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Influence of heat treatment condition on passivity of titaniumaluminum-vanadium alloy in sodium chloride solution

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ABSTRACT

Corrosion of Ti6Al4V was study with different heat treatments in 3,5% NaCl solution by electrochemical measurements, included potenthiodynamic polarization curves, linear polarization resistance (LPR) measurements and electrochemical impedance spectroscopy (EIS), in order to focus on exploring the effect of annealing on the electrochemical response in a quantitative manner. The samples were prepared in the state of the art; heat treatments were applied at four different temperatures of 550, 750, 950 and 1100°C. The microstructure of samples has been studied using the optical microscopy and the mechanical properties have been evaluated such as microhardness HV. The electrochemical test show that the corrosion rates of treated samples at temperature equal or more then 750 ° C; are much better for the untreated sample. Although, the corrosion product on the surface is identified as titanium dioxide by XRD in all © 2013 Trade Science Inc. - INDIA samples.

INTRODUCTION

The Ti6Al4V alloy is widely used in the aerospace, aircraft fabrication and in different industries fields. It presents good mechanical properties, low densities (around 4.5 g/cm^3) and interesting physicochemical properties. In particular due to their excellent resistance

KEYWORDS

Ti-6Al-4V: Alloy corrosion; Heat treatment; Corrosion product; XRD.

to corrosion, it's widely employed in the presence of sea water. However, the properties of this alloy can be modifying by different heat treatments used in the literature in order to improve their physico-chemical and mechanicals properties.

In this context, several studies have been initiated about the corrosion performance of heat treated

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TiAl6V4 alloy. Ueda and al are treated corrosion behaviors of nitriding heat treatment on this material, the results show an improvement in surface hardness which depends on the processing time^[5]. Moreover, M.M. Khaled and al were study the influence of different concentrations of NaCl on corrosion performance of nitrided Ti6Al4V alloy. They find an increase in the corrosion rate when increasing the chloride concentration^[6].

Zhongping Yao and al also studied the electrochemical behavior of the alloy Ti6Al4V, micro plasma oxidized in a 3.5% NaCl solution. The diagrams impedance spectroscopy (EIS) obtained show that the corrosion resistance increases with increasing oxidation time^[7].

The aim of the present work was to investigate the corrosion and passivation behaviors of annealing Ti6Al4V alloy in aerated 3.5% NaCl solution.

EXPERIMENTAL METHODS

The alloy used in this investigation was TA6V having the chemical composition of (mass fraction wt%): C=0.08, O=0.13, Fe=0.25, Al=6, V=4, H=0.02, N=0.05, Ti= rest.

Specimens were machined into 10X10 mm dimensions. All the samples are polished until the rank 1200, in continuation with the alumina paste, then rinsed with distilled water and are mechanically dried before each test. All the samples thus, have the same roughness. All specimens were treated in four temperatures: 550, 750, 950 and 1100°C for 2 and 4 hours, after this operation let cool with the free air.

The electrochemical tests were carried out using a model potentiostat/galvanostat/ZRA (GAMRY Instruments Ref. 600). A three-electrode cell consisting of the sample as the working electrode, the electrode potential was measured against a saturated calomel electrode (SCE) (E=240 mV/ENH) and a platinum foil was used as an auxiliary electrode.

The corrosion potential (Ecorr) and corrosion current density (Icorr) were determined using the Tafel fit. In the open circuit potential (OCP) measurement, changes in the open circuit potential (Ecorr) were monitored as a function of immersion time for about 1 hour in a saline solution (3.5% NaCl). All the electrochemical tests were performed at room temperature. *Research & Restens On*

earch & Reolews Dn Electrochemistry An Indian Journal Electrochemical impedance measurement was performed in the frequency range of $100 \text{ kHz}-5 \ 10^{-2} \text{mHz}$ at the open circuit potential, after 1 hour of immersion, by applying amplitude of 5 mV.

