

## INFLUENCE OF AGING TEMPERATURE ON THE ELECTROCHEMICAL BEHAVIOR OF THE Ti-15V-3Cr-3Sn-3Al ALLOY IN THE KROLL REAGENT

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**Abstract.** *The microstructure of the  $\beta$  Ti-15V-3Cr-3Sn-3Al alloy can be changed by aging, leading to  $\beta \rightarrow \alpha$  phase transformation and precipitation of intermetallic compounds. The electrochemical behavior of this alloy in the Kroll reagent (  $HNO_3$ , HF and  $H_2O$  mixtures) at room temperature, after aging during 2 hours in the 350-600°C temperature range was studied. A typical three-electrode cell (WE: Ti alloy; CE: Pt; RE: SCE) was used. The compositions of the Kroll reagent were 200 ml  $H_2O$  + 4 or 12 ml  $HNO_3$  (65%) + 2 or 6 ml HF (48%). The corrosion potentials oscillated between -0.85 and -0.45 V/SCE for all solutions and all samples but remained at the lower level during more time when higher HF concentrations were used. These potential variations showed the instability of the metal surface, which was successively in the active and passive states due to the reducing character of HF and oxidizing character of  $HNO_3$ . The polarization curves showed that the corrosion current, critical current and passive current densities increased with an increase of the HF concentration. We observed that the higher was the aging temperature, the higher were these current densities for all the compositions, which indicated that samples aged at higher temperatures were more susceptible to corrosion. This behavior was attributed to the formation of intra- and intergranular  $\alpha$ -phase precipitates, as revealed by microscopical analysis and X-ray diffractometry.*

**Key words:** Titanium alloy, Aging, Kroll reagent, Electrochemical behavior

## 1. INTRODUCTION

The Ti-15V-3Cr-3Sn-3Al alloy (Ti-15-3) belongs to the  $\beta$  Ti alloys group and presents high ductility, high mechanical resistance, good resistance/weight ratio and is indicated for the fabrication of structural components by plastic conformation processes (Froes & Bomberger, 1985 and Boyer, 1992).

Its mechanical resistance can be increased by aging, generally between 480 and 600°C. In this temperature range occurs the formation of precipitates of secondary  $\alpha$  phase in the grains and at the grain boundaries which create obstacles to the dislocation slips (Hein *et al.*, 1994).

Ti alloys exhibit good corrosion resistance in many diluted acid solutions but are severely attacked by HF where the formation of hydrides at the metal surface leads to embrittlement. In HNO<sub>3</sub> solutions occurs the passivation of these alloys due to the formation of oxides films containing TiO<sub>2</sub> oxide on the metal surface (ASM, 1992). Thus, the etching of the Ti alloys is usually carried out in a mixture of HNO<sub>3</sub> and HF in water (Kroll reagent)(E407-93, 1997).

In this work we studied the influence of aging temperature on the microstructure of the Ti-15V-3Cr-3Sn-3Al alloy and on its electrochemical behavior in Kroll solutions of different compositions.

## 2. EXPERIMENTAL

### 2.1. Aging procedure

The samples for aging treatment were cut from a shape of the Ti-15-3 alloy as received (i.e. solubilized at 790-815°C for 3 to 30 min in air) (AMS 4914, 1984). The chemical composition of the alloy is presented in Table 1. Their typical dimensions were 10x10x1mm. These samples were placed in a furnace whose temperature was increased from room temperature to aging temperature with a 10°C/min rate. They remained at this temperature 2 hours and were water-cooled. The aging temperatures were 350, 400, 450, 500, 550 and 600°C. The samples were mounted in resin, ground with SiC papers until 4000 grit, chemically polished using a suspension of colloidal silica in a H<sub>2</sub>O<sub>2</sub>-HF-HNO<sub>3</sub> mixture. The coupons were attacked in the Kroll reagent (aqueous solution of HNO<sub>3</sub> and HF) to reveal their microstructures and then observed using optical microscopy.

Table 1. Chemical composition of the Ti-15-3 alloy (wt%)

Ti	V	Cr	Sn	Al	Fe	O	C	N	H
bal.	14-16	2.5-3.5	2.5-3.5	2.5-3.5	0.25max	0.13max	0.05max	0.05max	0.015max

### 2.2. Electrochemical study

The electrochemical study was performed in the Kroll reagent at room temperature using different HF and HNO<sub>3</sub> concentrations. The solutions were prepared with deionized water (200 ml) and P.A. HNO<sub>3</sub> (d = 1.4 g.cm<sup>-3</sup>; 65%)(4 and 12 ml) and P.A. HF (d = 1.16 g.cm<sup>-3</sup>; 48%)(2 and 6 ml). Nor (des)aeration, neither agitation were used.

