HIGH TEMPERATURE OXIDATION PROCESS AFFECTED BY SHOT-PEENING: APPLICATION TO PURE ZR AND TI

Virgil OPTASANU, Armand KANJER and Tony MONTESIN

ICB UMR 6303 CNRS - Université de Bourgogne Franche-Comté, 9 Av Alain Savary, BP. 47870, 21078 Dijon Cedex, France

Abstract - An evaluation of the shot-peening effects on the oxidation rate of Zr and Ti between 350°C and 650°C for 100h is presented. It is shown that the oxidation rate can substantially be decreased by shot-peening at high temperatures (T>500°C) while at lower temperatures the effect is opposite. An investigation of the various factors that can play a role on the oxidation behaviour was realized in order to separate their influence. It was shown that the pollution of the surface that can eventually occur during the shot-peening process is not responsible for the oxidation rate decrease. It was proposed that, at temperatures giving mainly a bulk diffusion of the O^{2-} ions within the metal volume, the slowing of the oxidation rate could be explained by the mechanical stress.

Résumé – Influence du grenaillage sur l'oxydation haute température. Application au Zr et Ti purs. On présente une évaluation des effets du grenaillage sur l'oxydation du Zr et Ti entre 350°C 650°C pendant 100h. Il est montré que la vitesse d'oxydation peut-être substantiellement diminuée par le grenaillage aux hautes températures (T>500°C) alors que à des températures moyennes l'effet est opposé. Une investigation des divers facteurs pouvant jouer un rôle dans le comportement à l'oxydation est réalisée afin de séparer leur influence. On montre que la pollution de la surface qui peut éventuellement se produire lors du grenaillage n'est pas responsable de la baisse de la vitesse d'oxydation. A des températures auxquelles la diffusion des ions O^{2-} se fait majoritairement dans le volume peut-être expliquée, au moins partiellement par les contraintes mécaniques.

1. INTRODUCTION

The Zirconium and its alloy are used as cladding element in the nuclear industry due to the transparency to neutrons and good oxidation resistance at moderate temperatures. The Titanium presents huge industrial interest and is increasingly used in high temperature aeronautics and aerospace domains.

The shot-peening is one of the possible way to introduce high residual stress and residual stress gradients by producing strong plastic strains and hardening on the superficial layers of the samples. It is well known as a process used for fatigue life improvement. The influence of shot-peening on high temperature oxidation is much less investigated [1,2,3]. One remarked that at high temperatures, the strong hardening of the superficial layer produces a slowing down of the oxidation rate.

Tirés-à-part : V. OPTASANU, ICB UMR 6303 CNRS - Université de Bourgogne Franche-Comté, 9 Av Alain Savary, BP. 47870, 21078 Dijon Cedex, France

In our previous works we shown that shot-peened Zr samples have oxidation rates sensibly lower than the original material for short [1] (30 min), or longer oxidation times [2] (3 days) at 650°C. The Zirconium is generally not used uncoated at high temperature. The knowledge of the high temperature oxidation of this metal is important for security reason as it is used as first security barrier in nuclear reactors. Uncoated Titanium is used in aeronautic and aerospace engineering at high temperatures (jet engine rotors and deflector parts).

The high temperature oxidation (>450°C) of Zirconium is governed by the bulk diffusion of O^{2-} ions into the metal lattice while at medium temperatures the diffusion process mainly occurs in grain boundaries [4]. At high temperature the diffusion coefficient has sufficiently large values to give large diffusion zones of several tens of microns. The insertion of large quantities of oxygen into the zirconium lattice (up to 29% atomic) tends to expand the metal lattice and then gives important compression stress values in the plane parallel to the oxide/metal interface.

The diffusion process is closely influenced by the mechanical stress [5,6,7]. The apparent diffusion coefficient depends on the mechanical stress [8,9] as well on the stress gradients and can influence the oxidation based on anionic diffusion of the oxygen into the metal lattice [1,10,11]. By using pure thermodynamic developments the first Fick's law can be modified as follows:

$$\vec{J} = -D_0 \left[\left(1 + \frac{M_0}{RT} \eta_{ii} \sigma_{ii} \right) \vec{\nabla} c - \frac{M_0}{RT} c \vec{\nabla} (\eta_{ii} \sigma_{ii}) \right], \tag{1}$$

where $\vec{J}$ is the flux of oxygen into the metal, M_0 is the molar mass of the metal, c is the oxygen concentration, σ_{ij} is the stress tensor and $\eta_{ij} = \frac{\partial \varepsilon_{chem}}{\partial c}$ is the chemical expansion coefficient [5]. For example, in the Zr case, the average value of the chemical expansion coefficient is $\eta = 3.55 \ 10^{-5} m^3 \ kg^{-1}$.

