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Cyclic Potentiodynamic Polarization On Titanium Alloys Anodizing In Alkaline Solutions

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Titanium alloys are used in different industries such as biomedical, aerospace, aeronautic, chemical, and naval. Those industries have high requirements with few damage tolerances. The aim of this work was to study the corrosion behavior of titanium alloys anodizing and non-anodizing in alkaline (KOH and NaOH) solutions, exposed in 3.5%wt. NaCl and 3.5% wt. H_2SO_4 solutions at room temperature using cyclic potentiodynamic polarization (CPP) according to standards in order to obtain electrochemical parameters as the passivation range (PR), corrosion type, passive layer persistence, corrosion potential (Ecorr), and corrosion rate. The alloy Ti Beta-C anodized presented better corrosion resistance than Ti-6Al-4V in both media. The smallest corrosion rate is presented in Beta-C samples (4.72 E-8 A/cm^2) and the highest corrosion rate is CP2 (1.61 E-5 A/cm^2)

Introduction

Aeronautic materials have an important role regarding fuel efficiency which also are determined by its mechanical, physical, chemical electrical and thermal properties.
Material density reduction is the most effective way to decrease structural weight and enhance aircraft development.
Pure titanium is well known due to its low thermal conductivity, relatively low density and elasticity, moderate stiffness and excellent behavior against corrosion in several environments and reactivity of elements. [11]
Nowadays, aluminum is in top of most used materials in aircrafts but recently the use and implementation of titanium and composites is taking more visibility in charts.
Titanium replaced materials as steel and several superalloys due to the great difference presented in density and its consequences in fuel savings.
For example, Boeing 787 contains around 15% Ti, while past models as Boeing 747 used to show 2.6% and Boeing 777 8.3% of titanium leading to an increase of 40% in last two generations of Boeing Aircrafts
T. Fu in 2015, worked with titanium CP2 in a solution of sodium chloride at 3.5% through cyclic Potentiodynamic polarization (CPP), obtaining as results the increase of corrosion resistance when this alloy present a passive layer which difficult the penetration of chlorine ions. [2]
A. C. Alves in 2017 evaluating titanium CP2 using CPP and Spectroscopy of Electrochemical Impedance after an anodic treatment observed that chlorine ions struggle more to get inside the material. [3]

Analyzing titanium CP2 in H_2SO_4 using CPP, Dubent and Mazard obtained corrosion velocities of 20 μm per year being a greater value than inicially expected. [4]
L. Zhou in 2019 performed an investigation where they compared titanium alpha (CP), alpha + beta (Ti-6Al-4V) and beta metastable (Ti-13Nb-13Zr) resulting in a tendency to better corrosion resistance the closer to beta phase. [5]
In 2020 A. Nemtsov and P. Kirshkov studied anodic oxidation in laminates of pure titanium under a compilation of solutions (1.5 M sulfuric acid, 0.3 M phosphoric acid and 0.3 M of hydrogen peroxide) leading to a nanotubes layer with porosity between 40 and 70 nm. [1]

Enhancing the electrochemical properties in titanium alloys results in an extension of service lifespan leading to reduction of expenses in aeronautical industry. Titanium alloys are substituting steel alloys of aircraft's critical components helping to reduce structural weight and saving fuel. The use of alkaline solutions in anodizing process become easier its disposition and reduce environmental damage as acidic solutions.

Methodology

Experimental Procedure Preparation

Specimen preparation consisted in sectioning 16 samples (8 Ti Beta-C and 8 Ti CP2) measuring a thickness of 0.5 cm and then a mechanical cleaning using SiC sandpaper from 80P to 800P before anodizing.

Anodizing Process

Pretreatment consisted of ultrasonic cleaning in ethanol (C_2H_5OH) and deionized water.

Each of 16 specimens are connected to a circuit controlled by equipment using the following parameters.

- Solutions KOH and NaOH at 1M per liter of distilled water.
- Input current 0.025 and 0.010 A/cm^2.
- Duration of 300 and 600 s.

Solutions is at room temperature and as energy dissipation it is used circulating water around the container to cool down the system due to exothermal reaction occurring during the process.