Samples of 0.5 cm<sup>2</sup> area were cut from sheets of the Ti-15-3 alloy aged at 350 and 600°C and mounted in resin. An electrical connection was done on one face of the samples. The other face was ground with SiC papers until 600 grit. For the electrochemical study, a typical three-electrode cell was used. The working electrodes were the Ti-15-3 alloy samples, the counter electrode, a 10 cm<sup>2</sup> platinum sheet and the reference electrode, the saturated calomel electrode (SCE). The tests were carried out using a PAR 273A potentiostat monitored with a PC computer through the M352 corrosion software.

After immersion in the Kroll solutions, the corrosion potentials were measured during 10 min as a function of time and posteriorly cathodic and anodic polarization curves were obtained using a  $1\text{mV}\cdot\text{s}^{-1}$  potential sweep rate.

### 3. RESULTS AND DISCUSSION

#### 3.1. Influence of aging temperature

Figure 1 shows the microstructure of the Ti-15-3 alloy aged at 350, 450 and 600°C for 2 hours. We observed that the microstructure of the alloy aged at 350°C is similar to the microstructure of the alloy as received, i.e. equiaxial grains of  $\beta$ -phase. For aging at higher temperatures occurred the formation of precipitates of acicular form in the grains and at the grain boundaries. We noticed the larger amount of these precipitates for the alloy aged at 600°C. The X-ray spectra of these samples are presented in Fig. 2. Only the peaks of  $\beta$ -phase are detected for the samples aged at 350°C. For 450°C aging temperature, two new peaks related to the  $\alpha$ -phase are observed. For the sample aged at 600°C, three peaks of the  $\alpha$ -phase are present on the X-ray diffractogram. These results indicate that the precipitates observed during microscopical analysis (Fig.1) correspond to the  $\alpha$ -phase.

