EFFECT OF ATMOSPHERE ON OXIDATION OF Ti-6Al-4V ALLOY

Danieli Aparecida Pereira Reis
Instituto Tecnológico de Aeronáutica, São José dos Campos, Brasil. danielireis@universiabrasil.net

Cosme Roberto Moreira da Silva
Centro Técnico Aeroespacial, São José dos Campos, Brasil.

Maria do Carmo de Andrade Nono
Instituto Nacional de Pesquisas Espaciais, São José dos Campos, Brasil.

Miguel Justino Ribeiro Barboza
Escola de Engenharia de Lorena, Lorena, Brasil.

Francisco Piorino Neto
Centro Técnico Aeroespacial, São José dos Campos, Brasil.

Carlos de Moura Neto
Instituto Tecnológico de Aeronáutica, São José dos Campos, Brasil.

Sergio Frascino M.de Almeida
Instituto Tecnológico de Aeronáutica, São José dos Campos, Brasil.

Abstract. *The objective of this work was to evaluate the oxidation on creep behavior of the Ti-6Al-4V alloy focusing on determination of the experimental parameters related to the creep stages. Constant load creep tests were conducted with Ti-6Al-4V alloy in air and in nitrogen atmosphere at 500°C, 600°C and 700°C. Results indicated the creep resistance of the alloy in nitrogen atmosphere is greater than in air. Previously reported results about the activation energies and stress exponents' values indicate that the primary and stationary creep, for both test conditions, was probably controlled by dislocation climb. The decrease in ductility after creep in air is larger than creep under nitrogen atmosphere due to oxidation and surfaces cracks.*
Keywords*: Ti-6Al-4V, creep, oxidation*

1- INTRODUCTION

The search for alloys with improved high-temperature specific strength and creep-resistance properties for aerospace applications has led in the last decades to sustained research activities to develop new alloys and/or improve existing ones [1]. Titanium and its alloys are excellent for applications in structural components submitted to high temperatures owing to their high strength to weight ratio, good corrosion resistance and metallurgical stability. Its high creep resistance is great importance in enhancing engine performance [2]. However, the affinity by oxygen is one of main factors that limit its application as structural material at high temperatures. The high solid solubility of oxygen in titanium results in material loss and in the formation of hard and brittle layer during elevated temperature air exposure. [3]. The development of titanium alloys with the objective of improving the creep properties have been observed, although the surface oxidation limits the use of these alloys in temperatures up to 600°C [4].

A substantial part of the creep research has been devoted to Ti-6Al-4V alloy due to its industrial and technological importance. Its creep properties in air have been well documented. However, its creep behavior in nitrogen atmosphere has only rarely been investigated. In this context, the purpose of this preliminary study is to evaluate the creep behavior of Ti-6Al-4V alloy focusing on determination of experimental parameters related to creep primary and the secondary creep.

2- EXPERIMENTAL PROCEDURE

The material chosen for the present study was hot-forged 12.7 mm diameter rod of commercial Ti-6Al-4V alloy with the same specifications as published by ASTM [5]. The microstructure consists of equiaxed α grains with average size about 10 μm. The β phase is present in the α grains boundaries. Tensile test was performed at 500ºC, 600°C and 700°C in air according to ASTM standard E 21 specification [6]. The tensile properties are summarized in Table 1 namely, 0.2% yield stress (YS), ultimate tensile stress (UTS), elongation (EL) and reduction of area (RA).

Table 1 - Tensile properties of Ti-6Al-4V alloy.

T (ºC)	YS (MPa)	UTS (MPa)	EL (%)	RA (%)
500	521	638	30	73.6
600	377	407	46	85.7
700	73	193	58.3	88.2

The initial creep stress levels were determined from the elevated temperature tensile properties given in Table 1. Constant load creep tests were conducted on a standard creep machine in air and nitrogen atmosphere, at stress of 312, 361, 465 and 520 MPa at a temperature of 500ºC, at stress of 125, 222, 250 and 319 MPa at 600ºC, and at stress of 14, 42 and 56 MPa at 700ºC. Samples with a gage length of 18.5 mm and a diameter of 3.0 mm were used for all tests. The creep tests were performed according to ASTM E139 standard [7].

3- RESULTS AND DISCUSSION

Representative creep curves of Ti-6Al-4V are displayed in Figure 1 in air and in nitrogen atmospheres.

