. The present work investigated the anodic behavior of Ti6Al4V alloy in citric acid/phosphate solutions pH 2, 4 and 5 in the presence of fluoride ion.

Experimental

Electrochemical measurements were carried out in a three-electrode conventional cell. The working electrode consisted of a Ti6Al4V disc. Cyclic voltammograms (CV), open circuit (OCP) and impedance (EIS) measurements were conducted in citric acid/phosphate solutions pH 2, 4 and 5 in the presence of 0.1 molL^{-1} sodium fluoride. Potential measurements are referred to a saturated calomel electrode (SCE) and the auxiliary electrode was a Pt wire.

Results and Discussion

OCP measurements (Figure 1) show that Ti6Al4V alloy remains in the passive zone after one hour immersion time in citric acid/phosphate solution pH 5 containing fluoride ion. However, in solutions with pH 4 and 2, the fluoride presence shifts the OCP to more negative values indicating the primary oxide film dissolution.

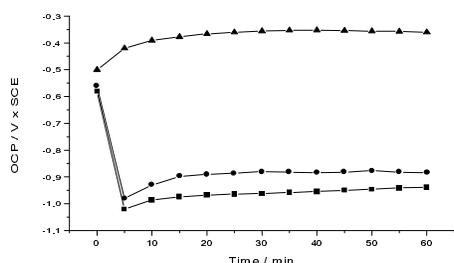


Figure 1: OCP of Ti6Al4V in citric acid/phosphate solutions containing fluoride; pH 2 (■), pH 4 (●), pH 5 (▲)

CV for Ti6Al4V run from -1.0 V to 1.0 V in pH 5 solutions containing fluoride show a passive behavior. On decreasing the pH a dissolution process appears in the presence of fluoride ion being observed high anodic currents at -0.5 V . The reverse scan shows a reactivation process indicating that a porous film was formed (data not shown).

The Bode plots for the alloy in pH 5 with fluoride present a capacitive behavior at high frequency followed by a diffusional process in the low frequency range (figure 2). The appearance of a shoulder on the phase angle curve at lower frequencies means that at least two different time constants are present. On decreasing the pH the maximum phase angle and the polarization resistance decrease. The calculated overall capacitance of the alloy in pH 5 solution is around $100 \mu\text{Fcm}^{-2}$ and 5 mFcm^{-2} at pH 2 evidencing a porous film formation.

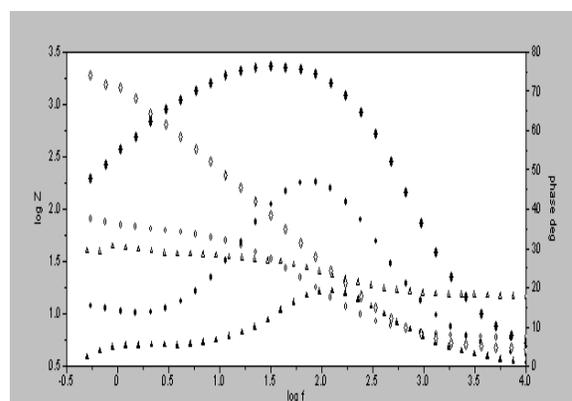


Figure 2: Bode plots for Ti6Al4V in citric acid/phosphate solutions containing fluoride after 20 minutes at OCP: pH 2 (▲ and △), pH 4 (● and ○), pH 5 (◆ and ◇)

Conclusions

This work shows that on increasing the solution pH up to 5 by adding phosphate the alloy passivation is improved even in the fluoride presence. On decreasing the pH in fluoride containing solution the film porosity increases.

Bibliography

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2. H. J. Raetzer-Sheibe, *Corrosion*, **34**, 437 (1978)

Acknowledgements

The authors acknowledge financial support from FAPERGS and CNPq.