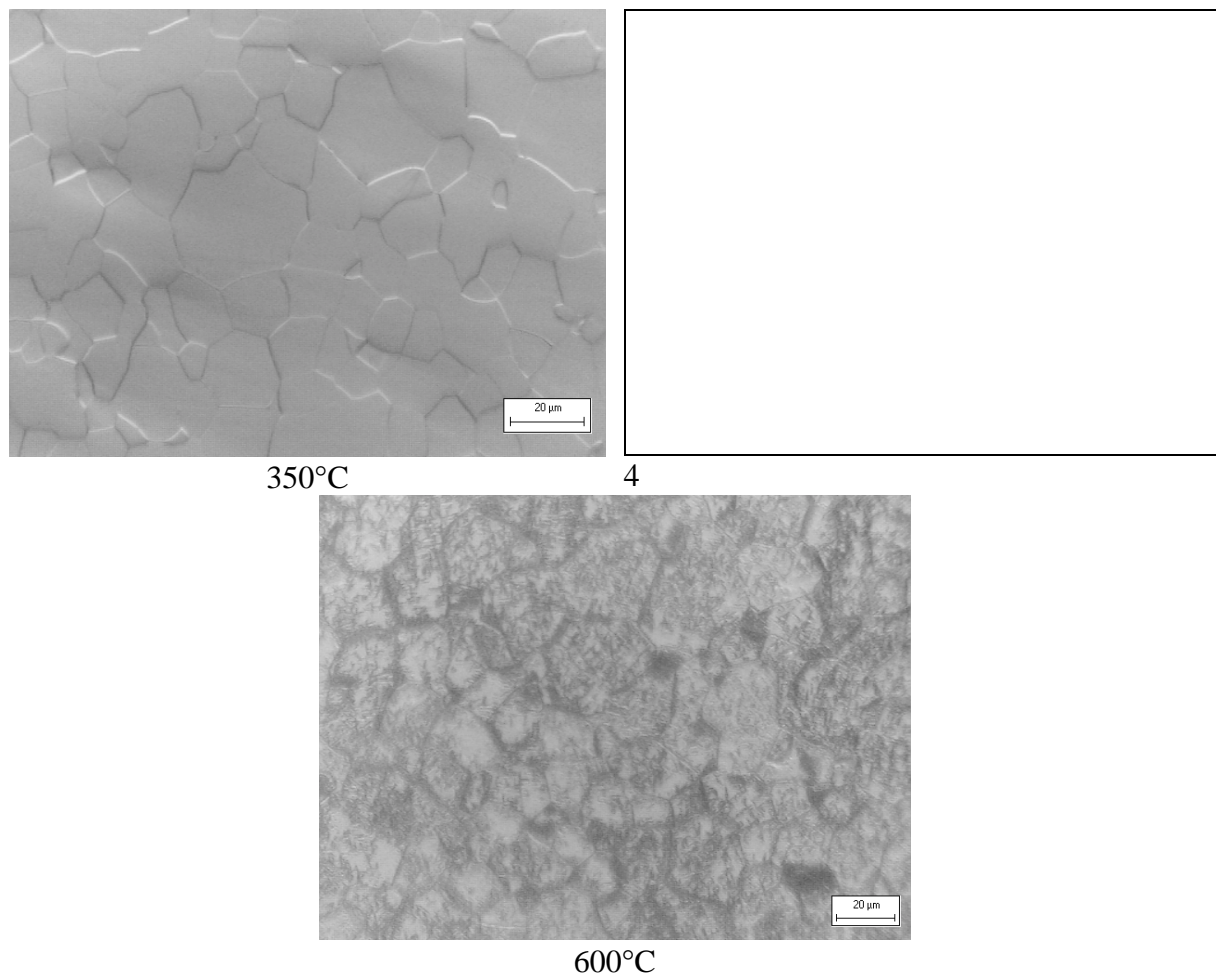


Figure 1- Optical photographs of the Ti-15-3 alloy aged at 350, 450 and 600°C

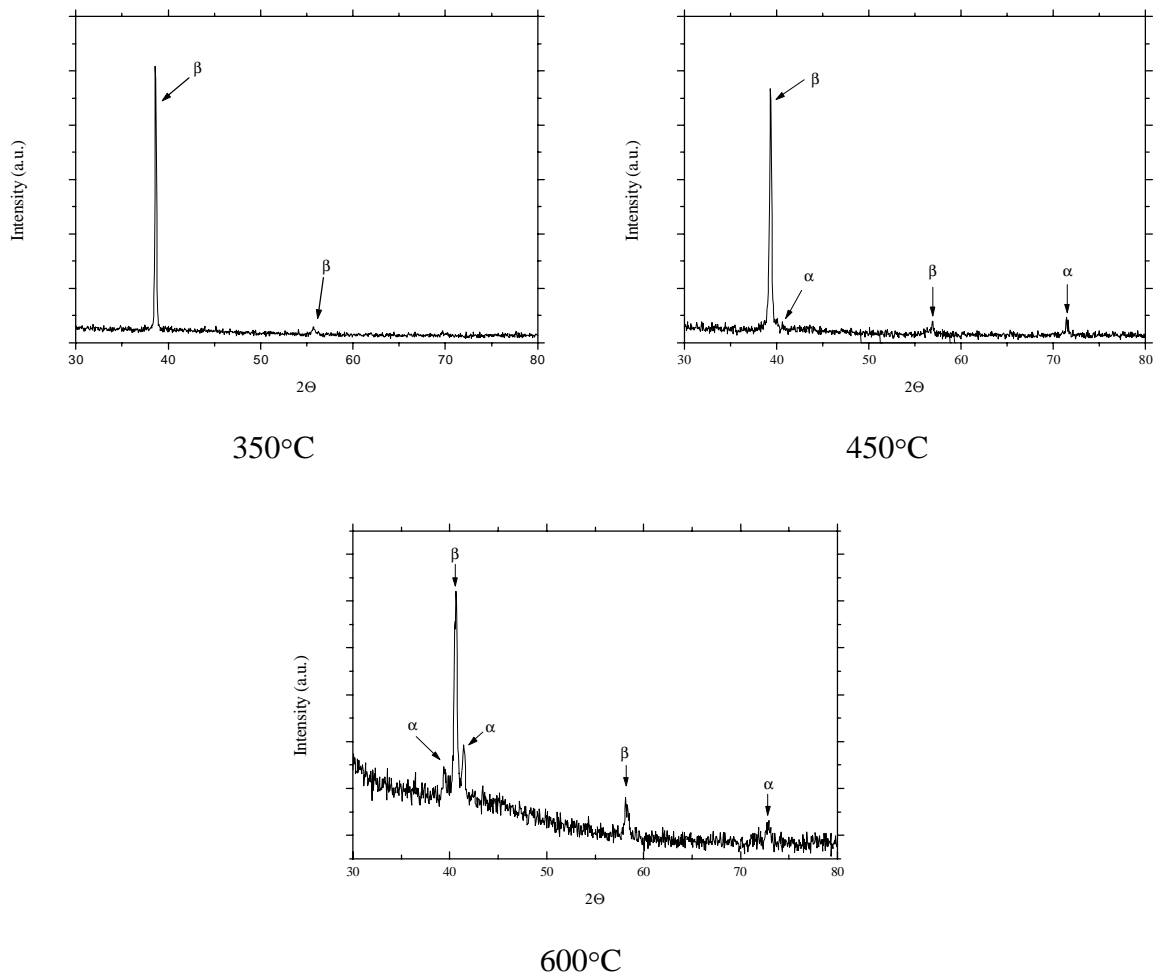


Figure 2- X-ray diffractograms of the Ti-15-3 alloy aged at 350, 450 and 600°C

### 3.2. Electrochemical results

Figures 3 and 4 show the evolution of the corrosion potential of the Ti-15-3 alloy aged at 350°C in two Kroll solutions with different HF concentrations. The oscillations of the potential between -0.85 and -0.45 V/SCE reveal the instability of the metal surface in such solutions. The surface is periodically active and passive. For the higher