Ti-6Al4V alloy exhibits a normal creep curve consisting of primary, secondary stages well defined. There is a relatively short initial period of decreasing primary creep rate that is associated with hardening due to the accumulation of dislocations. However, most of the creep life is dominated by a constant creep rate that is thought to be associated with a stable dislocation configuration due to recovery and hardening process [8,9].

Results from the creep tests at 500°C, 600°C and 700°C are summarized in Table 2, which show the values of primary creep time (t_p) defined as the ending of primary creep and secondary creep rate ($\dot{\varepsilon}_s$).

The results presented in Table 2 suggest that strain hardening during primary creep is dependent on the test temperature. The highest values of t_p and the reduction of the steady-state creep rate demonstrate that the higher creep resistance of Ti-6Al-4V in nitrogen atmosphere. This fact is related with the hard and thin nitride surface layer formed during creep tests [10]. Figure 2 and 3 show the stress dependence of primary creep time and steady-state creep rate for both test conditions.
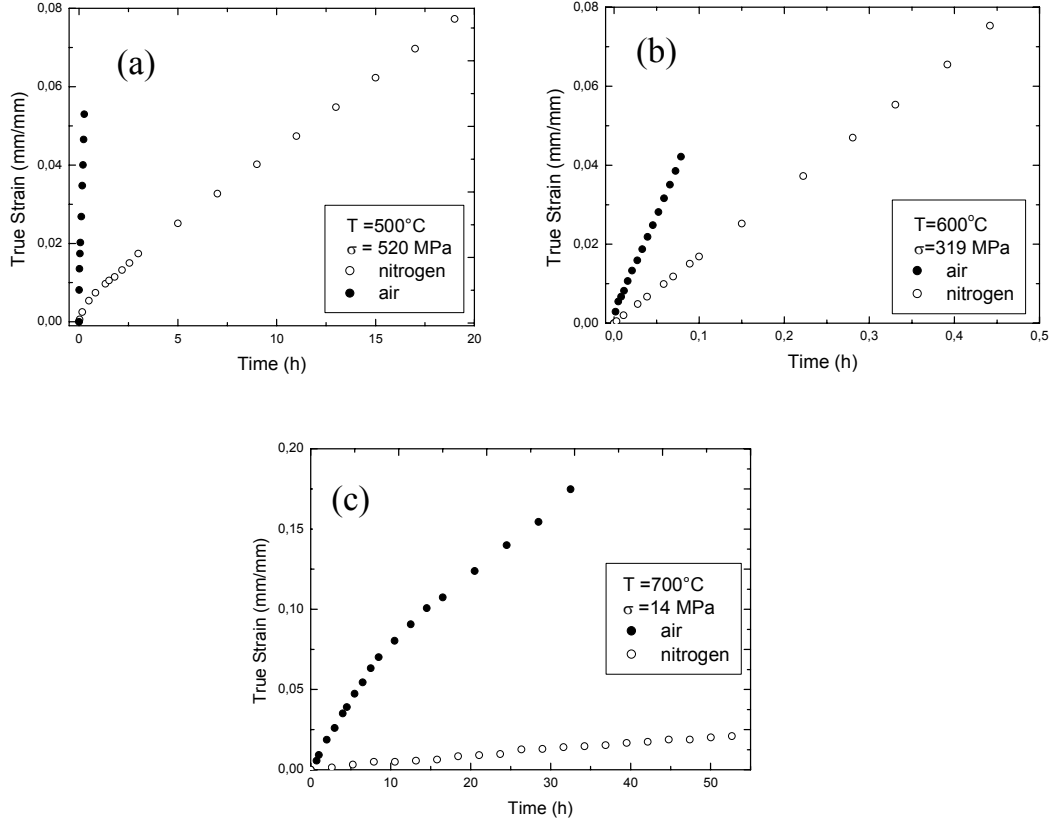
Fig. 1. Typical creep curves of Ti-6Al-4V: a) at 500°C / 520 MPa;
b) at 600°C / 319 MPa; c) at 700°C / 14 MPa.

By standard regression techniques, the results can be described in terms of power-law creep equations:

$$t_p = A\sigma^{-m} \tag{1}$$

$$\dot{\varepsilon}_s = B\sigma^n \tag{2}$$

The material parameters A, B, m and n are usually determined from a number of constant load creep tests. The parameters depend on temperature, composition and microstructure of material and also extend on applied stress level.