Surface microhardness measurements (Vickers indenter) were realized the load of 300gf. The microstructure and the corrosion product film were examined by optical microscope and XRD analysis. The diffractogram were recorded with radiation (CuK α = 1.54056 Å) at an angular range of 30-50 ° (2 θ) with a step of 0.04 °.

RESULTS AND DISCUSSION

Microstructure modifications

the microstructure of the Ti-6A1-4V used in our study is showed in the Figure 1, we can observe the presence of phase α (in white) and the phase β (in gray),¶ this alloy is duplex^[9].



Figure 1 : Optical micrographs of TA6V alloy untreated (G x500)

The influence of the heat treatments applied (Figure 2) shows that the microstructure is the same as the untreated sample, the presence of grains β and α homogeneously distributed and the microstructure obtained are fine when the temperature increases.

The most change in morphology, size and distribution phase for temperatures 550, 750 and 950°C (α domain) at 2h and 4h can be observed. In the case of β domain (1100°C: 2 and 4h), a new phase appear, it is the phase α '^[10].

Microhardness measurements



Figure 2 : Optical micrographs of TA6V alloy heat-treated (G x500).

The effect of heat treatments on hardness of samples was studied, using a Vickers microindenter. The results of the hardness obtained for annealed specimens are reported in Figure 3.



Figure 3: Microhardness data as a function of heat treatment for different samples.

The microhardness value of the sample treated at 1100 °C was four time as the microhardness of the untreated sample (230 HV_{0.3}). The higher hardness value obtained in the samples at various temperatures can be related to the refinement of the microstructure.

Electrochemical testing

For electrochemical tests we opted for stationary and non stationary methods regarding: the evolution of the potential, potentiodynamic and Electrochemical impedance spectroscopy.

Potential evolution $(E_0 = f(t))$:

The figure 4 a, b presents the evolution of the standard potential (E_0) as a function of time in NaCl solution. The potential values recorded for samples treated at 2h fluctuating between -0.150 and -0.310 (mV/SCE), however, for 4h treatment the interval -0.180 and -0.370 (mV/SCE) was recorded.

In the case of two treatments, we observe for temperatures below 950 ° C, the E_0 stabilizes quickly. However, from 950 ° C the standard potential takes more time to stabilize.

In general, all samples studied show a rapid increase at the beginning and become stable after one hour of immersion, probably due to the formation of a protective film of corrosion product on the surface.

Potentiodynamic polarisation technique:

Potentiodynamic polarization technique has been widely used to study these corrosion systems^[11,12]. the Curves plotted for the both treatments (Figure 5 a, b) consist of cathodic and anodic branches and a wide range of free passivation.

The cathodic current density of this system should be attributed to the reduction of oxygen dissolved in the solution^[13].





Figure 4 : Open circuit potentials versus time for TA6V after 1h of immersion in aerated 3.5% NaCl solution: a) 2h and b) 4h.



Figure 5 : Potentiodynamic polarization curves obtained for TA6V in aerated 3.5% NaCl solution at different processing cycle: a) 2h and b) 4h.

We note that the untreated sample has a wide range of pasivation wich begins from 0 mV / SCE with a corrosion potential -690 mV / ECS. However, for temperatures 550, 750, 950 and 1100 ° C, the formation of the passivation film begins at potential which tends to values nobler.

For the sample treated at 1100 °C, it indicates a rupture of the film in around of 500mV/SCE for both processing time but with rapid self regeneration.

Potentiodynamic tests show that the treated and untreated samples show the same tendency to spontaneously form an oxide film which improves the protection features and the polarization curves of TA6V alloy depend greatly on the procedure of heat treatments.

The results deduced from the polarization curves \mathcal{R} sesence & \mathcal{R} corres \mathcal{D} n

Electrochemistry An Indian Journal "TABLE 1", show that when the temperature of treatment increases the corrosion potential tends towards more positive values, and the best electrochemical performance in chloride medium are attributed to the sample treated at 750 ° C for 2 hours with a low corrosion current, it is about 12 μ A and a potential tends toward noble values -417mV/SCE. In addition, the corrosion potential values obtained show that the heat treatments applied on very little influence on the corrosion behavior of the alloy.

