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Electrochemical Studies of Heat Treated Ti-6Al-7Nb alloy used in Surgical Implant Application

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Abstract

Titanium and its alloys are widely used for orthopedic applications due to their high biocompatibility. Vanadium-free Ti-6Al-7Nb alloy has been developed as a potential alloy for providing improved corrosion and wear resistance for orthopedic implant devices, and to avoid the toxicity of vanadium ion.

This work deals with the dependence of corrosion parameter of Ti-6Al-7Nb alloy on compositional variation in the phases resulting from various heat treatments. Electrochemical examinations were applied made in blood plasma solution involving potential –time and dynamic polarizations for Ti-6Al-7Nb alloy of various heat treatments.

The corrosion parameters obtained from open circuit potential, and potentiodynamic polarization for the alloy Ti-6Al-7Nb were superior for specimen developed by solution treatment at 950^{o}C and air cooled followed by aging in comparison with that of other treatments.

الخلاصة

اخذ استخدام للتيتانيوم وسبائكه ينتشر بصورة واسعة في جراحة العظام والمفاصل وذلك لملائمته البايولوجية العالية . لقد تطورت السبيكة الخالية من الفناديوم ذات التركيب Ti-6Al-7Nb من اجل تحسين خواص التاكل والبلي للزوارع الجراحية ،وكذلك لتجنب سمية ايون الفناديوم في السبيكة التقليدية Ti-6Al-4V .

ان العمل المعروض في هذا البحث يتعامل مع التغيرات في التركيب الدقيق بفعل المعاملات الحرارية على التاكل للسبيكة Ti-6Al-7Nb . تم اجراء الاختبارات الكهروكيميائيةعلى السبيكة في مشبهات محاليل الجسم من خلال قياس الجهد –الزمن ثم قياس الاستقطاب الداينميكي (Dynamic Polarization) للسبيكة عند انواع مختلفة من المعاملات الحرارية .

لقد بينت نتائج الدراسات الكهروكيميائية ان للمعاملات الحرارية تاثيرفي خواص التاكل الناتجة من التغيير الطوري الذي بدوره يؤدي الى تغيير تركيب العناصر داخل الاطوار والتي تحدد نوع الاكاسيد المتكونة في وسط التاكل .تشير النتائج المستنبطة من فحوصات التاكل على سبيكة Ti-6Al-7Nb المعاملة حراريا عند درجة حرارة 950 م^{0} ووسط تبريد الهواء بالمقارنة مع بقية المعاملات الحرارية الاخرى بانها تمتلك خواص تاكل ممتازة.

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Introduction

The use of artificial body implants is rising in rapidly and at present, titanium and titanium alloys seem to be well established systems for heavy load-bearing skeletal implants, such as artificial tooth roots or joint endoprostheses [1]. Titanium is widely used for making orthopedic implant devices as it can form a stable passivating surface in the biomedium that is compatible with the tissue surroundings. Titanium is well known for its high corrosion resistance due to the instant formation of an inert oxide surface layer with *n*-type semiconducting characteristics [2, 3]. This has given titanium a reputation of being a biocompatible material compared to other conventional implant materials [4].

Titanium and its alloys have been increased widely to be used as biomaterials in surgical implants due to the low inertness in the body, so that corrosion resistance seemed likely to be good in the human environment [5].

Titanium alloys have been clinically applied since 1970 when surgical implants were made with high strength Ti-6Al-4V alloys [6]. As vanadium oxide VO_2 is thermodynamically unstable some vanadium atoms could be released in human body and cause toxic effects [7,8]. These drawbacks of Ti-6Al-4V alloy have led to the development of new titanium alloys without vanadium such as Ti-6Al-7Nb and Ti-5Al-2.5Fe [9].

Raja et al [10] investigated the effect of microstructure on the corrosion behavior of titanium alloys. They studied the pitting corrosion in (1M) NaBr solution of three different microstructures (Widmanstätten, acicular martensite and α-phase) which were produced through suitable heat treatments for the near alpha alloy Ti-6Al-2Sn-4Zr-2Mo(0.1Si).

Aziz-kerrzo et.al [3] studied the corrosion susceptibility of Ti, Ti-6Al-4V and Ti-45Ni in a buffered saline solution using anodic polarization and electrochemical impedance spectroscopy. Ti and Ti-6Al-4V exhibited high resistance to the onset of localized corrosion, but pits were found to initiate at potential as low as 250 mV (SCE) on Ti-45Ni and the passive film formed on these electrodes comprising an inner barrier and an outer porous layer. The nature of the porous layer was found to depend on the nature of the alloy and the solution anion species.