The stress exponents obtained are in the range from 2,23 to 11.73. Previously reported results about the apparent activation energies of creep in air indicate that $Q_p = 309$ kJ/mol and $Q_s = 319$ kJ/mol for primary and secondary creep, respectively [11, 12]. Values estimated at 319 MPa to nitrogen were $Q_p = 361$ kJ/mol and $Q_s = 437$ kJ/mol. The measured creep stress exponents at 500°C, in air and in nitrogen atmosphere, were 11.73 and 6.90 for primary creep and 9.67 and 7.86 for secondary creep, respectively. However at 600°C, in air and in nitrogen atmosphere, creep stress exponents were 4.55 and 5.96 for primary creep and 4.25 and 5.31 for secondary creep, respectively and at 700°C were 3.26 and 2.23 for primary creep and 2.62 and 2.64 for secondary creep, in air and in nitrogen atmosphere, respectively. Harrigan Jr. [13] conducted constant load creep tests for Ti-6Al-4V alloy at 315°C and 650°C. The results indicate that the steady-state strain rate $\dot{\varepsilon}_s$, may be described by the equation (2). In this case, the author consider that the value founded, n = 3.8, is

low for a two-phase system, but is in agreement for the stress dependence founded in pure metals and solid solutions. The stress exponent for pure titanium at 650°C is 5, which is reasonable for a pure metal.

Table 2 - Creep data at 500, 600 and 700°C.

Temperature (°C)	Atmosphere	σ (MPa)	t_p (h)	$\dot{\varepsilon}_s$ (1/h)
500	air	312	20.0	0.00116
		361	5.33	0.00347
		465	0.30	0.04295
		520	0.0462	0.1596
	nitrogen	312	58.0	0.0000617
		361	26.0	0.0001791
		465	4.00	0.00111
		520	1.801	0.00377
600	air	125	0.8333	0.00901
		222	0.0958	0.09162
		250	0.03055	0.1597
		319	0.01167	0.499
	nitrogen	125	24.0	0.00104
		222	1.713	0.01996
		250	0.353	0.03169
		319	0.089	0.1665
700	air	14	12.5	0.00396
		42	0.325	0.06426
		56	0.141	0.15656
	nitrogen	14	49.36	0.00034
		42	5.35	0.00673
		56	2.00	0.0128

However, Evans and Harrison [14] present for a Ti-6Al-4V alloy at 400 and 500°C stress exponents in the range of 8 to 16. A detailed study has been conducted in air by Warren, Hsiung and Wadley [15] about the high temperature creep and microstructural evolution accompanying the creep deformation of a nanocrystalline Ti-6Al-4V alloy, for the range of 600 to 900°C. At 600°C involves creep of predominately α-phase whilst above of 680°C the microstructure exhibits superplastic behavior of a two phases (α +β) structure. At 600°C the average value of the activation energy for all stress was 240 kJ/mol, this is identical to the activation energy determined by Harrigan Jr. [13]. The value of the creep stress exponent n = 3.4, of the nanocrystalline alloy is similar to n = 3.8 obtained for as-cast Ti-6Al-4V alloy tested with coarse grain at 650°C. In this case, micromechanical creep models based on a dislocation glide-climb predict creep exponents of 3. At 760°C and low applied stress when concomitant grain growth is introduced the mechanisms model predicts a creep stress exponent of n = 2.6.