The specimen is totally submerged in KOH or NaOH a determined time with bubbling.

Electrochemical Tests

Measurements were conducted at room temperature using a Solartron 1286 potentiostat/galvanostat/ZRA (Zero Resistance Ammeter) in 3.5 wt.% NaCl solution.

A conventional three-electrode cell configuration was used for electrochemical corrosion studies, which consisted of a working electrode, WE (Titanium and its alloys), a

reference electrode, RE (saturated calomel electrode (SCE), and a counter electrode, CE (platinum mesh).

The CPP measurements were conducted over a potential scan range between −1.2 and 1.2 V vs. SCE from corrosion potential (Ecorr), using a scan rate of 1 mV/sec.

Results

Chemical Composition

Alloys used in this investigation showed elements presented in table I, according to supplier information.

TABLE I. Chemical composition of titanium alloys

Alloy	Elements (% wt.)						
	Ti	**Al**	**V**	**Zr**	**Mo**	**Cr**	**Sn**
Ti CP2	99.8	--	0.2	--	--	--	--
Ti Beta-C	75.2	4.2	8.1	4.3	3.9	3.3	--

Electrochemical Characterization

Figure I below present Potentiodynamic Polarization Curves immerged in potassium hydroxide using a current input of 0.010 A/cm^2 interacting with NaCl at 3.5% as test solution. This chart show potential (V) vs. ECS against natural logarithm of the current. CP2 alloy present passivation/activation cycles shown as fluctuations.

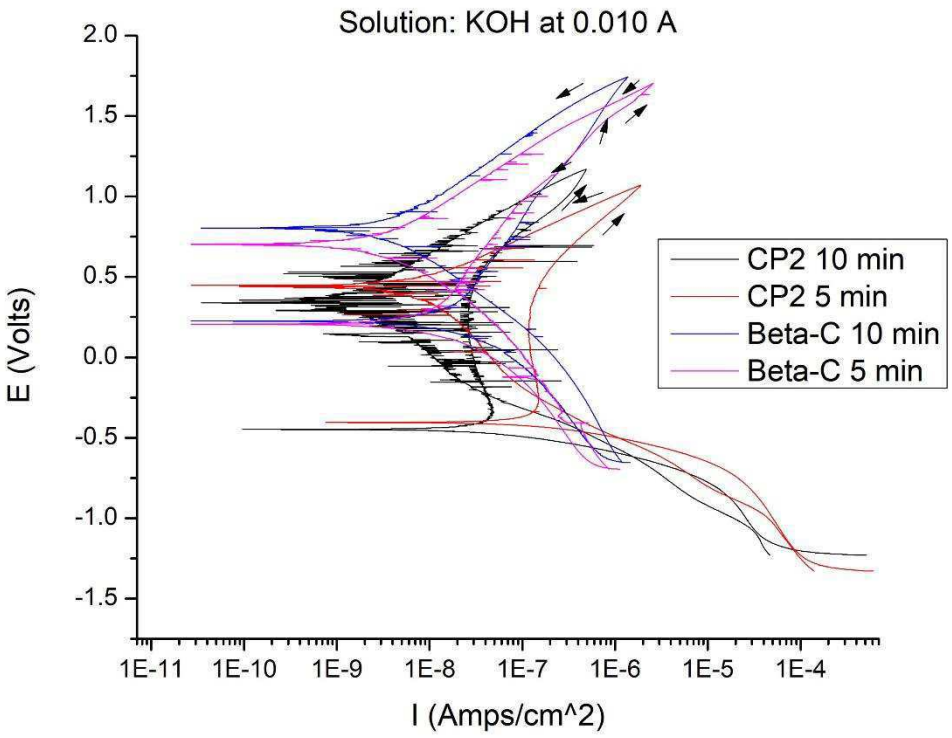

Figure 1. PPC for titanium alloys anodized in KOH using a current density input of 0.010 A/cm^2 and exposed in NaCl at 3.5% during the test using 2 different immersion time.

