Experimental and numerical study of the effects of a nanocrystallisation treatment on high-temperature oxidation of a zirconium alloy


1. Introduction

Surface Mechanical Attrition Treatment (SMAT) is a recent process designed to nanocrystallise the surface of metallic alloys [1–4]. It can thus enhance the mechanical properties of the material treated by inducing grain refinement down to the nanometer scale in the top surface layer [3]. This nanocrystallisation process has different effects that have been successively studied on several metallic materials (not only pure metals such as copper, but also steels and other alloys [1–4]). In the present work, its physicochemical effects on an M5 zirconium alloy are investigated. This material is of great interest to the nuclear industry because of its neutron resistance [5]. High-tech applications in high-temperature environments are thus of particular interest. SMAT should effectively change the surface properties of these zirconium alloys. From a general viewpoint, an increase in the grain boundary fraction going from the core of the material to the top surface of the sample, due to the grain size refinement induced by SMAT, can modify the diffusion parameters. It is now well established that the surface reactivity can also be modified by nanocrystallisation treatment [6]. As a result, the oxidation properties are assumed to be affected and possibly improved by SMAT. First, the effects of the Surface Mechanical Attrition Treatment process on the initial metallic specimens were studied using X-ray diffraction and roughness measurements. Second, the oxidation effects were investigated using thermogravimetric analyses and Raman spectroscopy measurements. Both these techniques can be used to identify the kinetic parameters characteristic of the oxidation process and the local chemical composition of the phases. Oxidation mechanisms were then investigated by modelling the phenomena concerned, including its numerical aspects. Finally, the mechanisms involved were analysed in order to understand how SMAT can improve the corrosion resistance of such an M5 Zr alloy.

2. Material and surface treatment conditions

The material studied is a commercial M5 zirconium alloy containing a zirconium base with niobium (1% mass) and 1000 ppm of oxygen, as used in the nuclear industry. Half the samples were treated using the nanocrystallisation process (SMAT). They were SMATed for 15 min on each of the main surfaces (symmetrical treatment). Steel balls of 3 mm diameter were used with a sonotrode frequency of 20 kHz. Fig. 1 shows a simple geometrical representation of the process. Details of the experimental method have been given in previous works [3]. Oxidation at different temperatures was also investigated. However, only the case of a furnace temperature of 550 °C in ambient air and an oxidation time...
of 20 h is considered here. This temperature was chosen and carefully studied not only in relation to stresses typically used in industry on zirconium alloys [5], but also to preserve the benefits of SMAT [1–3]. If the temperature becomes too high, the grains can grow and cause the superficial nanostructure to disappear [1–3].

3. Results of SMAT on non-oxidised surface properties

3.1. X-ray diffraction results

Various surface modifications can be expected when Surface Mechanical Attrition Treatment is used. Both the grain size and roughness, for example, are known to be modified by the SMAT process [1–4]. The first can be investigated indirectly using diffraction experiments. More specifically, the diffracting domain size and second order residual stresses were studied simultaneously using X-ray diffraction (XRD) by measuring peak broadening [7–8]. The experiments were performed with a Seifert 3000PTS goniometer and a Cr radiation source (\( \lambda = 0.22897 \) nm). The Full Width at Half Maximum intensity (FWHM) was then evaluated on each of the diffraction peaks. Two data treatment methods were performed to extract information from the FWHM. First, the Laue-Scherrer formula was considered based on the assumption that the mesoscopic strain is equal to zero. With this assumption, the FWHM is directly linked to the coherent diffracting domain size [7–11]. By comparing the FWHM for SMATed specimens with the FWHM for untreated specimens, a ratio was calculated according to Eq. (1):

\[
\frac{FWHM_{SMAT}}{FWHM_{noSMAT}} = \frac{r}{Rt}
\]  

The above ratio as a function of the Bragg peak position is shown in Fig. 2. The mean ratio calculated is thus 2.590 ± 0.122. This approach, however, is too simplistic in relation to the previous stress/strain assumption. Second, the Halder–Wagner–Langford method was used to refine our predictions [7–11]. This method enables the mesoscopic distortions and the size of the coherent diffracting domains (assumed to be linked to the grain size) to be deconvoluted simultaneously. Using this approach, a variable change was performed by means of the relations in Eq. (2):

\[
\begin{align*}
\delta & = \frac{2 \sin(\theta_B)}{\lambda} \\
\beta & = \frac{FWHM \times \cos(\theta_B)}{h}
\end{align*}
\]  