The Equation (1) is purely thermodynamic and do not contains any phenomenological parameter. It shows two driving forces one governed by the concentration gradient but influenced by the mechanical stress, the second governed by the stress gradients.

For the physical interpretation of the stress influence on the diffusion law we will consider in the following explanations the case of a material that expands when oxygen diffuses within its crystallographic lattice (the chemical expansion coefficient, $\eta > 0$).

The influence of the stress on the first term $-D_0 \left(1 + \frac{M_0}{RT} \eta_{ii} \sigma_{ii} \right) \vec{\nabla} c$ can be illustrated as a flux increase in tensioned regions of the material. We notice that the presence of a compressive stress decreases the effective diffusion coefficient.

The influence of the second term $D_0 \frac{M_0}{RT} c \vec{\nabla} (\eta_{ii} \sigma_{ii})$ can be illustrated like a mechanical pump: the oxygen migrates from the more compressed to less compressed regions. We also notice that the sign of this term is opposite to the concentration gradient term (Fick's term). A compression stress decreases the value of the apparent diffusion coefficient. As an example, a triaxial compression stress of about 400 MPa applied on Zr decreases the effective diffusion coefficient of about 30% at 650°C. While the stress value is limited by the mechanical properties of the material, the stress gradient can reach very strong values if the variation of the stress is made within a very short depth. The term in Equation (1) containing the stress gradient can then be very influent and can act in some cases as an up-wind driving force for the dissolved oxygen, by opposing the "natural" flow from "rich" to "poor" concentration. The stress taken into account can be due to external forces or to thermal and mechanical processes. In previous simulation works was shown that the diffusion can be "manipulated" by the mechanical stress [1]. Works on the Surface Mechanical Attrition Treatment (SMAT) [3] effects on high temperature oxidation of M5 zirconium alloy revealed also a slowing down of the oxidation introduced by the nanocrystallization of the surface. We previously studied [2] the influence of several factors on the oxidation of Zr at 650°C: shot-peening duration, nature of the oxidant atmosphere and annealing influence. We shown that the longer is the shot-

peening treatment the bigger is the influence on the oxidation. The present work investigates the oxidation behaviour of the shot peening plates at temperatures between 350°C and 650°C.

2. EXPERIMENTAL PROCEDURE

Commercially pure Zr and Ti plates (99.8% purity, 2 mm thick Zr plates, and 99.6% purity, 1 mm thick Ti plates, Goodfellow) have been used in this study. Rectangular samples 50 x 25 mm^2 were cut, annealed at 750°C for 2h under dynamic secondary vacuum in order to decrease the eventual post-manufacturing residual stress. The samples were then shot-peened both sides by alternate steps of 5 min/side in order to avoid a too strong Almen's deformation. The shot-peening is realized using 20 g of 2mm tungsten carbide balls and a sonotrode vibrating at 20 kHz with an amplitude of 12μm. In this study, the chosen shot-peening durations were 5, 10 and 20 min for Ti respectively 30 min for Zr.

After shot-peening, small samples of 10 x 10 mm^2 were cut and used for thermo-gravimetric analysis. Samples were subjected to oxidation at temperatures between 350°C and 650°C for few days. SEM and optical microscopy were realized and we found that during the high temperature exposure the grains of the metal do not grow. In contrast, the temperature is high enough to produce (at least partially) the dislocations recovery and then decrease the residual stresses. For example, at 650°C the recovery is produced in less than 1h for Zircalloy 2 [12].