Thair et.al [11] studied the effect of solution treatment and aging of Ti-6Al-7Nb alloy on the corrosion behavior of this alloy in simulated body fluid (Ringer's solution).They have exposed the alloy to solution treatment at different temperatures in $\alpha+\beta$ field range (850^{o}C to 970^{o}C) and β field

range (1010^{o}C) followed by aging at 550^{o}C. They have found that solution treatment at 950^{o}C followed by aging gives superior corrosion resistance due to the absence of selective dissolution of the phases.

The microstructure and its characterization of the alloy used in this work at different type of heat treatments (quenching, air-cooling and slow furnace cooling) from solution temperatures (namely 850 C^0 ,930 C^0 and 950 C^0) are investigated previously by Ajeel et.al [12].

Experimental part Materials

The materials used in this work are Ti-6Al-7Nb alloy which was prepared by DMRL (Defence Metallurgical Research Laboratories, Hyderabad-India)

Specimen Preparation

Specimens of 10-mm diameter with thickness of 4 mm were cut out from the rolled sheet Ti-6Al-7Nb alloy. The shaped specimens were molded using fast cold setting material up to 20 mm thickness leaving the topside of the specimen exposed. The mounted specimens were allowed to set for half an hour and care was taken to ensure that the mould does not contain any cracks or bubbles at the mould/specimen interface. The mounted specimens were grinded with SiC emery papers with different grits started from 80 grit, and continued by 120, 230, 400, 600, 800 and 1000 grit to get flat surface. The final polishing was carried out using alpha alumina 1µm, 0.3µm and 0.05µm. For electrochemical studies, suitable provision was made on the other side for electrical contact. The schematic diagram of the molded specimen for electrochemical studies is shown in Figure 1.

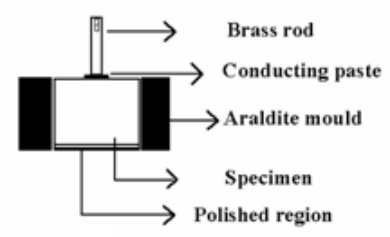

Figure 1: Specimen reparations for electrochemical studies.

Electrochemical Studies

In this work, open circuit potential (OCP) – time measurements, and potentiodynamic polarization were used as the techniques for evaluating corrosion parameters of the heat treated Ti-6Al-7Nb alloy in comparison to untreated specimens. The localized corrosion characteristics of the specimens were studied in simulated body fluids. The electrolyte, cell assembly and the electrode preparation for *in vitro*

electrochemical studies are detailed below.

NO.	CONST-ITUENT	WEIGHT (gm/l)
1	NaCl	0.700
2	KCl	1.200
3	KSCN	0.330
4	$NaHCO_3$	1.500
5	Na_2HPO_4	0.260
6	KH_2PO_4	0.200

Solutions

For electrochemical studies Ringer's solution, Artificial Saliva and Synthetic Blood Plasma (Chemical composition in Tables 1 – 3) were used in this study with adjusted pH. 7.4.

Table 1: Chemical composition of Ringer's solution [13].

NO.	CONST-ITUENT	WEIGHT (gm/l)
1	NaCl	9.00
2	*KCl*	0.43
3	$CaCl_2$	0.24
4	$NaHCO_3$	0.20

Table 2: Chemical composition of Artificial Saliva [14].

NO.	CONST-ITUENT	WEIGHT (gm/l)
1	NaCl	6.800
2	KCl	0.400
3	$CaCl_2$	0.200
4	$NaHCO_3$	2.200
5	Na_2HPO_4	0.126
6	NaH_2PO_4	0.026
7	$MgSO_4$	0.100

Table 3: Chemical composition of Synthetic Blood Plasma [14]

Electrochemical Cell

The electrochemical cell used in this study was locally fabricated according to the ASTM standards G5-87 [15]. The electrochemical cell containing six-necked flask of 500 ml capacity and it was equipped with a platinum electrode, which acts as the auxiliary electrode. A standard calomel electrode (SCE) was used as the reference electrode for measuring the electrode potential. A Luggin capillary was kept in such away that the working electrode and its tip remain at a distance of about 2mm in between to avoid ohmic drop. The temperature of the polarization cell was maintained at $37\pm1^{o}C$ by means of thermostated water bath to simulate the human body

temperature. Before immersing the specimen into the electrolyte, purging of the solution was carried out using purified nitrogen in order to remove the dissolved gases such as oxygen, carbon dioxide etc. and purging was maintained throughout the experiment. Figure 2 shows schematic representation for the potentiodynamic polarization arrangements.