where \( \theta_B \) is the peak position for which the Bragg condition is fulfilled for \( hkl \) reflection. The peak position and FWHM were determined independently for each peak, using a least square fitting procedure based on the theoretical pseudo-Voigt function [9]. In this model, the inverse value of the slope is directly related to the size of the coherent diffracting domains [7–11]. The identification results can then be used to calculate the ratio of the mean size without SMAT to the mean size with SMAT, as in Eq. (1). These two mean values correspond to the average penetration length of the X-rays (for chromium radiation, the length is estimated at 1.873 \( \mu m \) [12]). The ratio is thus about 2.7. Consequently, and comparing both methods, an irrefutable decrease in the diffracting domain size is observed on the M5 zirconium alloy being investigated. This observation corresponds to a decrease in the associated grain size due to the attrition treatment, with a local factor that can be higher at the extreme surface than the mean ratio derived from XRD. Complementary measurements were performed in the Berkeley ALS synchrotron using monochromatic wavelength. The diffraction patterns are shown in Fig. 3a (untreated specimens) and 3b (SMATed samples). The latter shows continuous rings that could be explained by the refinement of the microstructure. We assume that no significant crystallographic texture results from the SMAT process. Also, the rings in the SMATed samples are wider which indicates an increase in the diffracting domain size (because the instrumental function is the same). The diffracting domain size has thus been modified by the SMAT process.

3.2. Roughness results

Roughness was also investigated as the SMAT process is known to modify the geometric surface properties [13,14]. A Taylor Hobson Surtronic 3+ was used to measure the arithmetic average of the absolute values \( Ra \) and the maximum height of the profile \( Rt \) [15]. Measurements were carried out on both treated and untreated samples. \( Ra = 0.34 \pm 0.01 \mu m \) and \( Rt = 3.73 \pm 0.17 \mu m \) were obtained for the untreated samples and \( Ra = 0.40 \pm 0.02 \mu m \) and \( Rt = 3.60 \pm 0.25 \mu m \) for the SMATed samples. Because of the uncertainties involved, \( Rt \) is not a very efficient way of describing the effect of SMAT on the surface. However, \( Ra \) shows a slight increase which is easily explained by the impact of the balls during the SMAT process and is directly visible on the surface of the samples. Finally, we observed that the roughness is only slightly modified by the SMAT process considered (with the steel balls used). As a result, roughness does not seem to be a relevant parameter to quantify the effect of SMAT on an M5 Zr alloy.
4. Results of SMAT effects on oxidation at 550 °C

4.1. Kinetics results

The oxidation of an M5 zirconium alloy was studied using several techniques. The problem was first considered from a chemical and macroscopic point of view. A classical thermogravimetric analysis in a Setaram TGA 92 thermobalance was thus used. The sensitivity of the balance is 1 µg. Samples were heated at a rate of 50 °C/min up to the required oxidation temperature of 550 °C under an argon atmosphere. The temperature selected is thought to be stable after 1000 s to within ± 0.1 °C. Oxidation was then performed under artificial air at 1 bar (20% O2; 80% N2) with a gas flow rate of 0.6 l/h in the thermobalance. The weight change curves (per surface unit) as a function of the exposure time are shown in Fig. 4 for both treated (solid line) and untreated (dashed-dotted line) specimens. The experimental values and the theoretical values (dashed line) obtained from the diffusion model of the ZrO2 oxide growing on the Zr metal are superimposed. This theoretical curve does not include the SMAT effects, as discussed further on. Kinetic constants were also extracted. The transformation curves are shown in Figs. 5 and 6 resulting in a parabolic law (at a first approximation). These parabolic results are consistent with other research on untreated zirconium based materials [16,17]. According to the Wagner theory, it corresponds to a purely diffusional regime [18]. For the SMATed samples, a parabolic rate constant $k_{MP}$ of $1.677 \times 10^{-9}$ kg/m² was obtained, with $k_{MP} = 2.134 \times 10^{-9}$ kg/m² for the untreated samples, corresponding to a relative increase of 21% (more than the experimental uncertainties). However, Figs. 5 and 6 show a slight
difference between the linear fit and the experimental points, which means that the oxidation kinetics are not completely due to the diffusion mechanism. Consequently, a complete law based on Huntz’s successful approach [19] was used with the following equation:

\[ t = \frac{1}{k_{1}} \Delta M + \frac{1}{k_{\text{MP}}} \left( \frac{\Delta M}{S} \right)^{2} \]  

