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Jean-Philippe Couzinie, Bassem Barkia, Véronique Doquet, Ivan Guillot

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INFLUENCE OF HYDROGEN AND OXYGEN CONTENT ON THE MECHANICAL BEHAVIOR OF Zr AT 300°C AND Ti AT 20°C

COUZINIE J.P.¹
ICMPE, UMR 7182 CNRS-UPEC,
F-94320 Thiais, FRANCE

DOQUET V.²
LMS, UMR 7649 CNRS-Ecole
Polytechnique, F-91128 Palaiseau,
FRANCE

BARKIA B.^{1,2}
ICMPE, UMR 7182 CNRS-UPEC,
F-94320 Thiais, FRANCE
LMS, UMR 7649 CNRS-Ecole
Polytechnique, F-91128 Palaiseau,
FRANCE

GUILLOT I.¹
ICMPE, UMR 7182 CNRS-UPEC,
F-94320 Thiais, FRANCE

ABSTRACT

The mechanical behaviors of α -Zr and α -Ti with various oxygen and hydrogen contents were investigated by loading/relaxation/unloading tensile tests and tests with strain rate jumps, at 300°C and 20°C, respectively. Solute oxygen and hydrogen atoms were found to have antagonist effects. While the former increases the yield stress and hardening exponent, reduces the activation volume and enhances static and dynamic strain aging phenomena, the latter significantly reduces these effects, as long as the O content is not too high.

INTRODUCTION

At room temperature, commercial purity titanium and zirconium have an hexagonal compact (hcp) structure. Despite the large number of deformation modes of these hcp metals, plastic deformation is mainly accommodated by the glide of $a/3\langle 1-210 \rangle$ dislocations (so called $\langle a \rangle$ dislocations) in the prismatic $\{10-10\}$ planes [1-3]. The core structure of $\langle a \rangle$ screw dislocations is complex but now well-established [4]. Such a non-planar core is source of a high-lattice friction and of an important deviation from Schmid and Boas law [3,5]. Plastic deformation is controlled by the mobility of screw dislocations, which *post-mortem* TEM observations show lying in Peierls valleys [5,6] and *in-situ* dynamic TEM observations show gliding by jerky movements [7]. Different mechanisms have been proposed to explain the behavior of these dislocations subjected to such Peierls frictional forces: the Friedel and Escaig cross-slip mechanism (movement from a sessile to a glissile configuration before glide in the prismatic planes [8]), the kink-pair mechanism (jump between adjacent Peierls valleys) and the alternative locking-unlocking model (existence of a metastable configuration by jumps over lengths larger than the distance between Peierls valleys [9]). These models are temperature and stress-dependent.

The impurity content in solid solution – especially H and O – plays a crucial role in the plastic deformation of hcp crystals [10,11], but the interaction

mechanisms between interstitial solutes and dislocations are still not clearly understood. Numerous studies give evidence of the hardening effect of O on hcp metals [10,12]. Sastry *et al.* evoke local ordering of O close to the defects to explain the hardening effect [13] while Naka *et al.* evokes a modification of dislocation cores [5]. By contrast, solute H was reported to soften α -Ti [14] and α -Zr and to enhance creep [15]. Hydrogen would reduce the activation energies in the prismatic planes and thus make dislocation glide easier. According to the *in-situ* dynamic TEM observations of Shih *et al.* [16], H seems to increase dislocations velocity in α -Ti-4Al.

The aim of this paper is to analyse the mechanical behavior of α -Ti and α -Zr in the presence of different hydrogen and oxygen contents.

EXPERIMENTAL PROCEDURES

Both materials were extracted from hot-rolled commercial sheets denoted by Zr_1/Zr_2 and Ti_1/Ti_2 , respectively. A few specimens were also cut perpendicular to the axis of a forged titanium billet (Ti_0). The initial chemical compositions of the different materials are given in Table 1.

Material	O (wt. ppm)	Oeq. (at%)	H (wt. ppm)	H (at%)	Fe (wt%)
Zr_1	470±30	0.310	13±9	0.119	0.0126
Zr_2	1100±50	0.650	5±1	0.046	0.0129
Ti_0	450±30	0.135	5±2	0.023	0.0007
Ti_1	1600±50	0.510	6±2	0.028	0.0340
Ti_2	3200±100	1.020	15±3	0.075	0.1800

Table 1. Initial chemical compositions of the different materials used in the study.