Open Circuit Potential (OCP) - Time Measurements

The aim of the OCP-time measurements is to understand the corrosion behavior of the heat treated specimens under equilibrated conditions in the simulated body environment. The open circuit potential versus time measurement is considered as an important parameter for evaluating the stability of the passive film of the alloys. The specimens were immersed into the electrolyte and immediately the initial potential of the specimens was noted and monitored as a function of time up to 60 min.

Potentiodynamic Polarization Measurements

Potentiodynamic polarization was carried out in Ringer's solution (Table 3 the chemical composition) at pH adjusted to 7.4 and temperature 37.4±1^{o}C for both as rolled and heat treated specimens. Nitrogen gas was continuously purged into the electrolyte throughout the study to eliminate the dissolved oxygen. All the potential measurements were made with reference to a saturated calomel electrode (SCE). A platinum foil was used as counter electrode and potentiostate (Potentiostate type PRT 10-0,5-TACUSSEL ELECTRONIQU Co. France) was used for conducting the polarization experiments. When the specimen attained a constant potential, Potentiodynamic polarization was started from an initial potential of 250 mV below the open circuit potential and the scan was continued up to 1500 mV. The specimen was scanned in the positive direction at a sweep rate of 10 mV/sec and the current was monitored with respect to the potential.

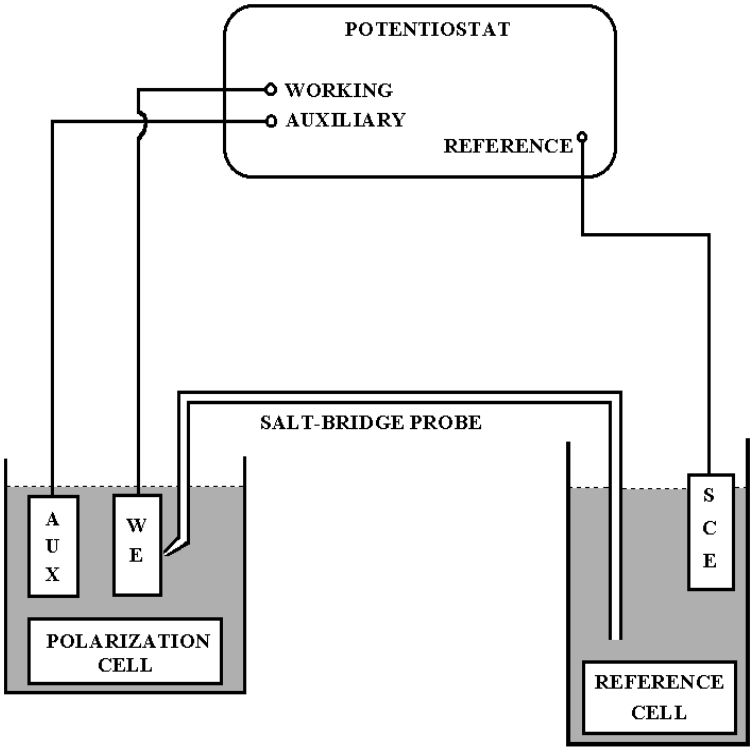

Figure 2 schematic representations of the potentiodynamic polarization arrangements.

Results

Open Circuit Potential (OCP)-Time Measurements

The stability of passive condition of the as rolled, solution treated and aged Ti-6Al-7Nb alloy at different temperatures is illustrated by the potential-time curves in Figures 3 to 5. The OCP's measured for the specimens heat-treated at 950^{o}C/WQ, 930^{o}C/WQ and aged (Figure 3) were found to shift towards passive direction continuously with the time and very low OCP values were recorded (-70 mV_{SCE} and –90 mV_{SCE} respectively) indicating strong surface passivation. This ensures the absence of chemical dissolution of Ti oxide and the formation of oxyhydroxides on the alloy containing elemental oxide. Yu et al [16] confirmed that alloys with Nb contents are strong candidates for formation of complex homogenous oxyhydroxides.