(3)

where \( t \) is the oxidation time, \( \Delta M \) is the weight gain per surface unit, \( k_{\text{MP}} \) is the parabolic rate constant and \( k_{1} \) is the linear constant correlated to a pure reaction step. With this model, the fit process leads to more accurate kinetic parameters (the corresponding curves are not shown in the present paper). For SMATed samples, we obtain \( k_{\text{MP}} = 1.402 \times 10^{-9} \text{kg/m}^{2} \text{s} \), with \( k_{\text{MP}} = 1.872 \times 10^{-8} \text{kg/m}^{2} \) for untreated samples (similar values have been found in literature [18]), corresponding to a relative increase of 25% (more than the experimental uncertainties). Consequently, and regardless of the data processing method chosen, experiments show that SMAT can lead to a decrease in the degradation of M5 materials during high temperature oxidation at 550 °C after 20 h.

4.2. Oxide phase composition

In order to complete the previous experimental observations, the composition of the oxide layer was also studied using a high-resolution XY Dilor-Jobin–Yvon Raman spectrometer equipped with a CCD detector and a high-temperature cell. Its wavenumber resolution is the integrated peak intensity and the exponents \( I \) note quadratric and monoclinic zirconia respectively. This method was applied using peaks M(218) and Q(280) for SMATed samples and M(176), M(189) and Q(280) for untreated samples. SMAT seems to increase the quadratic phase, which can reach a value of 60% indicating stabilisation (while the corresponding value in the untreated specimen is only 35%). Several authors have already observed stabilisation of the quadratic phase, as mentioned in [21]. This will be discussed further on.

5. Modelling and numerical results of oxidation at 550 °C

5.1. a) Modelling

In order to explain the previous results during oxidation, a simple model was established taking into consideration both the oxygen diffusion in the Zr alloy and the oxide growth over the metal due to diffusion mechanisms, and a moving interphase [18,22,23]. No mechanical coupling effect is assumed, i.e. the stresses are taken to be zero. First, we consider an effective diffusion coefficient of oxygen in the zirconium alloy, according to Hart’s relation [23]:

\[ D_{\text{eff0–Zr}} = x_{gb}(r) \times D_{gb} + (1 - x_{gb}(r)) \times D_{\text{grain}} \]  

(5)

where the subscript “gb” stands for grain boundaries and \( x_{gb}(r) \) is the corresponding volume fraction which can depend on the spatial position \( r \). Eq. (5) is often used to determine the diffusion parameters at macroscopic scale based on the mesoscopic scale. This transition scale relation corresponds to a parallel model between the grain boundary flux and the grain flux. Other models can be used however such as the following serial model:

\[ D_{\text{eff0–Zr}} = \left( x_{gb}(r) \times D_{gb} \right) + \left( 1 - x_{gb}(r) \right) \times D_{\text{grain}}^{-1} \]  

(6)

Both models correspond to the extreme limits of the real effective diffusion coefficient. The numerical values of the diffusion parameters \( D_{gb}, D_{\text{grain}} \) in M5 materials can be identified from the exhaustive work of Richie et al. [24]. A relation depending on the temperature \( T \) is thus obtained:

\[ D_{gb} = 6.998 \times 10^{-11} \exp\left( \frac{-21800}{RT} \right) \]  

(7)

\[ D_{\text{grain}} = 2.747 \times 10^{-6} \exp\left( \frac{-180235}{RT} \right) \]

where \( R \) is the ideal gas constant, the activated energy is expressed in J/mol and the pre-exponential factor is in m²/s. Eqs. (5) and (6) indicate how the nanocrystallised layer can modify the oxidation kinetics. These two equations can be computed by considering different ratios between the diffusion coefficient in the grains and the diffusion coefficient in the grain boundaries (as well as the realistic ratio for the present diffusion parameters given in Eq. (7) at \( T = 550 \) °C). Both models (serial and parallel) are depicted in Fig. 8. It shows that the numerical value of the effective diffusion parameter increases with the grain boundary fraction. However, the choice of a particular micro-diffusional model leads to a maximum relative difference of 70% (for \( x_{gb}(r) = 0.5 \) and \( D_{\text{grain}}/D_{gb} = 0.08896 \) for zirconium at \( T = 550 \) °C). A more realistic value of \( x_{gb} \) fraction was also introduced equal to 2% [16,17] (for untreated samples). The relative difference is then only 15% and does not have any significant influence on the results. Similarly, the diffusion parameters in SMATed samples are gradually modified from the metal core toward the top surface due to the decrease in the grain size by means of \( x_{gb}(r) \).