The residual stress has been measured by incremental hole-drilling method (IHDM). Experimental details are presented elsewhere [1]. *Figure 1* shows the profile of the residual stress in Zr plate in a direction parallel to the sample surface with respect to the depth. The stress curve has a particular shape characteristic to shot-peening: there is a first region on the first 150 μm with a negative gradient, followed by a zone with positive gradient. In the case of the oxidation, according to the Equation (1), the first zone will contribute to decrease the oxygen flux into the metal bulk. Due to the positive stress gradient in the second zone (>150μm), the apparent diffusion coefficient value increases. The first zone slows down the diffusion, while the second zone accelerates it.
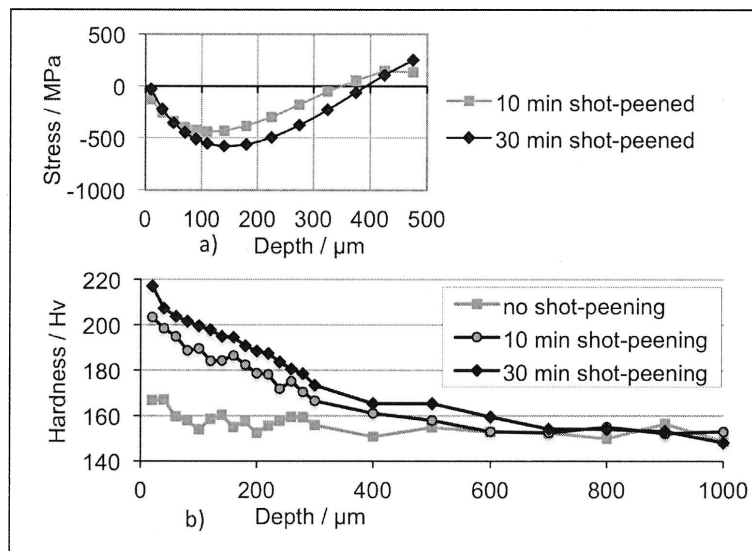
**Figure 1**. Residual stress measured (a) by IHDM and hardness after shot-peening (b).

As shown in our previous works [1,2,13] on Zr plates, shot-peening can substantially decrease the high temperature oxidation rate. Figure 2 presents mass gain curves for short and long oxidation periods at 650°C. The mass gain have parabolic shape at early stages of the oxidation (t<7h) which

represents about 8μm of oxide, then there is a transition region which is short in the case of un-shot-peened samples and much longer in the case of the shot-peened sample. The un-shot-peened sample reaches rapidly a linear regime, which means that the protective oxide layer thickness remains globally constant. In the case of the shot-peened sample the linear regime shows a much slower rate. At this temperature the annealing is total and only a difference in the oxide morphology and phase composition formed in the early stage of oxidation can explain this oxidation behaviour. Deeper investigations will be made in order to characterize the oxide nature.

In the range of temperatures that we investigate the oxidation of Zr and Ti are anionic processes. The oxidation occurs by diffusion of the oxygen in the metal lattice followed by the transformation of the oxygen-richest zones into oxide. The concentration profile of the dissolved oxygen goes progressively from 29% atomic at the oxide/metal interface to zero in the pure-metal region. *Figure 3* presents the morphology of the oxide, interface and solid solution zone (of the oxygen in the metal), for pure Zr oxidized at 650°C for 3 days. One can remark that the oxide layer is cracked, with cracks parallel to the oxide/metal interface. The interface between metal and oxide is undulated. Also, between the pure metal and the oxide there is a zone with a variable amount of dissolved oxygen, as remarked on EDX measurements presented also in *figure 3*. In the pure metal zone, the apparent amount of oxygen measured by EDX is about 12%. This is due to the pollution of the superficial layers of the metal by the atmospheric oxygen during the polishing of the sample. Here, the depth of diffusion of the oxygen into the metal lattice is about 15 μm. We published elsewhere [14] evidences that EDX measurements show length of diffusion shorter than other more accurate techniques like Nuclear Reaction Analysis.

At 650°C (see *figure 2*) the mass gain at the beginning is parabolic, then linear, which is the sign that during the late stages of oxidation the protective un-cracked oxide layer thickness remains constant. This thickness is difficult to measure precisely on micrographic images because it is not constant. Also, the protectiveness of this layer is made by the non-connection of the cracks, which is impossible to quantify by micrographic techniques. At 650°C, after 72h of oxidation, the mass gain is reduced by 80% - the rate of oxidation is divided by 5! The mechanical treatment of the samples produces a relative protection of the material at high temperature by slowing down the oxidation.
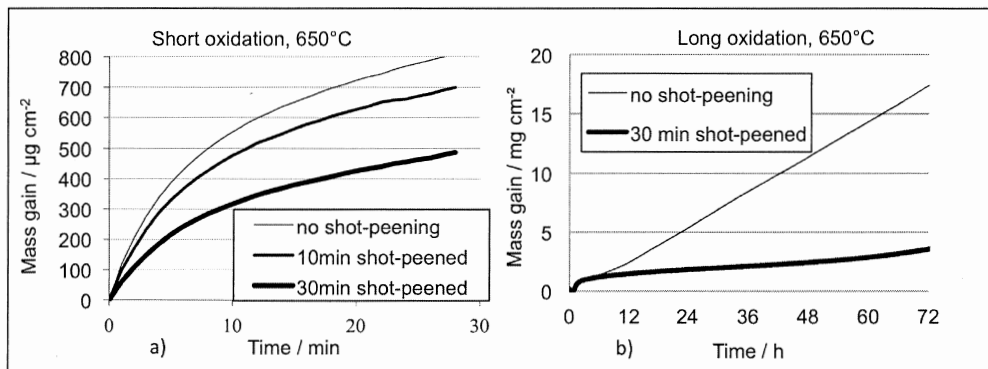