Figure II, below show the behavior of coupons anodized in potassium hydroxide applying 0.025 A/cm^2 interacting with NaCl at 3.5% as test solution. This chart show potential (V) vs. ECS against natural logarithm of the current. CP2 alloy present passivation/activation cycles shown as fluctuations.

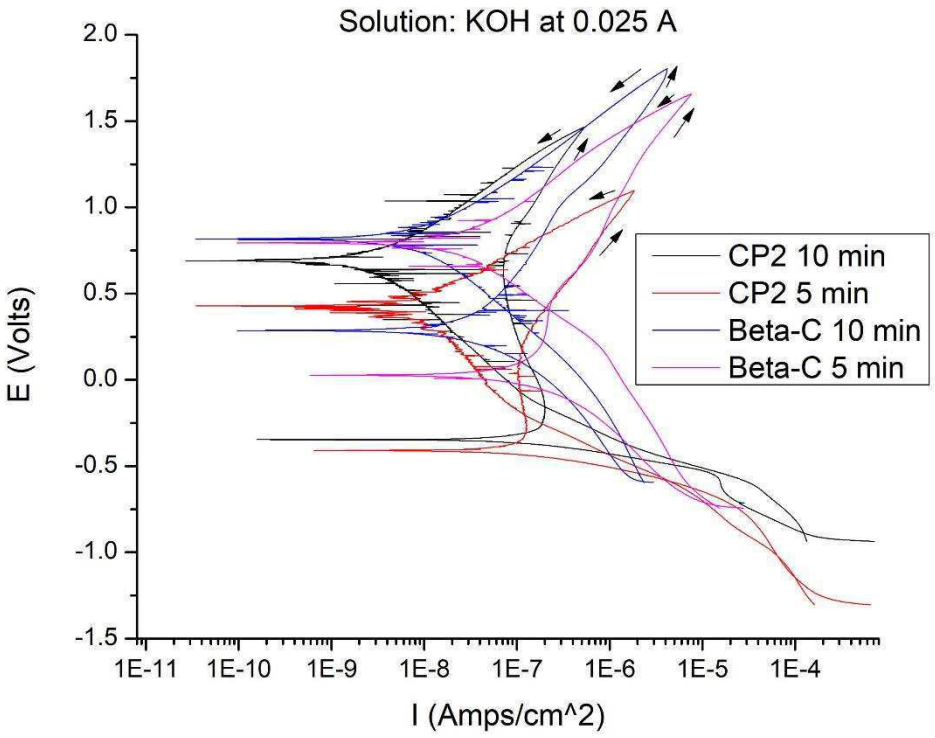

Figure II. PPC for titanium alloys anodized in KOH using a current density input of 0.025 A/cm^2 and exposed in NaCl at 3.5% during the test using 2 different immersion time.

Figure III, below show the behavior of coupons anodized in sodium hydroxide applying 0.010 A/cm^2 interacting with NaCl at 3.5% as test solution. This chart show potential (V) vs. ECS against natural logarithm of the current. CP2 alloy present passivation/activation cycles shown as fluctuations.