Some specimens were charged with hydrogen at 500°C (Ti) and 400°C (Zr), so as to remain below the solubility limit at the testing temperatures (23ppm and 30ppm at 20°C in Ti_1 and Ti_2 , respectively, and 60ppm in Zr at 300°C). A similar thermal treatment, but under secondary vacuum was applied to as-received Ti specimens, including those from the billet (Ti_0), this leaving the O and H content unchanged and producing a similar microstructure and internal stress state as in H-charged specimens.

The textures of all materials extracted from sheets were qualitatively similar, with a <10-10> direction parallel to DL and <c> axes distributed in the DN-DT plane, 20 to 70° away from DN. As a consequence, tension along DT favors basal slip compared to tension along DL, more favorable to prismatic slip. Twinning, inhibited by high O contents, is expected to be very limited in Ti_2 and Zr_2 [17]. The mean grain size of the materials is summarized in Table 2.

Material	(DN,DL)	(DN,DT)	(DL,DT)
Zr_1	52	50	54
Zr_2	57	57	52
Ti_1	30	30	17
Ti_2	40	40	32

Table 2. Mean grain sizes of the materials (μm).

For Zr, strain-controlled loading/relaxation/unloading tensile tests were carried out on cylindrical samples with $\phi=5\text{mm}$ at $2\times 10^{-4}\text{s}^{-1}$ and a temperature of 300°C . Loading/relaxation/unloading sequences were repeated for plastic strains levels from 2×10^{-4} to 6×10^{-2} . For Ti, tension tests were done on cylindrical samples with $\phi=8\text{mm}$ at fixed strain rate ($2\times 10^{-4}\text{s}^{-1}$) or with tenfold strain-rate jumps to explore the range 2×10^{-6} to $2\times 10^{-2}\text{s}^{-1}$. Tests with 20h-relaxation-periods followed by unloading until reverse plastic flow and reloading to a higher strain were also performed, as well as creep tests, always at 20°C .

RESULTS AND DISCUSSION

Figure 1 presents the results of the tensile tests on Zr at 300°C . The plastic flow is clearly affected by the H and O contents.

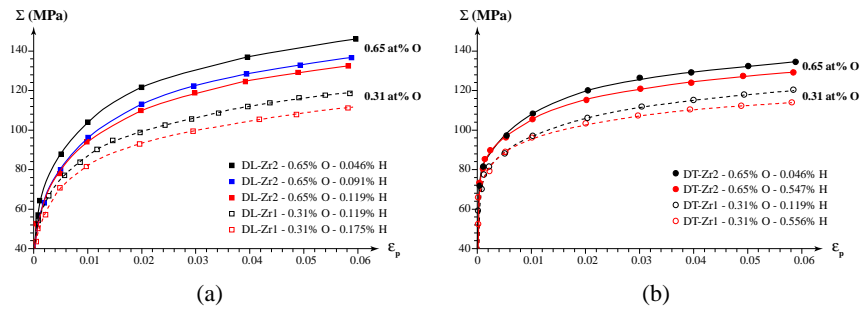


Figure 1. Stress-strain curves of Zr at 300°C : (a) tests along DL ; (b) tests along DT.

The increase in oxygen content leads to an increase of the yield and flow stresses, especially in the DL direction (Fig. 1.a.). Solute H tends to reduce the O-induced hardening. The effect is more discernible when approaching the hardening curve $\Sigma=f(\epsilon_p)$ by a power law (1):

$$\Sigma = \Sigma_0 \times \epsilon_p^n \quad (1)$$

Figure 2 displays the evolution of Σ_0 and n with the atomic percentage of hydrogen in the materials.

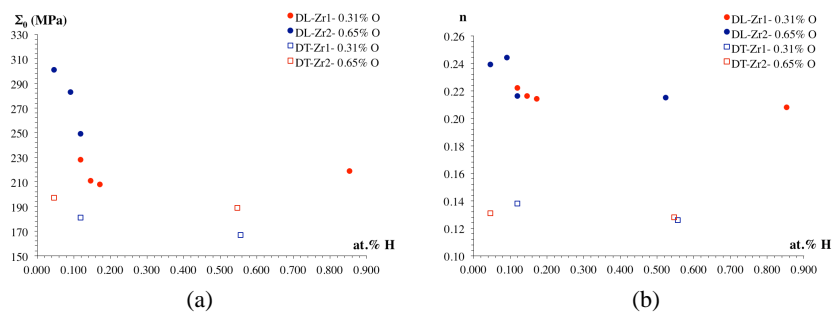


Figure 2. Evolution of the hardening parameters of Zr with H at 300°C : (a) Σ_0 ; (b) n .