Electrochemical impedance spectroscopy (EIS):

Electrochemical impedance spectroscopy (EIS) testes is required to provide an overview of the characteristics and kinetics of electrochemical processes oc-





Temperature	Untreated	550°C		750°C		950°C		1100°C	
		2h	4h	2h	4h	2h	4h	2h	4h
E _{cor} (mV/SCE)	-690	-459	-459	-417	-463	-412	-548	-490	-483
$I_{cor}(\mu A)$	16,0	28,7	32.8	12,0	1,6	8.0	1,48	3,26	11,4
V _{cor} mm/an	0.495	0.550	0.019	0.004	0.043	0.014	0.012	0.016	0.064

 TABLE 1 : Electrochemical results of potentiodynamic polarization of TA6V in 3.5% NaCl solution

curring at the interface of titanium alloy in NaCl solution.

From the table below (TABLE 2), we can see an amelioration of a corrosive performance with increasing temperature, but with a remarkable increase in value for Rt corresponding for heat treatments at 2h.

Figure 5, shows the Nyquist plots for the untreated and heat-treated samples, there was only one capacitive loop corresponding to a capacitive phenomenon for all specimens. The treatment at 750 $^{\circ}$ C for 2h and 4h has better corrosion behavior in NaCl solution.

X-ray diffraction analysis

X-ray diffraction analysis (Figure 7) of corroded

products were formed on samples surface in 3.5% sodium chloride solution confirmed the presence of TiO₂,



Figure 7 : X-ray spectra obtained after immersion test.

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TABLE 2 : Results of the impedance spectra obtained for TA6V in aerated 3.5% NaCl solution at different processing cy	ycle:
a) 2h and b) 4h.	

Temperature(°C) Time of treatment (h)	$C_f(\mu F.cm^{-2})$	R _t (k.ohm.cm ²)	R _p (ohm.cm ²)	
State initial	untreated	53,49	156,9	7,911	
550	2	56,40	167,3	5,804	
550	4	86,30	83,14	10,24	
750	2	47,22	108,6	5,804	
750	4	60,01	47,26	15,88	
050	2	52,41	177,9	7,899	
930	4	217,4	6,45	7,044	
1100	2	66,43	84,73	5,423	
1100	4	26,09	6,38	18,04	
160000 a) 140000 - 120000 - 100000 - 100000 - 100000 - 80000 - 40000 - 20000 - -20000 0 2000					
	Zr(ohms/cm ²)		Zr (ohm/cm ²)		

Figure 6 : Impedance diagram of TA6V in 3.5% NaCl solution after 1h: a) heat treatment for 2h and b) heat treatment for 4h.

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which implies that in the temperature or the different conditions of heat treatment does not affect the nature of corroded products formed but increase the capacity for self regeneration.

CONCLUSIONS

In this paper, we have shown that the behavior of Titanium-Aluminum-Vanadium alloy having undergone heat treatment for different conditions and placed in corrosive influence that:

- The heat treatments applied to the titanium alloy α + β (Ti6Al4V) have an influence on the microstructure and phases distribution;
- The microstructure of titanium alloys depends both on the proportion of each phase and the heat treatment applied to the material.
- The microstructures obtained after heat treatments are fine with interesting mechanical properties. The electrochemical tests in saline 3.5% NaCl show that the treated and untreated samples present the same tendency to spontaneously form an oxide film that improves protection features. With improved capacity for self regeneration indicated for the treatment of 750 ° C 2h and 4h.
- Analysis by X-ray diffraction at grazing incidence reveals the formation of TiO₂ at the surface for all samples. The heat treatments applied did not flock to the nature of the corrosion products.

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