Figure 2. Short (a) and long (b) oxidation durations for Zr plates, at 650°C
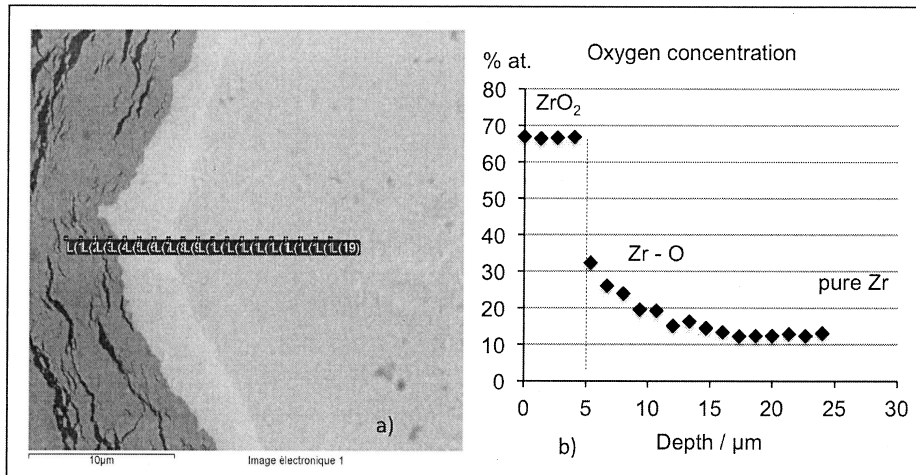
Figure 3. Morphology of the oxide, interface and oxygen solid-solution zone (a). Corresponding EDX measurements of the oxygen concentration (b).

The oxidation of the Zr was made at several temperatures: 350°C, 400°C, 450°C, 500°C, 650°C. *Figure 4* shows the influence of the shot peening on the oxidation for 400°C and 500°C. For temperatures under 450°C the shot-peened Zr samples oxidize more than natural Zr samples. Under 450°C the mass gain is parabolic, which is the sign that the diffusion is the rate limiting process during the oxidation. For temperatures above 500°C the shot-peening slows down the oxidation rate.

The different behaviour at high and lower temperature can be explained by the lattice diffusion at high temperature while at lower temperatures the diffusion occurs mainly via grain boundaries and dislocations [15]. For Zr, under ~450°C the oxygen diffuses mainly by grain boundaries and dislocation, while above this temperature occurs mainly the lattice diffusion. The density of dislocation is highly increased by shot-peening in the superficial layer. The oxide formed on shocked metal, can produce small oxide grains and subsequently many grain boundaries, which are the preferential way for the oxygen ions to reach the metal. At low temperatures, short-circuits of diffusion in the metal can also participate to increase the oxidation rate [15].
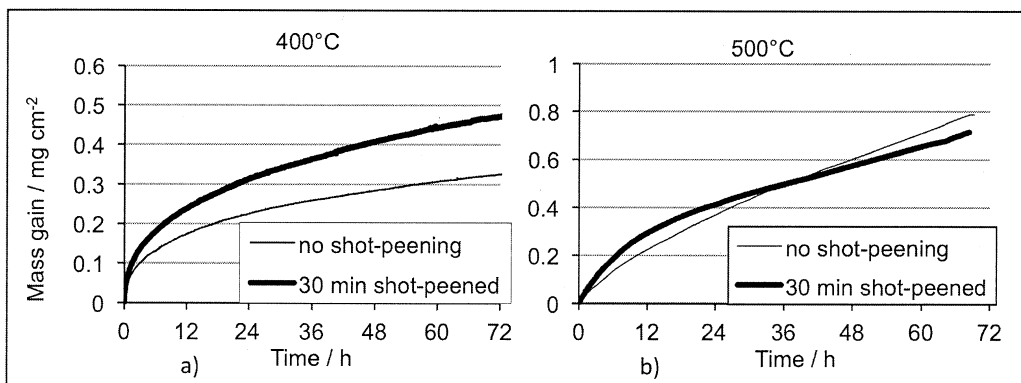
Figure 4. Mass gain at 400°C (a) and 500°C (b) for Zr samples.