Hydrogen reduces both Σ_0 and n (Fig. 2). The effect is more significant for the DL direction and seems to saturate for a H content above 0.2 at.%. Activation volumes were computed based on stress relaxation data (Fig. 3.a.). It was found to be independent of the loading direction, to decrease with the plastic strain and with the O content. By contrast, H increases the activation volume, but only for the moderate O levels (0.31at.%) while at higher O levels (0.65at.%), H has no impact on this parameter. Considering that at 300°C the kink-pair mechanism is still predominant to describe the screw dislocation mobility, the dislocation jump length h in steady flow has been calculated from (2) for the different tests and plotted versus the H content (Fig. 3.b.).

$$V = \left(\frac{\mu b^3 h^3}{8\pi\tau^*} \right)^{1/2} \quad (2)$$

with τ^* the thermally activated stress (viscous stress).

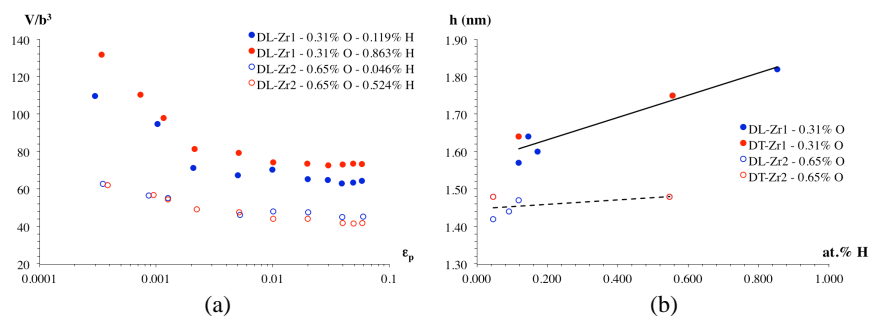


Figure 3. (a) Evolution of the activation volume with H and O content for Zr at 300°C (DL direction) ; (b) Evolution of the jump length h with H content for Zr at 300°C.

The influence of hydrogen on the jump length is clear for the Zr₁ alloy (0.31% O) whatever the loading direction. At moderate O levels, H could shield the interactions between oxygen and screw dislocations.

For Ti, the influence of H charging on the flow stress was small (10 to 60MPa upward or downward variation, depending on the strain level and strain rate) and more complex than in Zr, since the tensile curves of base and charged metals sometimes crossed each other. Duplicate tests are needed to check the reproducibility of these observations. However, such effects can be expected according to Beck [18]. Based on compression tests on Ti single crystals with a H content between 0 and 22ppm he reported a significant H-induced increase in the critical shear stress for dislocations glide on the prism and basal planes and a reduction in the critical stress for twinning. Contrary to what was observed in Zr, the activation volume in Ti was found to vary with the loading direction (it was 20 to 30% higher along DL than along DT) but not with the H content, at least for $O_{eq} \geq 0.51$ at.%. But as for Zr, it also tended to decrease with the plastic strain and with the O content.

H-charging was found to enhance slightly room-temperature creep along the DL direction (time to fracture reduced by a factor of 0.92 for Ti₁ loaded at $1.21\sigma_{0.2}=400$ MPa and Ti₂ loaded at $1.14\sigma_{0.2}=540$ MPa) (Fig. 4). Additional tests at lower stress levels and along the DT direction are in progress.

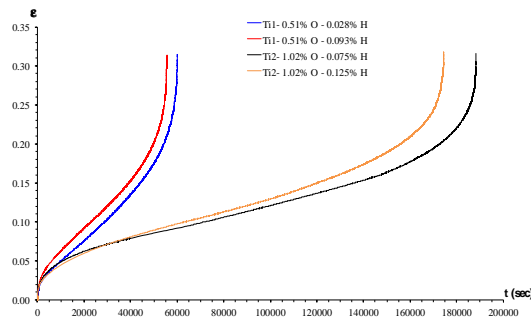


Figure 4. Creep behavior for Ti_1 and Ti_2 along the DL direction at 20°C .