HF concentration, the corrosion potential remains more time in the active potential range due to the reducing character of this acid. Similar observations were made for the alloy aged at 600°C.

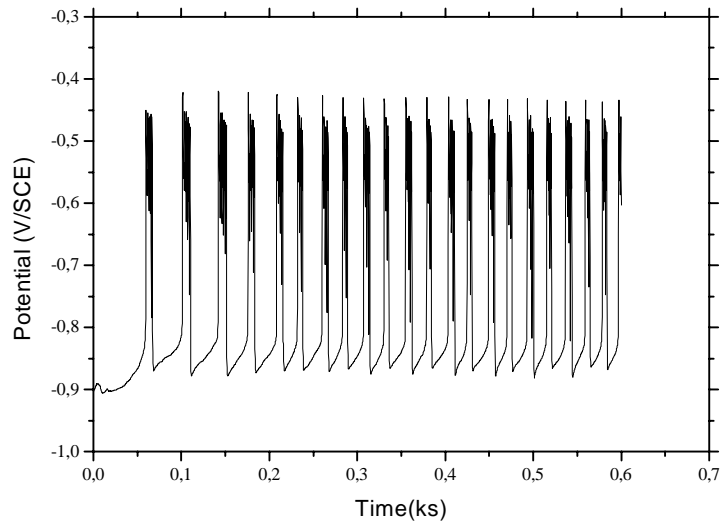


Figure 3- Evolution of the corrosion potential of the Ti-15-3 alloy aged at 350°C during 2 h in 200ml H<sub>2</sub>O + 4ml HNO<sub>3</sub> + 2ml HF at room temperature

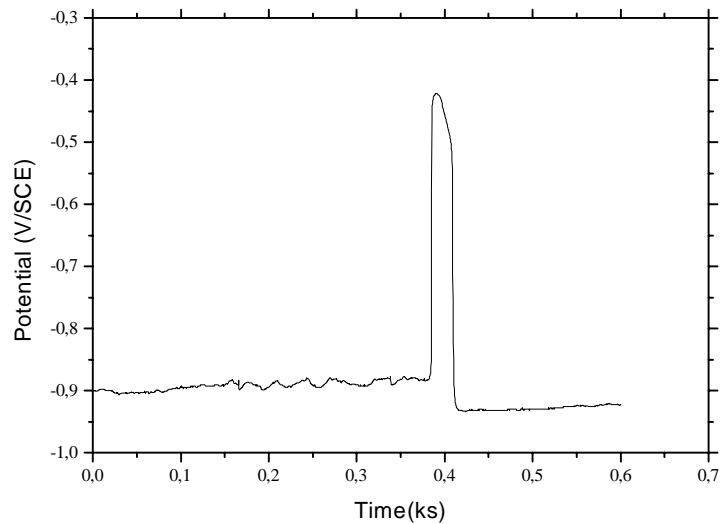


Figure 4- Evolution of the corrosion potential of the Ti-15-3 alloy aged at 350°C during 2 h in 200ml H<sub>2</sub>O + 4ml HNO<sub>3</sub> + 6ml HF at room temperature