In the context, for different titanium alloys, the values of activation energy determined by Tang et. all [16] from 327 to 416 kJ/mol and correspond to climb controlled creep. The apparent activation energy of self-diffusion usually reported for α-Ti was in the range of 242 to 293 kJ/mol [17]. In recent paper, Köppers et. all [18] reviewed the values reported. They showed that the amount and nature impurities, particularly the fast diffusing impurities Fe, Ni and Co had several effects on Ti self-diffusion. In high-purity α-Ti activation energies of 303 and 329 kJ/mol were found, respectively, for Ti-self diffusion and Al solute diffusion.
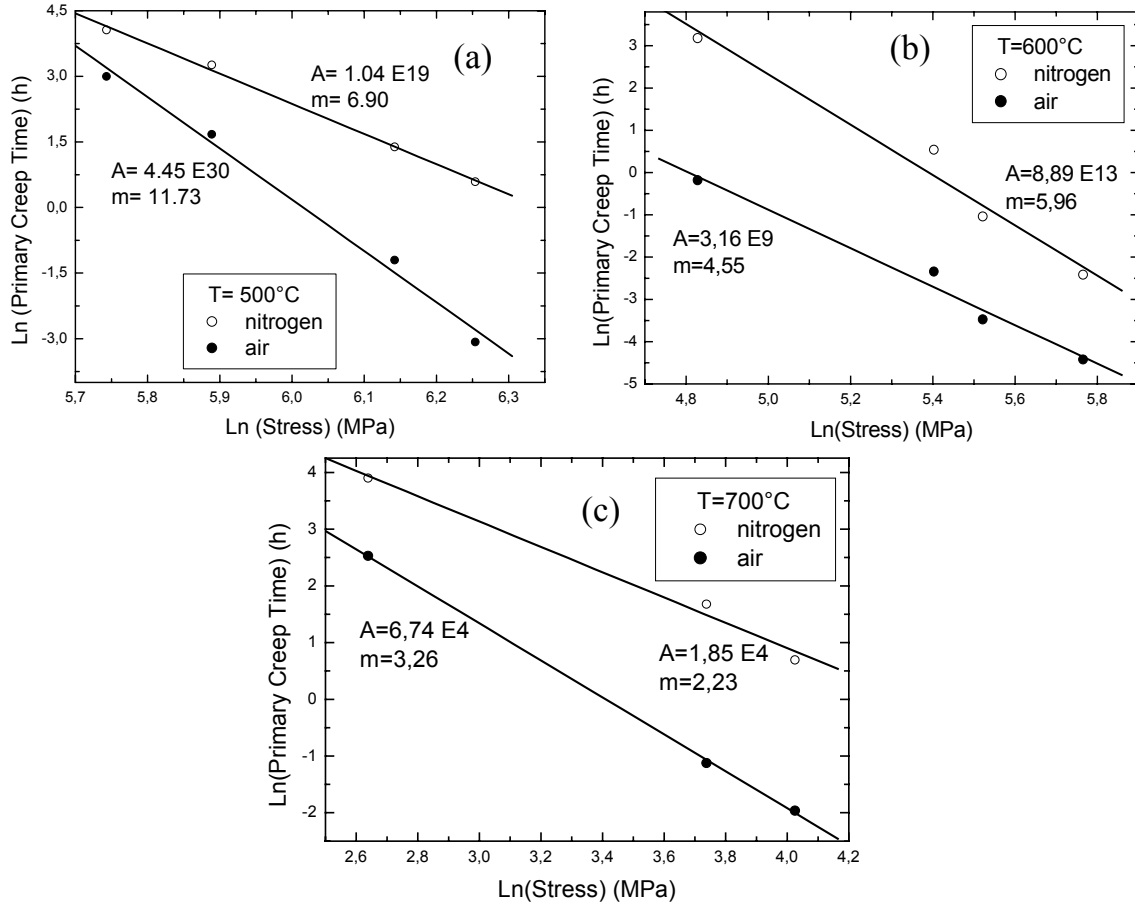
Fig. 2. Stress dependence of primary creep time in air and nitrogen atmosphere
(a) at 500°C, (b) at 600°C and (c) at 700°C.

Based in the information mentioned, the activation energies for primary creep and steady state determined in the present work fall within the range of the values determined by Köppers et. all [18] and target all thus, the correlation between Q_p and Q_s and the stress exponents may indicate that the creep in the both stages is controlled by dislocation climbs.

The relation between primary creep time and steady-state creep obeyed the equation (3), where N and P are constants over limited stress and temperature ranges, such that:

$$t_p(\dot{\varepsilon}_s)^N = P \tag{3}$$

The proportionality between $\dot{\varepsilon}_s$ and t_p is presented in Figs. 4. At 500, 600 and 700ºC in air and nitrogen atmosphere, the proportionality by standard regression techniques is obtained for N = 0.974 and P = 0.014.

Kellerer and Wingert [19] showed that the changes caused by oxidation in air of Ti-6Al-4V alloy lead to a several mechanisms, which can contribute to deformation. The increase of the "c" lattice parameter with increasing oxygen content accounts for most of the volume expansion. Because oxygen stabilizes α, the surface layers contain a higher than equilibrium α concentration. Higher thermal expansion of α and its larger volume per unit cell cause additional deformation. These mechanisms apparently can introduce surface stresses which result in extensive creep deformation.