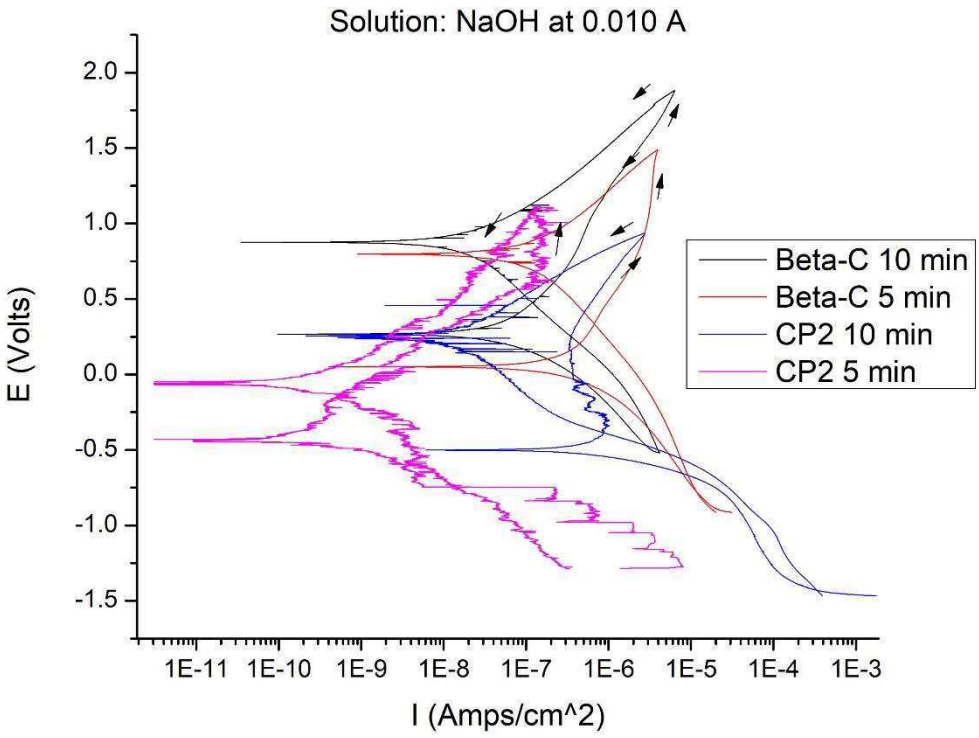

Figure III. PPC for titanium alloys anodized in NaOH using a current density input of 0.010 A/cm^2 and exposed in NaCl at 3.5% during the test using 2 different immersion time.

Figure IV, below show the behavior of coupons anodized in sodium hydroxide applying 0.025 A/cm^2 interacting with NaCl at 3.5% as test solution. This chart show potential (V) vs. ECS against natural logarithm of the current. CP2 alloy present passivation/activation cycles shown as fluctuations.

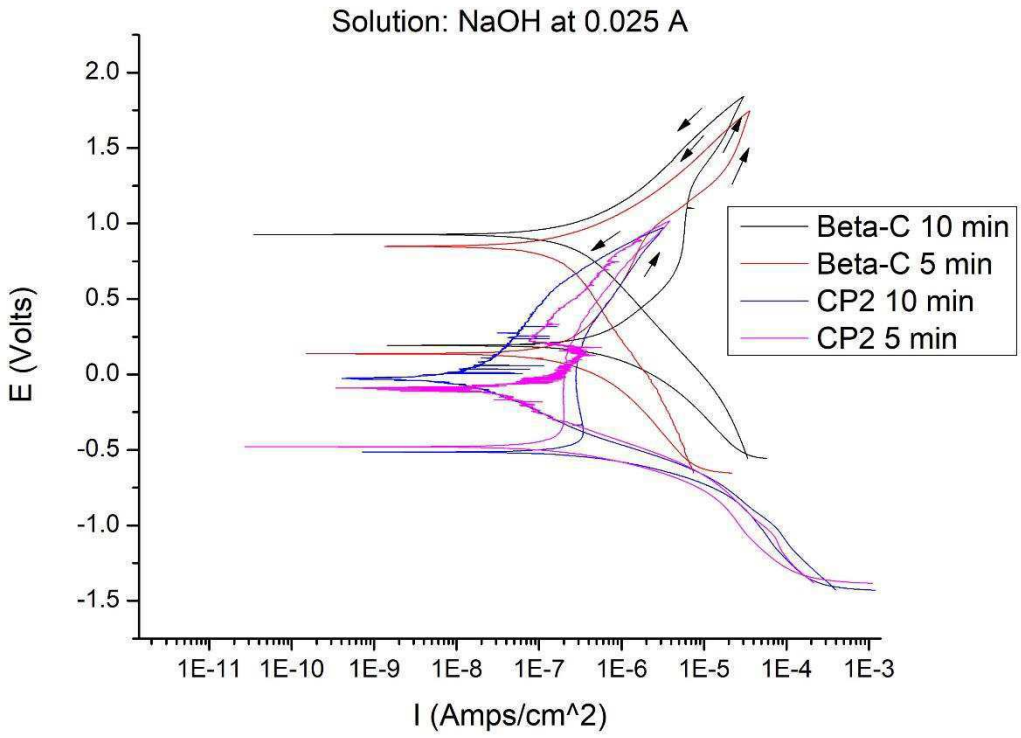

Figure IV. PPC for titanium alloys anodized in NaOH using a current density input of 0.025 A/cm^2 and exposed in NaCl at 3.5% during the test using 2 different immersion time.