The polarization curves of the Ti-15-3 alloy aged at 600°C during 2 h in 200ml H<sub>2</sub>O + 12ml HNO<sub>3</sub> + 2ml or 6 ml HF confirm the reducing character of HF. Indeed, for the same HNO<sub>3</sub> concentration, the corrosion current ( $i_{\text{corr}}$ ), critical current ( $i_{\text{crit}}$ ) and passive current ( $i_{\text{pass}}$ ) densities increase with an increase of the HF concentration. This behavior is observed for the other solutions and for the alloy aged at 350°C too, as depicts in Table 2. From these results, we note that the HNO<sub>3</sub> concentration has little influence on the values of  $i_{\text{corr}}$ ,  $i_{\text{crit}}$  and  $i_{\text{pass}}$  for the same HF concentration. On the contrary, for the same HNO<sub>3</sub> concentration, the current densities increase nearly 5 times as the HF volume increases from 2 to 6 ml.

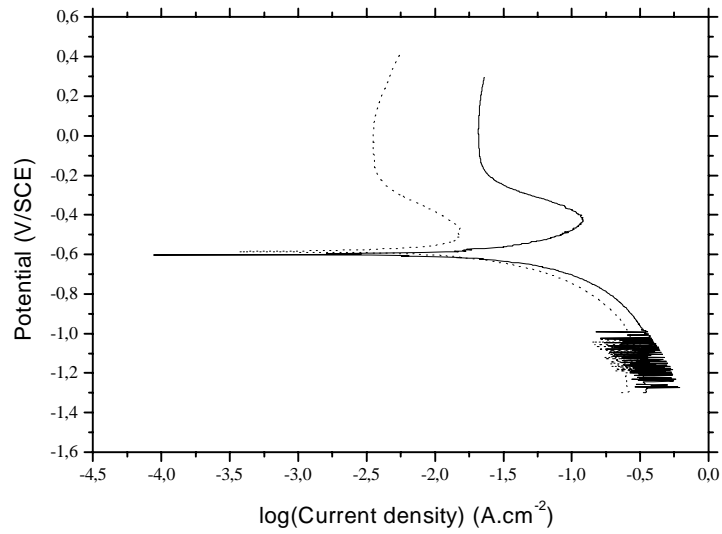


Figure 5- Polarization curves of the Ti-15-3 alloy aged at 600°C during 2 h in 200ml H<sub>2</sub>O + 12ml HNO<sub>3</sub> + 2ml HF (.....) and in 200ml H<sub>2</sub>O + 12ml HNO<sub>3</sub> + 6ml HF (—) at room temperature

Table 2. Corrosion current, critical current and passive current densities (in mA.cm<sup>-2</sup>) of the Ti-15-3 alloy aged at 350 and 600°C in different Kroll solutions

Aging temp.(°C)	HNO <sub>3</sub> (ml)	HF (ml)	$i_{\text{corr}}$ (mA.cm <sup>-2</sup> )	$i_{\text{crit}}$ (mA.cm <sup>-2</sup> )	$i_{\text{pass}}$ (mA.cm <sup>-2</sup> )
350	4	2	9.2	13.3	2.9
350	12	2	8.7	14.3	2.8
350	4	6	21.1	59.1	10.6
600	4	2	13.2	20.1	4.4
600	12	2	11.2	15.0	3.5
600	4	6	-	81.8	17.9
600	12	6	75.5	121.9	20.8

We observe in Table 2 and Fig.6 that for the same Kroll solution, all the  $i_{\text{corr}}$ ,  $i_{\text{crit}}$  and  $i_{\text{pass}}$  values measured for the Ti-15-3 alloy aged at 600°C are higher than those obtained for the alloy aged at 350°C. This shows that the presence of precipitates of  $\alpha$ -phase in the  $\beta$ -matrix decreases the corrosion resistance of the alloy. It is known that a two-phase alloy is generally more susceptible to corrosion than a single-phase alloy, due to galvanic effects (Fontana, 1986).