Table 4 shows the OCP of Ti-6Al-7Nb specimens in Ringer's solution ST at different

temperatures. In the case of specimens air-cooled after solution treatment, the specimen ST at 950^{o}C and aged (Figure 4) did not exhibit potential drops associated with surface activation during 1 hour exposure in the Ringer's solution. This kind of behavior strongly suggests that the air-formed native oxide consisting TiO_2, Al_2O_3 associated with traces of Nb_2O_5 and Ta_2O_5 on this specimen is kinetically resistant to chemical dissolution in the environment under study and this also confirmed by Cittig et al [5].

Titanium oxide can be presented on the titanium surface at normal or slightly elevated temperatures as rutile, a tetragonal form of titanium dioxide, and the presence of this surface film confers upon titanium excellent corrosion resistance in a wide range of corrosive media [17]. The presence of Nb_2O_5 can reduce migration of active ions like Cl^- through the passive film and improves the structural integrity of the oxide film such that pit initiation can be reduced [10]. It is well known that Al impairs the resistance of the alloy against pitting, thus the repassivation can occur in preference to dissolution in alloys with Nb and Ta alloying elements [16,18].

It can be seen from Figures 4 and 5 that the corrosion potential transient for the AC and FC specimens ST at 850^{o}C in Ringer's solution shows sudden drop after short time of immersion. This sudden decrease in the potential is ascribed to the chemical dissolution of sub oxides.

It may conclude that the depassivation and activiation by reducing the chemical dissolution rates strongly depend on surface nature after different heat treatments which play a role in the elemental distribution. The OCP data for the above two treatments suggests the presence of Ti^{+4} during the activation instead of complete reduction of TiO_2 to TiOOH [11].

Table 4: OCP of Ti-6Al-7Nb specimens in Ringer's solution ST at different temperatures.

Heat treat-ment	**OCP after 60 minute in Ringer's Solution (mV_{SCE})**		
	WQ	**AC**	**FC**
850°C	-120	-483	-345
930°C	-90	-274	-298
950°C	-70	-132	-288
As Rolled	-327		

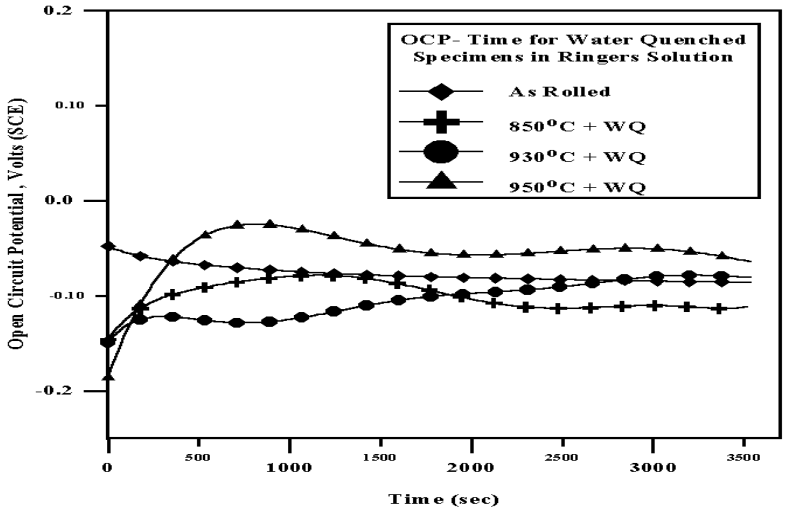

Figure 3 Open circuit potential (OCP) versus time in Ringer's Solution for Ti-6Al-7Nb alloy water quenched from different ST temperatures in α+ β phase fields and aged at 550°C/4hours.

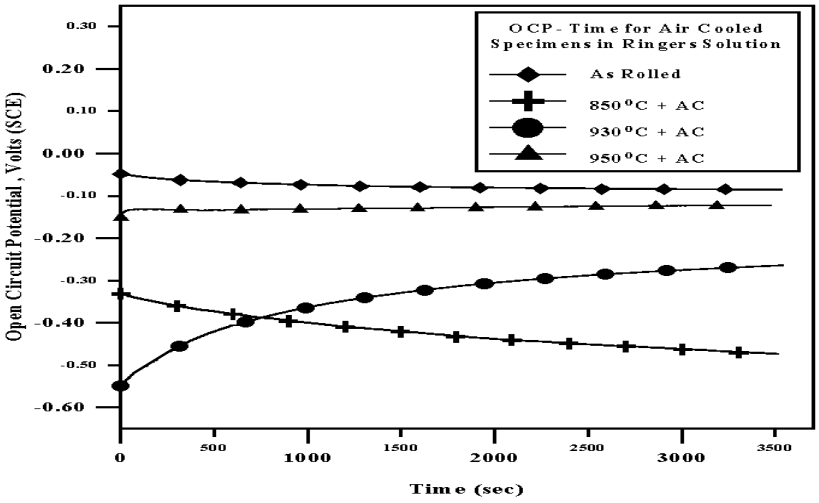

Figure 4 Open circuit potential (OCP) versus time in Ringer's Solution for Ti-6Al-7Nb alloy air cooled from different ST temperatures in α+ β phase fields and aged at 550°C/4hours.