Table II and III summarize results observed in figures I to IV

TABLE II. Summary beta-C alloy

Alloy	Solution	Duration (min)	Input (A/cm^2)	I Corr (A/cm^2)	E Corr (V)	Hysteresis	Passivation range (V)
Beta-C	KOH (1)	10	0.010	4.72 E-8	0.226	Negative	1.426
		10	0.025	1.16 E-7	0.285	Negative	1.342
		5	0.010	5.29 E-8	0.206	Negative	1.280
		5	0.025	3.60 E-7	0.026	Negative	1.478
	NaOH (2)	10	0.010	2.72 E-7	0.267	Negative	1.491
		10	0.025	1.01 E-6	0.192	Negative	1.543
		5	0.010	6.32 E-7	0.050	Negative	1.332
		5	0.025	4.04 E-7	0.137	Negative	1.495

The smallest current density is presented in Beta-C sample anodized in potassium hydroxide during 10 minutes using an input current of 0.010 A/cm^2 while the greatest current density is shown in sample anodized in sodium hydroxide during 10 minutes with an input current of 0.025 A/cm^2. The more and less susceptible to corrosion were anodized using KOH and both with an input of 0.025 A/cm^2 being duration of immersion the difference (5 mins and 10 mins respectively). The shortest passivation range is coupon under conditions of potassium hydroxide during 5 minutes with input current of 0.010 A/cm^2 and, in the other hand, the longest passivation range is presented in the same iteration as the greatest current density.

TABLE III. Summary CP2 alloy

Alloy	Solution	Duration (min)	Input (A/cm^2)	I Corr (A/cm^2)	E Corr (V)	Hysteresis	Passivation range (V)
CP2	KOH (1)	10	0.010	4.08 E-6	-0.448	Negative	1.551
		10	0.025	2.38 E-5	-0.346	Negative	1.756
		5	0.010	9.68 E-6	-0.404	Negative	1.375
		5	0.025	1.61 E-5	-0.409	Negative	1.438
	NaOH (2)	10	0.010	2.23 E-5	-0.500	Negative	1.311
		10	0.025	1.67 E-5	-0.514	Negative	1.373
		5	0.010	7.38 E-7	-0.431	Negative	1.337
		5	0.025	2.75 E-6	-0.479	Negative	1.435

The greatest current density is presented in CP2 sample anodized in potassium hydroxide during 5 minutes using an input current of 0.025 A/cm^2 while the smallest current density is shown in sample anodized in sodium hydroxide during 10 minutes with an input current of 0.010 A/cm^2. The more and less susceptible to corrosion were anodized with an input of 0.025 A/cm^2 and duration of 10 minutes of immersion being the anodizing solution the difference (NaOH and KOH respectively). The longest passivation range is coupon under conditions of potassium hydroxide during 10 minutes with input current of 0.025 A/cm^2 and, in the other hand, the shortest passivation range is presented sodium hydroxide during 10 minutes using a current input of 0.010 A/cm^2.

SEM analysis

Figure V and VI are superficial metallography of Ti CP2 and beta-C respectively. Ti CP2 present alpha phase matrix while beta-C show beta phase matrix