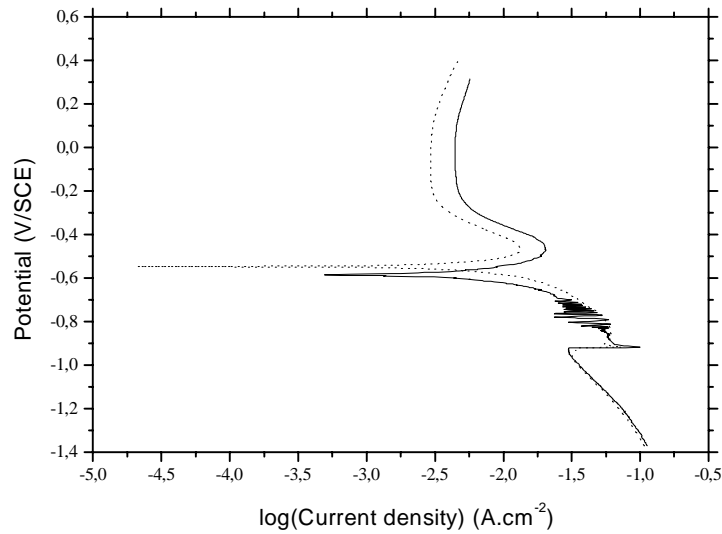


Figure 6- Polarization curves of the Ti-15-3 alloy aged at 350°C (.....) and 600°C (—) during 2h in 200ml H<sub>2</sub>O + 4ml HNO<sub>3</sub> + 2ml HF at room temperature

These results were confirmed by measuring the ideal etching time to reveal the microstructures of the Ti-15-3 alloy aged in the 350-600°C temperature range in different Kroll solutions (Fig. 7)(Ribeiro *et al.*, 1998). In one hand, we observed that the HNO<sub>3</sub> concentration has little influence on the etching time for the same HF content. On the contrary, an increase of HF content decreases significantly the etching time for the same HNO<sub>3</sub> concentration. In the other hand, an increase of the aging temperature leads to the decrease of the etching time. As the corrosion current densities in Kroll solutions increase when higher aging temperature is used, the time necessary to observe the microstructure of the alloy by etching in these solutions consequently decreases.

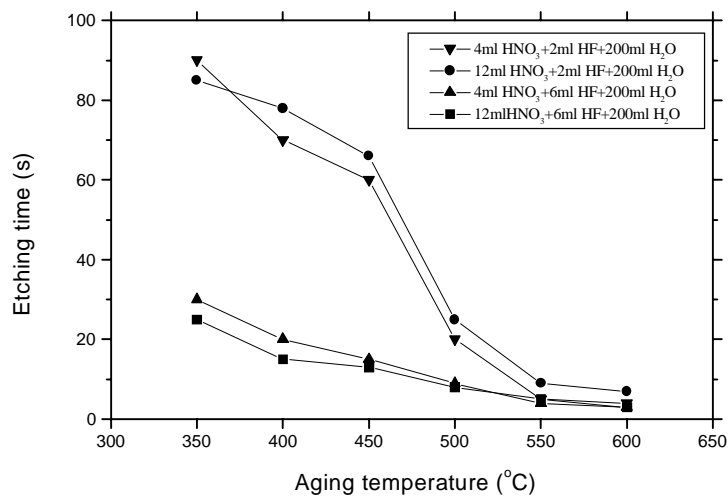


Figure 7- Influence of the aging temperature and the composition of Kroll solutions on the ideal etching time for the Ti-15-3 alloy

#### 4. CONCLUSIONS

Aging of the  $\beta$  Ti-15V-3Cr-3Sn-3Al alloy (Ti-15-3) for 2 hours at temperatures equal or higher than 450°C led to the precipitation of  $\alpha$ -phase in the grains and at the grain boundaries, as revealed by optical microscopy and X-ray diffraction analysis.

The Ti-15-3 alloy aged at 350°C and 600°C were successively active and passive in Kroll solutions (H<sub>2</sub>O+HNO<sub>3</sub>+HF) at room temperature, showing the instability of the alloy surface in such solutions.

The Ti-15-3 alloy aged at 350°C was more corrosion resistant than the alloy aged at 600°C probably due to the precipitation of  $\alpha$ -phase during aging at 600°C and to the consequent galvanic effects.

An increase of HF concentration in Kroll solutions increased significantly the corrosion rate of the alloy, whereas the HNO<sub>3</sub> concentration only showed a slight influence.

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