Static Aging

A typical static aging (SA) peak has been revealed during the reloading process after relaxation and unloading phases in Zr. For Ti, a Lüders plateau was observed in Ti_1 and yield points in Ti_2 , (with a higher load drop at high strain rates), but only in tension along DT direction. The decrement of stress $\Delta\Sigma$ between upper and lower yield stresses is plotted in Fig. 5 for Zr. $\Delta\Sigma$ increases with the plastic strain until a maximum between 2% and 4%. $\Delta\Sigma$ is also function of the O level, the loading direction and the amount of solute H : the effect is more pronounced for the highest O level and in the DT direction (as well as for Ti). The most striking result is the H-induced reduction in SA. This effect is stronger along DT and is dependent on the O level.

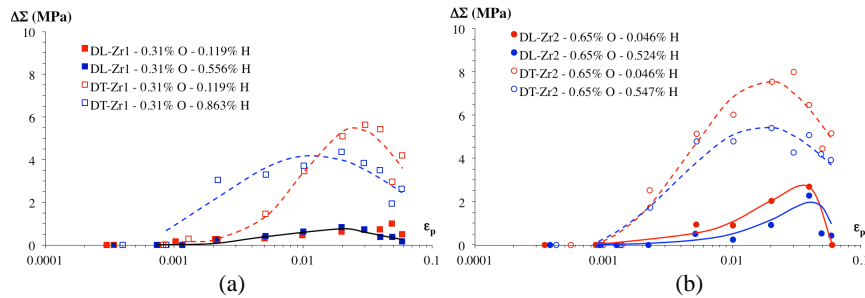


Figure 5. Static aging of Zr at 300°C . Evolution of the stress drop $\Delta\Sigma$ with plastic deformation ϵ_p : (a) Zr_1 (0.31at.% O); (b) Zr_2 (0.65at.% O).

The presence of a stress drop has been highlighted in numerous studies for Ti and Zr alloys [19,20]. The phenomenon is generally interpreted as static aging due to solute atoms in interstitial positions. Following the Schoeck and Seeger model [21] SA is due to the short-distance redistribution of the interstitials in the dislocation stress field, leading to the pinning of mobile dislocations. In the case of Zr, O atoms in the octaedral sites could be responsible for the observed SA at 300°C . The phenomenon is all the more important for the material loaded along DT when the $\langle c+a \rangle$ slip system is activated. This result could be interpreted by the redistribution of O atoms on $\langle c+a \rangle$ and $\langle a \rangle$ dislocations. Using a simplified atomic diffusion model (mere

geometrical approach), the jump frequencies between octaedral sites in the basal plane (Γ_1) and along the $\langle c \rangle$ axis, (Γ_2) can be estimated and the former is found to be smaller than the latter:

$$\Gamma_1 = \frac{1}{6} \left(\frac{c}{a} \right)^2 \times \Gamma_2 = 0.42 \times \Gamma_2 \quad (2)$$

Oxygen atoms redistribution should thus be faster on dislocations with a $\langle c \rangle$ component. The effect could even be enhanced by the stronger stress field associated with $\langle c+a \rangle$ dislocations compared to $\langle a \rangle$ dislocations.

In the presence of hydrogen, SA is clearly reduced (Fig. 4). According to Sofronis and Birnbaum this softening could originate from the hydrogen-induced "elastic shielding" of the interactions between dislocation stress fields and localised obstacles [22]. This mechanism implies that in the presence of hydrogen, dislocations will be less sensitive to obstacles and could start moving at lower stresses. Other authors explain the H-induced softening in terms of increased mobility of screw dislocations based on *in-situ* dynamic TEM observations of dislocation glide [23]. The TEM results gave evidence that the triggering effects of hydrogen on dislocations mobility was enhanced in materials containing other interstitial species, which is the case in our materials [24]. Considering that in most hcp metals hydrogen is present in tetrahedral sites and is also likely to decrease the density of octaedral sites available for oxygen, Feaugas and Conforto [25] pointed out that it could lead to an increase of the activation volume and thus a softening of the materials.

Dynamic Strain Aging

Small serrations were observed on the stress-strain curves, starting as soon as plastic flow began, for all Ti vacuum-annealed materials. The amplitude of these serrations increased from 1 to 6 MPa as the strain-rate decreased from $2 \times 10^{-2} \text{s}^{-1}$ to $2 \times 10^{-6} \text{s}^{-1}$ (Fig. 6). It is higher in Ti_2 than in Ti_0 , with the smallest O content, whereas twinning is very limited in the former and intense in the latter. These serrations are thus not due to twinning but to the repeated breakaway of dislocations from solute atoms atmospheres and reforming of these atmospheres (dynamic strain aging, DSA). As for static aging, an increase in the solute H content led to a reduction in the amplitude of the serrations.