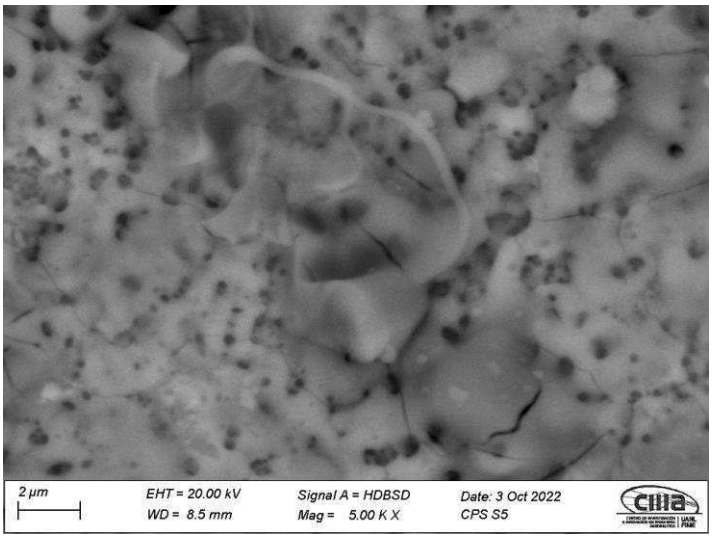

Figure V. Superficial metallography Ti CP2 after anodizing process and electrochemical test.

Figure V present alpha phase expected in Ti alloys CP2 while Figure VI below shows alpha + beta phase expected in Ti alloys beta-C

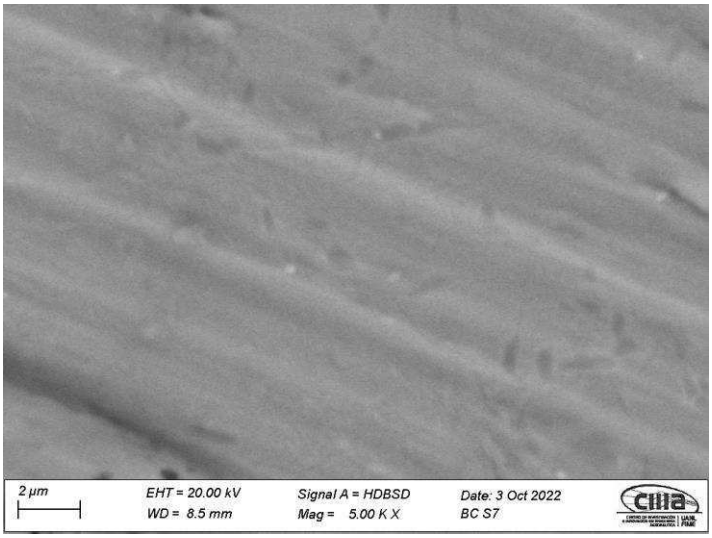

Figure VI. Superficial metallography Ti beta-C after anodizing process and electrochemical test

Conclusions

Summary and interpretation

CP2 tests show noise attributed to activation/passivation cycles.

- CP2 in KOH at 0.010 Amps during 10 mins presents the noisiest performance.
- CP2 in NaOH at 0.010 Amps during 5 mins shows cycles after the hysteresis.
- CP2 in NaOH at 0.025 Amps during 5 mins displays similar behavior as in 0.010 Amps.

Beta-C performed lowest corrosion rate (4.72 E-8 A/cm^2) compared to CP2 showing the highest current density (1.61 E-5 A/cm^2) meaning a longer lifespan for beta-C sample.

Cases considering 0.025 A present lower values of E Corr leading to more susceptibility to corrosion.

Combination Beta-C, 10 mins, KOH, 0.010 A shows the lowest density current. In the other hand, iteration CP2, 10 min, KOH, 0.025 A is the highest corrosion kinetics tending to loss more material.

In general, CP2 is more susceptible to corrosion (-0.514 V) than Beta-C presenting the lower potentials (0.285 V) in all samples.

Specimens of 5 mins immersion are less susceptible to corrosion considering anodic solution and alloy while the E Corr is lower in each iteration.

Samples under 0.010 A condition struggle less to get into passivation (1.280 V) and present density current lower than 0.025 A samples.

General conclusion

Service lifespan of beta-C alloy anodized by potassium hydroxide will be longer than CP2 alloy under same conditions due to susceptibility and current density presented in this investigation. Every test presented negative hysteresis leading to uniform corrosion along specimens.

Limitations and Recommendations

Scope of this work was achieved which is compare anodized alloys varying current, duration and alkaline solutions. These results are relevant and part of future researches to compare results using different electrochemical characterization as Electrochemical Impedance Spectroscopy and Electrochemical Noise. Additional to investigation matrix, obtaining results from conventional acidic anodization processes collecting data from same three electrochemical methods.

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