At high temperature the slowing can be explained, at least during the initial stages, by the mechanical stress acting as a driving force. Another factor that can play a role is the stabilization of the quadratic phase of zirconia by the high compression stress and the small crystallites size in the

shocked area. After few hours at high temperature the stress must decrease but probably the recovery is not total. There is also probably a difference in the morphology of the protective oxide layer due to the hardening, as remarked for Zircalloy by Panicaud et al [3] by XRD techniques. However, after the annealing of the metal, which occurs rapidly at high temperature (~ few hours at T> 500°C), only the early oxide can be morphologically different. Thus, the reason of this oxidation behaviour at high temperature is not obvious and has to be studied further. This particular point will be the object of our future works.

Oxidation made on shot-peened then chemically etched samples, where superficial layers of about 3μm thick have been removed (see *figure 5*), shows the same behaviour in oxidation: more the sample is shot-peened lower is the mass gain. This shows that the eventual pollution of the surface by the WC balls is not responsible of the oxidation rate slowing down. However, by comparing the mass gain of etched and un-etched samples (see *figures 2* and *5*), etched samples oxidize more than un-etched specimens, which indicate that the highly shocked few μm thick superficial layer has an important influence on the oxidation.

In order to summarize all the TGA experiments, a coefficient evaluating the relative difference between shot-peened and natural samples in terms of mass gain during oxidation can be defined as follows:

$$\delta = \frac{\Delta m_{s-p} - \Delta m_0}{\Delta m_0} \qquad (2)$$

where Δm_{s-p} and Δm_0 are the mass gain for shot-peened and respectively natural samples. This coefficient is positive when the shot-peening accelerates the oxidation and negative when it slows it down. The bigger is the absolute value of δ, the greater is the influence of the shot peening on the oxidation. *Figure 6* presents values of the coefficient δ with the temperature for 30 min shot-peened Zr samples. A linear trend line shows that the influence of the shot-peening vanishes around 500°C. However at 500°C, Figure 4 shows an important difference between the shapes of the two mass-gain curves. A longer oxidation time should give more difference between the final mass gains.
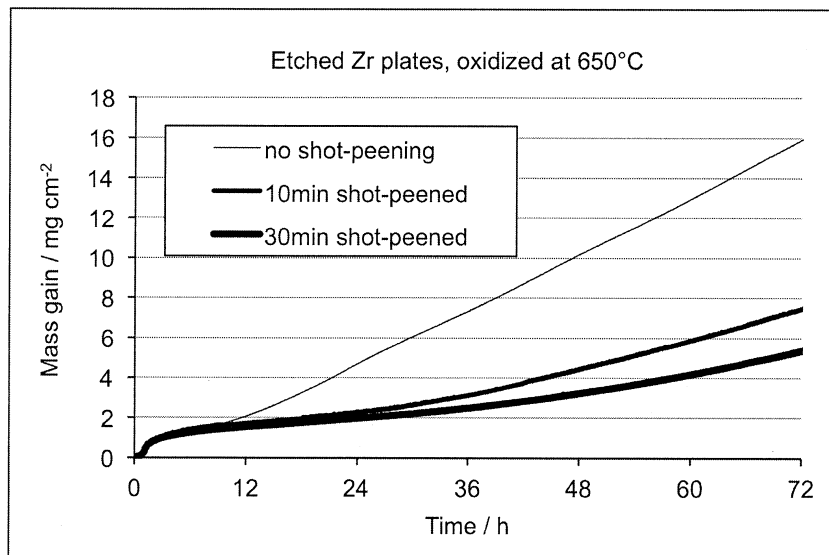
**Figure 5.** Oxidation at 650°C of etched Zr samples.
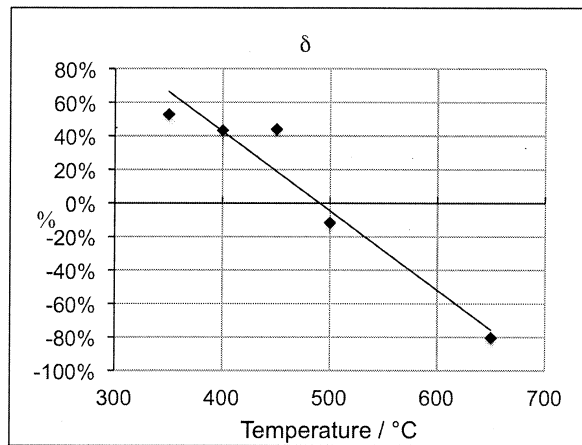
Figure 6. Relative difference between mass gain of shot-peened and natural samples, δ coefficient.