Thus, a decreasing of steady state creep in function of the reduction of oxidation process showed that for the Ti-6Al-4V alloy their lifetime can be strongly affected by the atmosphere that was submitted because the oxidation suffered by the material to the tests realized in this work.
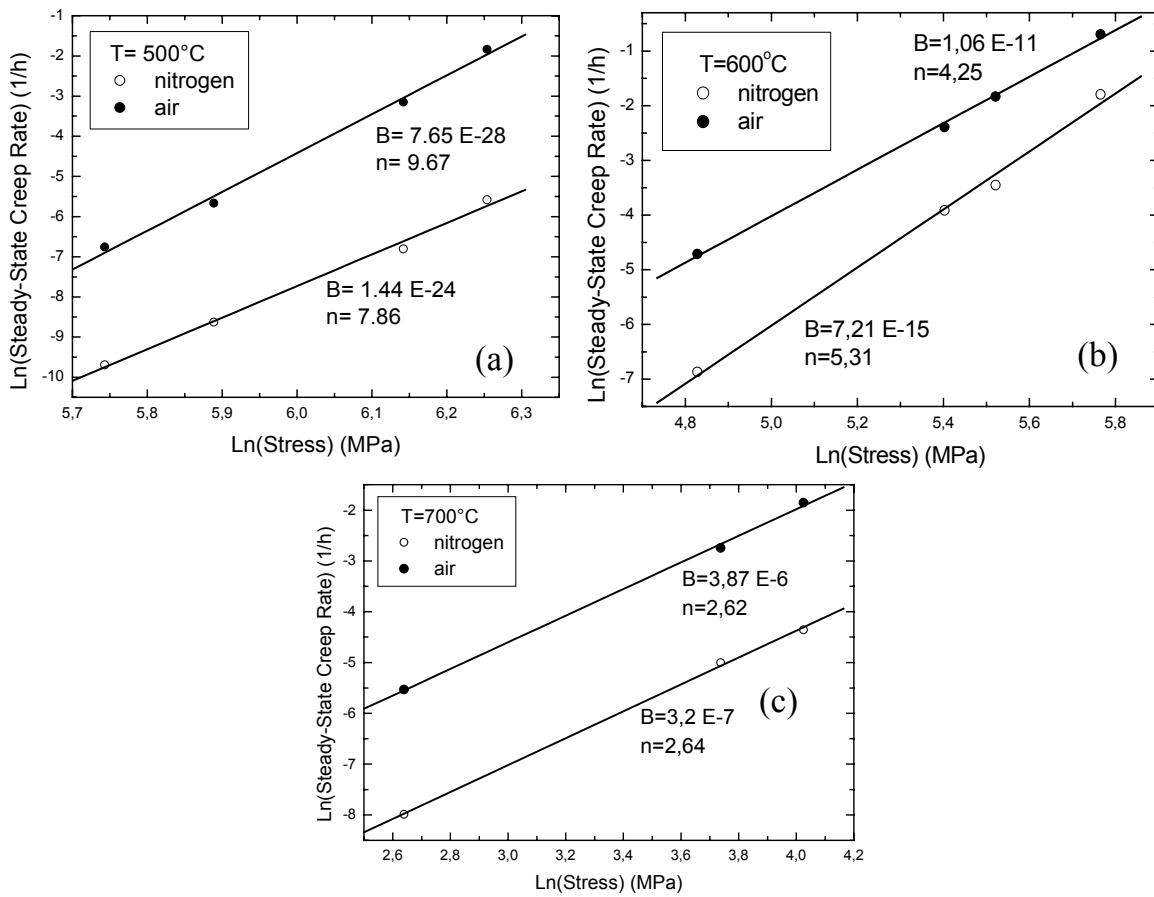

Fig. 3. Stress dependence of steady-state creep rate in air and nitrogen atmosphere
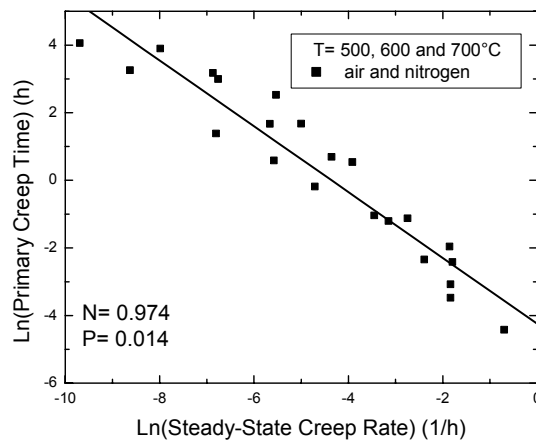(a) at 500°C, (b) at 600°C and (c) at 700°C.