Second, the oxide increase was modelled using a pure diffusional model. This assumption is supported by our experimental results for the sample kinetics (see in Figs. 5 and 6). An anionic diffusion is considered using the diffusion parameter \( D_{0–ZrO_{2}} \) in zirconia (zirconium oxide) given in [17]. The chemical reactions at the interphases are assumed not to be limiting. The second Fick law
First, for each time increment \( \Delta t \), two calculations are carried out. The first step results in an approximate concentration \( C_{x-1, t+1} \). The second improves the precision by estimating the diffusion coefficient at \( t + \frac{1}{2} \) by \( D_{eff}^{1/2, t} \) instead of \( D_{eff}^{t} \). This second calculation determines the value of the diffusion coefficient for every time increment \( t \) using the diffusion coefficient at \( t-1 \). The second calculation yields the value of the diffusion coefficient at every space node \( x \) at the average concentration between increments \( t \) and \( t+1 \) (using values at \( t + 1/2 \)) which has just been calculated. Although this method doubles the number of operations and increases the calculation time, it is much more precise.

Second, to take into account the variation in the diffusion coefficient with the space step, the basic expression of the Crank–Nicholson method must be modified. The diffusivity must be estimated at midpoint between two successive space nodes \( x \) and \( x + 1 \). Thus, the diffusion coefficient at the half-space step is interpolated linearly according to:

\[
D_{eff}^{1/2} = \frac{x_{c+1}^{t} + x_{c+1}^{t+1}}{2}
\]

(9)

\[
D_{eff}^{t} \equiv D_{eff}^{t} (C_{x}^{t}) \times \frac{\Delta t}{\Delta X}
\]

(10)

With this change, and if the space step \( \Delta X \) is sufficiently small, the non-linear partial differential equation can be brought back into the implicit Crank–Nicholson scheme to give the following expression Eq. (11), which can be expressed as a “three-diagonal” matrix. The improved Crank–Nicholson method can then be used to solve the non-linear diffusion problem, using the Thomas algorithm:

\[
-C_{x-1}^{t+1} \frac{x_{c+1}^{t+1} - x_{c}^{t+1}}{2} + 2C_{x}^{t+1} \left[ 1 + \frac{1}{2} \left( x_{c+1}^{t+1} + x_{c}^{t+1} \right) \right] - C_{x+1}^{t+1} \frac{x_{c+1}^{t+1} + x_{c}^{t+1}}{2} =
\]

\[
C_{x-1}^{t} \frac{x_{c+1}^{t} - x_{c}^{t}}{2} + C_{c}^{t} \left[ 1 - \frac{1}{2} \left( x_{c+1}^{t} + x_{c}^{t} \right) \right] + C_{x+1}^{t} \frac{x_{c+1}^{t} + x_{c}^{t}}{2}
\]

(11)

The unknown concentrations are on the left-hand side of the equation and the known concentrations on the right-hand side. This numerical scheme has been successfully applied to various problems such as nitriding and aluminisation [28].

5.3. Numerical parameters and results

The numerical parameters include 200 space nodes for the metal (zirconium alloy) with an initial length of 0.5 mm, 100 space nodes for the growing oxide (zirconia) with an arbitrary initial length of 1 mm (to avoid numerical divergence at \( t = 0 \)), and 3600 time nodes for a recording time of 20 h. The initial oxygen concentration was taken equal to zero for both the metal and the oxide. Finally, the Hart model was considered in order to obtain the effective diffusion coefficient in Zr at 550 °C. The moving interphase between M5 and the growing oxide was then calculated according to [25] using the following equation (Stefan relation):

\[
\dot{\nu}_{int}(t) = \frac{\dot{F}_{oxygen}(x_{int}, t) - \dot{F}_{oxygen}(x_{int}, t)}{C_{int}(x_{int}, t) - C_{oxygen}(x_{int}, t)}
\]

(12)

where \( \dot{\nu}_{int} \) is the speed of the interphase, \( x_{int} \) is the interphase position and \( \dot{F}_{oxygen} \) is the oxygen flux in the phase considered, determined according to the first Fick law [23]. The boundary conditions at this interphase were extracted from the thermodynamic phase diagram [16,17].