In the case of Ti the shot-peening produces visible microstructure changes as remarked *figure 7*. One can remark strong grain refinement up to 50 μm to the surface, as well twinning up to 200 μm (for the 20 min shot-peened sample).

Figure 7 shows also the mass gain for Ti at 650°C for different shot-peening durations. As for Zr, the shot-peened Ti plates oxidize less than natural Ti plates. At this temperature, the most shot-peened sample shows a remarkable slowing down of the oxidation rate ($\delta = -47\%$).

Investigations at lower temperatures were not yet realized for Ti because of the good resistance to oxidation of this material, which need long oxidation tests. Long exposure periods at lower temperatures are however interesting for industrial purposes and will be made in our future works.
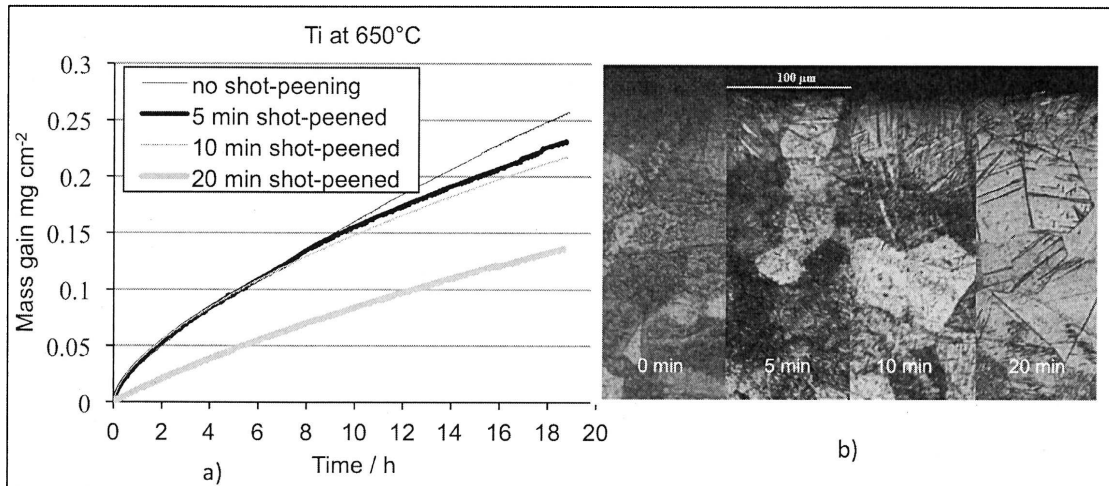
Figure 7. Mass gain for Ti samples at 650°C (a) and micrographics of the hardened layer (b).

4. CONCLUSIONS

In this work we have shown that a mechanical treatment, namely the shot-peening, can produce substantial modification of the oxidation rate for Zr and Ti. For Zr, at temperatures under

450°C, in the domain of the preponderant grain boundary and dislocation diffusion, the shot-peening increases the oxidation rate. At T>500°C, the shot-peening produces a slowdown of the oxidation rate. This phenomenon is partially explained by the presence of the stress state that produces a mechanical driving force. However, at temperatures T>550°C the annealing of the samples, which occurs during the oxidation, tends to annihilate the stresses. Then, the differences between the mass gains can be explained only by the morphologic differences of the earlier oxide, which is grown on a nanostructured substrate.

The acceleration of the oxidation rate at medium temperatures (T<500°C) can be explained by the nanostructure of the superficial layers, which produces small oxide grains and many grain boundaries. The increase of the density of diffusion paths boosts the oxygen supply to the metal to oxidize.

The eventual pollution of the surface during the shot-peening by the WC balls is not responsible for the slowing down of the oxidation rate because etched shot-peened samples still oxidize less than etched un-shot-peened specimens.

This study proves that shot-peening is then one of the simple mechanical methods for life-time improvements of Zr and Ti exposed at high temperature oxidation. Further works will be made on industrial grades of Ti and its alloys.

5. ACKNOWLEDGEMENTS

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