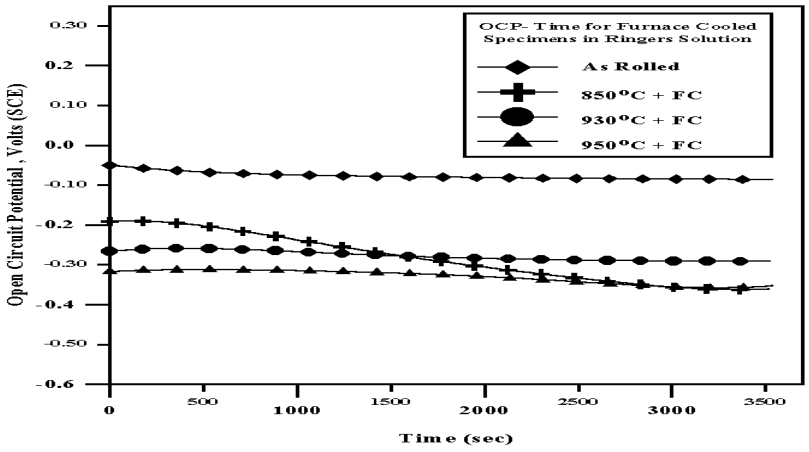

Figure 5 Open circuit potential (OCP) versus time in Ringer's Solution for Ti-6Al-7Nb alloy furnace cooled from different ST temperatures in α+ β phase fields.

Potentiodynamic Polarization

It is very important to evaluate the susceptibility to localized corrosion of the material under study, which can be determined by means of potentiodynamic polarization curves. The main parameters that can be obtained from these curves are the corrosion potential, E_{corr} and the passivation current density, i_p. The potentiodynamic polarizations curves of the specimens, solution treated and aged (STA) are presented in Figures 6 to 8. The passivation current density at 500 mV_{SCE} [13] measured for the solution treated and aged (STA) specimens are given in Tables 5.

The specimens ST at 950^{o}C followed by air cooling and aged shows the lowest passivation current density (0.533 $\mu A/cm^2$) as compared to other specimens indicating stability of the passive film of the specimen against any dissolution. The potentiodynamic polarization curves show that Ti-6Al-7Nb specimens heat treated under different conditions are passive in a wide potential region up to the breakdown occurrence at $E_b \approx 1$ to 1.1 V_{SCE}.

Table 5: Passive Current Density (i_p) $_{at}$ 500 mV_{SCE} of Ti-6Al-7Nb Specimens in Ringer's solution ST at different temperatures.

Heat treatment	Passive Current Density (i_p) at 500 mV_{SCE} in Ringer's Solution ($\mu A/cm^2$)		
	W Q	AC	FC
850°C	2.528	3.292	3.382
930°C	2.543	2.356	2.669
950°C	1.812	0.533	2.731
As Rolled	1.489		