The numerical concentration results are given in Fig. 4 (dashed line). This curve corresponds to modelling without SMAT, i.e. with a constant diffusion coefficient along the metal depth. Although simple and far from being perfect, this model corresponds well to the experimental results. Furthermore, the same model was computed with a specific variation in the grain size with depth to take the SMAT effect into account [1–4], leading to an increase in the grain boundary fraction as the metal depth decreases. The calculations are given in Fig. 9 with the oxygen concentration for both SMATed and untreated configurations as a function of depth. As expected, the oxide thickness in the SMATed samples is smaller than in the untreated specimens. The effective diffusion parameter in the SMATed zirconium is higher which means that the oxygen diffuses more easily in this phase, and is therefore less available for the creation of oxides. The characteristic diffusion length in the SMATed samples is higher. The theoretical difference in the oxide thickness is about 4 μm (with the Hart model at 550 °C during 20 h of oxidation). The choice of a serial model would lead to an ultimate difference of only 3.68 μm (fairly similar) between the SMATed and untreated conditions. This direct effect of SMAT via
the grain boundary ratio seems to correspond to a very slight effect, in accordance with the above remarks. However, it is sufficient to fully explain both the experimental and observed differences (the relative difference in mass for the numerical results is 33.6% while the relative difference in mass for the experimental results is only 11.2% at the final oxidation time of 20 h).

6. Discussion

The experimental data lead to two major conclusions. First, the SMAT process seems to be adapted to an M5 Zr alloy, as it reduces the grain size, but has no significant effect on the roughness. Second, SMAT is able to slightly increase the oxidation resistance of the grain size, but has no significant effect on the roughness. The SMAT process seems to be adapted to an M5 Zr alloy, as it reduces the grain size due to the underlying nanocrystallised metal layer [21]. This indirect effect of SMAT, which occurs as the result of a chemical crystallographic modification of the growing oxide (monoclinic to the quadratic phase) has not been considered in the modelling because an average diffusion coefficient for the oxide layer was chosen according to [17] (but with no particular link to the underlying microstructure of zirconia). A second oxidation resistance mechanism has also been identified and described in detail in the present paper, i.e. the direct effect of the SMAT process by means of a grain size gradient of \( \langle \chi_{\text{MS}}(r) \rangle \). The numerical calculations performed have shown that this effect can be significant and could explain experimental results.

From a modelling point of view, the predominant effect is linked to the ratio \( D_{\text{eff}, \text{O}_{2} \rightarrow \text{Zr}} / D_{\text{O}_{2} \rightarrow \text{ZrO}_{2}} \) for both SMATed and untreated samples. The main problem with this ratio is that it has not really been established, in particular because there are too many uncertainties in the literature concerning zirconium oxide diffusion parameters [17]. Complementary experimental investigations therefore need to be carried out at different temperatures in order to quantify and define the main mechanism responsible for oxidation resistance. For example, the methodology previously used indicates that it might be possible to identify the diffusion parameters and development of the grain size with depth from an inverse analysis combining thermogravimetric analyses, the micro-hardness profile and modelling.

The SMAT process has very different effects. First, it reduces the grain size on the top surface. This increases the diffusion of oxygen into the M5 alloy reducing the thickness of the oxide layer. This could also increase the growth stresses. Therefore, because of the underlying nanostructure of the M5 alloy and/or the higher compressive stresses (the Pilling and Bedworth ratio is 1.56 [5]), the quadratic zirconia phase seems to be stabilized. This could then influence the oxidation mechanism of the growing oxide because of diffusion in the main quadratic phase in the case of SMAT samples. A schematic summary representation of the SMAT effects is given in Fig. 10.

7. Conclusion

In the present work, different experiments have been performed on a nanocrystallised M5 alloy. The decrease in grain size has been clearly established from macroscopic measurements using XRD. This aspect needs to be investigated further to obtain the quantitative development of grain size with depth and time. The high-temperature oxidation of these materials has also been studied with both macroscopic (thermogravimetric analysis) and mesoscopic (local Raman spectroscopy) experiments that show the slight but irrefutable benefits of SMAT. This can be explained by two different mechanisms: the direct effect of the SMAT process via a grain size gradient and/or an indirect effect of the SMAT process via a chemical modification of the growing oxide (monoclinic towards the quadratic phase). From the numerical investigations, it has been possible to show that the first can explain the experimental kinetics. Moreover, although the numerical results are linked to strong assumptions, especially the micro-diffusional relation (Hart’s model), they lead to good qualitative predictions. The second mechanism has not been considered in the model because of discrepancies found in the literature in relation to different zirconia diffusion coefficients. It would also be interesting to quantify these two mechanisms as a function of the temperature. Finally, and from a modelling viewpoint, numerical models also need to be developed in order to relate them to mechanical effects inside the oxide layer as suggested in other works [29–31].

References