Fig. 4. Dependence of steady-state creep rate on the primary creep time.

4- CONCLUSIONS

The creep properties of Ti-6Al-4V alloy in air and in nitrogen atmosphere were investigated at 500ºC, 600°C and 700°C. The exposure at high temperature in nitrogen atmosphere increases the creep resistance of the alloy at 500ºC in the range from 312 to 520 MPa, at 600ºC in the range from 125 to 319 MPa and at 700ºC in the range from 14 to 56 MPa.

The results for creep tests in air and under nitrogen atmosphere indicated that the primary creep, as well as the steady-state creep, is controlled by dislocation climb at 500, 600 and 700ºC. The decreasing of steady state creep in function of the reduction of oxidation process showed that for the Ti-6Al-4V alloy can be lifetime was strongly affected by the atmosphere that was submitted because the oxidation suffered by the material.

ACKNOWLEDGMENT

REFERENCES

[1] Es-Souni, M. **Mater. Characterization**, v.46, p. 365, 2001.
[2] Boyer R.R. **Mater. Sci. Eng. A**, v. 213, p. 103, 1996.
[3] Abkowitz S.; Burke J.J.; Hiltz Jr., R.H. **Technology of Structural Titanium.** D. Van Nostrand Company, p.31-32, 1955.
[4] Seco, F.J.; Irissari, A. M. **Fatigue Fract. Eng. Mater. Struc.**, v. 24, p.741, 2001.
[5] **Metals Handbook**, Desk edition, Howard E. Boyer and Timothy L. Gall, eds., ASM International, 1985.
[6] ASTM E 21-92 Standard test methods for elevated temperature tension tests of metallic materials. In **Annual Book of ASTM Standards**. American Society of Testing and Materials, Philadelphia, PA., 1989.
[7] ASTM E139 Standard test methods for conducting creep, creep rupture and stress-rupture of metallic materials. In **Annual Book of ASTM Standards**, American Society of Testing and Materials, Philadelphia, PA., v. 30.01, 1989.
[8] Dyson, B.F.; Mc Lean, M. **ISIJ Int.**, v. 30, p.802, 1990.
[9] Barboza, M.J.R., ITA, São José dos Campos, Brazil, **Doctoral Thesis**, p. 194, 2001.
[10] Rosen, A.; Rottem, A. **Mater. Sci. Eng.** v. 22, p.23, 1976.
[11] Barboza, M. J. R.; Moura Neto, C.; Silva, C. R. M. **Mater. Sci. Eng. A**, v.369, p. 201-209, 2004.
[12] Es-Souni, M. **Mettal. Mater. Trans. A**, v.32, p. 285, 2001.
[13] Harrigan Jr., W.C. Creep fracture characteristics of weld-repaired cast Ti-6Al-4V, **Metal. Transactions**, v. 5, p.565-572, 1974.
[14] Evans, W.J.; Harrison, G.F. Validity of friction stress of measurements for high-temperature creep. **Metal. Science,** p.346-350, 1979.
[15] Warren, J.; Hsiung, L.M.; Wadley, H.N.G. High temperature deformation behavior of physical vapor deposited Ti-6Al-4V. **Acta Metall. Mater.,** v. 43, p. 2773-2787, 1995.
[16] Tang, F.; Nakazawa, S.; Hagiwara; Transient creep of Ti-Al-Nb alloys. **M. Mater. Sci. Eng. A**, v. 325, p.194, 2002.
[17] Palchan, I.; Rosen, A. History dependent creep of Ti-6Al-4V alloy. **Metal. Sci.** p.163-165, 1978.
[18] Köppers, M.; Herzig, C.H.R.; Friesel, M.; Mishin, Y. Diffusion intrinsic self-diffusion and substutional Al in α-Ti. **Acta Mater.** V.45, p.4181-4191, 1997.
[19] Kellerer, H.; Wigert, L. Deformation of titanium by surface oxidation. **Metallurgical Transactions.** v.2, p.113-115, 1971.