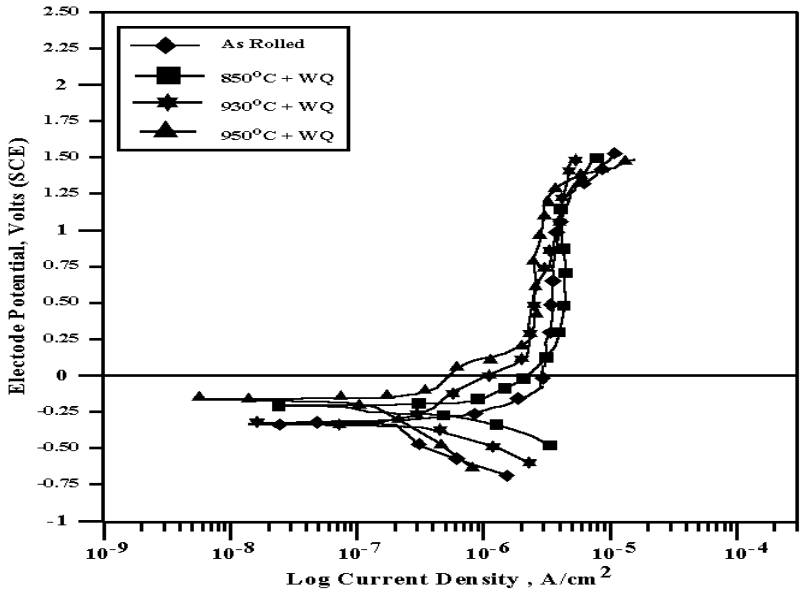

Figure 6 Potentiodynamic polarization behaviors for the hot rolled Ti-6Al-7Nb specimens in Ringer's Solution at sweep rate of 1mV/s after water quenching from different solution treatment temperatures in α+β phase field and aged at 550°C/4hours followed by air-cooling.

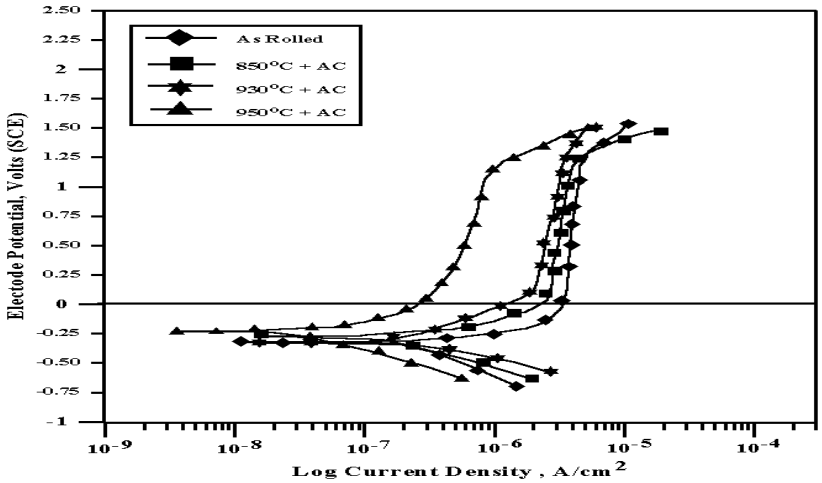

Figure 7 Potentiodynamic polarization behaviors for the hot rolled Ti-6Al-7Nb specimens in Ringer's Solution at sweep rate of 1mV/s after air cooling from different solution treatment temperatures in α+β phase field and aged at 550°C/4hours followed by air-cooling.

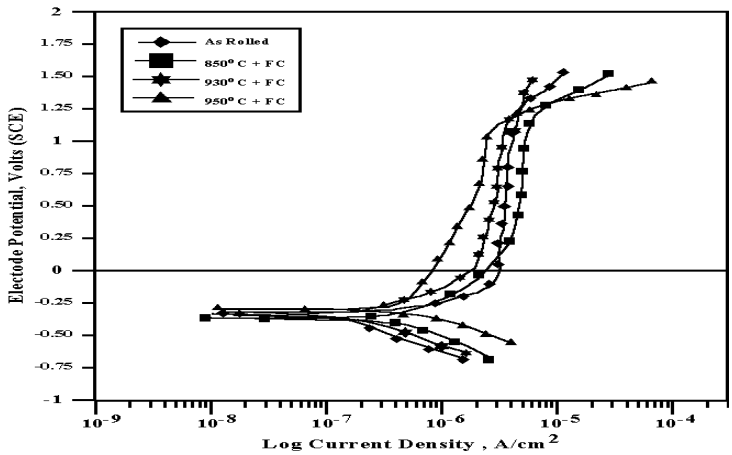

Figure 8 Potentiodynamic polarization behaviors for the hot rolled Ti-6Al-7Nb specimens in Ringer's Solution at sweep rate of 1mV/s after furnace cooling from different solution treatment temperatures in α+β phase field.

Conclusions

- The electrochemical investigations on the rolled and heat-treated specimens show that the alloy Ti-6Al-7Nb remains in passive state over more than 1.0 V_{SCE} under various heat-treated conditions whereas, 0.5 V_{SCE} above – 0.25 V_{SCE} is adequate for satisfactory performance of orthopedic implants.
- The anodic polarization studies clearly reveal that compositional variation in the phases plays a major role on the corrosion behavior of the hot rolled specimens. The specimen ST at 950^{o}C/AC and aged at 550^{o}C for 4 hours exhibits superior corrosion behavior due to the absence of selective dissolution of the phases.

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