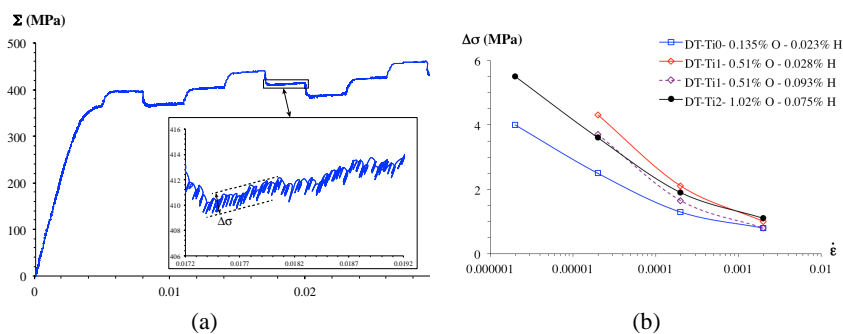


Figure 6. (a) Tension test of Ti_1 along DT at a strain rate of $2 \times 10^{-4} \text{s}^{-1}$. Note the presence of serrations ; (b) Evolution of the amplitude of the serrations ($\Delta\sigma$) with the strain rate.

Which solute atoms are responsible for the observed DSA is not a trivial question. Ti exhibits aging phenomena in several distinct temperature ranges that have been related to H, O, C, N and even substitutional Fe atoms, considering their respective bulk diffusivities [26]. Hydrogen was held responsible for DSA between 200 and 400K [26]. However, Nemat-Nasser *et al.* [27] observed room-temperature DSA in nearly H-free titanium and suggested that diffusion of O, C and N in the core of dislocations, much faster than bulk diffusion, can explain it. Like in the present case, a H-induced reduction in DSA was noticed in Ti6246 [28] at 20°C and in commercially pure Ti at 500°C [14].

By contrast, in a Ti₁ specimen charged by error to 0.140at.% H, above the solubility limit – although without any drop in ductility – "large" serrations, with amplitudes around 5MPa suddenly appeared around 5% strain, during a tensile test at $2 \times 10^{-4} \text{ s}^{-1}$ along DT. Such serrations, significantly larger than those observed in vacuum-annealed metal at the same loading rate, might be due to twinning. This would be consistent with the H-induced decrease in critical stress for twinning reported by Beck [18], who suggested that hydrides provide stress concentrations likely to trigger twin nucleation.

CONCLUSIONS

Solute oxygen and hydrogen atoms have antagonist effects on the mechanical behavior of both α -Zr and α -Ti. While the former increases the yield stress and hardening exponent, reduces the activation volume and enhances static and dynamic strain aging phenomena, the latter significantly reduces these effects, as long as the O content is not too high.

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REFERENCES

- [1] Akthar, A., Teghtsoonian, E., 1975, "Prismatic slip in α -titanium single crystals", *Metal. Mater. Trans.*, **6A**, pp. 2201–2208.
- [2] Biget, M. P., Saada, G., 1988, "Low-temperature plasticity of high-purity α -titanium single crystals", *Phil. Mag. A*, **59** (4), pp. 747–757.
- [3] Akthar, A., Teghtsoonian, E., 1971, "Plastic deformation of zirconium single crystals", *Acta Metall.*, **19** (7), pp. 655-663
- [4] Legrand, B., 1985, "Core structure of screw dislocations $1/3[1120]$ in titanium", *Phil. Mag. A*, **52** (1), pp. 83–97.
- [5] Naka, S., Lasalmonie, A., Costa, P., Kubin, L. P., 1988, "The low-temperature plastic-deformation of α -titanium and the core structure of a-type screw dislocations", *Phil. Mag. A*, **57** (5), pp. 717–740.
- [6] Tanaka, T., Conrad, H., 1972, "Deformation kinetics for (1010)(1120) slip in titanium single-crystals below $0.4T_m$ ", *Acta Metall.*, **20** (8), pp. 1019-1030.
- [7] Farenc, S., Caillard, D., Couret, A., 1993, "An in-situ study of prismatic glide in α -titanium at low-temperatures", *Acta Metall. Mater.*, **41** (9), pp. 2701-2709.

- [8] Friedel, J., 1959, "Dislocation interaction and internal strains", *Proceedings, Symposium on Internal Stresses and Fatigue in Metals* G.M. Rasswieler and W.L. Grube eds, Elsevier Publishing Corp. (Amsterdam), pp. 220-262.
- [9] Couret, A., Caillard, D., 1991, "Dissociations and friction forces in metals and alloys", *J. Phys. III*, **1** (6), pp. 885-907.
- [10] Mills, D., Craig, G. B., 1968, "The plastic deformation of zirconium-oxygen alloy single crystals in range 77 to 950K", *Trans. AIME*, **242** (9), pp. 1881-1890.
- [11] Conrad, H., 1981, "Effect of interstitial solutes on the strength and the ductility of titanium", *Prog. Mat. Sci.*, **26** (2-4), pp. 123-404.
- [12] Soo, P., Higgings, G. T., 1968, "The deformation of zirconium-oxygen single crystals", *Acta Metall.*, **16** (2), pp. 177-186.
- [13] Sastry, D. H., Prasad, Y. D., Vasu, K. I., 1971, "An evaluation of rate-controlling obstacles for low-temperature deformation of zirconium", *J. Mat. Sci.*, **6** (4), pp. 332-341.
- [14] Senkov, O. N., Jonas, J. J., 1996, "Dynamic strain aging and hydrogen-induced softening in alpha titanium", *Metal. Mater. Trans.*, **27A**, pp. 1877-1887.
- [15] Gao G.Y, Dexter S.C, 1987, Effect of hydrogen on creep behaviour of Ti-6Al-4V alloy at room temperature, *Met. Trans* **18A**, pp 1125-1130
- [16] Shih, D. S., Robertson, I. M., Birnbaum, H. K., 1988, "Hydrogen embrittlement of α -titanium – in-situ TEM studies", *Acta Metall.*, **36** (1), pp. 111-124.
- [17] Zaeferrer, S., 2003, "A study of active deformation systems in titanium alloys: dependence on alloy composition and correlation with deformation texture", *Mat. Sci. Engng*, **A344**, pp. 20-30.
- [18] Beck, F. H., 1975, "Effect of hydrogen on the mechanical properties of titanium and its alloys", NASA CR-134796 final report.
- [19] Hong, S. I., Ryu, W. S., Rim, C. S., 1983, "Elongation minimum and strain rate sensitivity minimum of zircaloy-4", *J. Nucl. Mat.*, **116** (2-3), pp. 314-316.
- [20] Veevers, K., Rotsey, W. B., 1968, "Effect of irradiation on strain ageing in annealed zircaloy-2", *J. Nucl. Mat.*, **27** (1), pp. 108-111.
- [21] Schoeck, G., Seeger, A., 1959, "The flow stress of iron and its dependence on impurities", *Acta Metall.*, **7** (7), pp. 469-477.
- [22] Sofronis, P., Birnbaum, H. K., "Mechanics of the hydrogen-dislocation-impurity interactions. 1. Increasing shear modulus", *J. Mech. Phys. Sol.*, **43** (1), pp. 49-90.
- [23] Birnbaum, H. K., Robertson, I. M., Sofronis, P., 2000, "Hydrogen effects on plasticity", *Proceedings, Conference of the NATO-Advanced-Study-Institute on Multiscale Phenomena in Plasticity - From Experiments to Phenomenology* J. Lepinoux et al. eds, *Nato Advanced Science Institutes Series E, Applied Physics*, **367**, pp. 367-381.
- [24] Tabata, T., Birnbaum, H. K., 1984, "Direct observation of hydrogen enhanced crack propagation in iron", *Scripta Metall.*, **18** (3), pp. 231-236.
- [25] Feaugas, X., Conforto, E., 2009, "Influence of hydrogen on the malformation mechanisms and damage to alloys of titanium and zirconium", *Proceedings, Conference on Mechanisms and Mechanics of Plasticity-Environment Interactions* B. Viguier eds, EDP Sciences, pp. 161-178.
- [26] Garde, A. M., Santhanam, A. T., Reed-Hill, R. E., 1972, "The significance of dynamic strain aging in titanium", *Acta Met.*, **20**, pp. 215-220.
- [27] Nemat-Nasser, S., Guo, W. G., Cheng, J. Y., 1999, "Mechanical properties and deformation mechanisms of a commercially pure titanium, *Acta Met.*, **47**, pp. 3705-3720.
- [28] Gerland, M., Lefranc, P., Doquet, V., Sarrazin-Baudoux, C., 2009, "Deformation and damage mechanisms in an α/β 6242 Ti alloy in fatigue, dwell-fatigue and creep at room temperature. Influence of internal hydrogen", *Mater. Sci. Engng.*, **507**, pp. 132-143