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On the mechanical effects of a nanocrystallisation treatment for ZrO_2 oxide films growing on a zirconium alloy

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ABSTRACT

In the present work, mechanical features are investigated in the case of ZrO_2 thermal oxide films growing on a Zr alloy at the temperature of 550 °C. The effects of a nanocrystallisation treatment on high temperature oxidation of a zirconium alloy are specifically studied. High temperature oxidation is performed in order to show benefits of such a nanocrystallisation on corrosion resistance and its influence on the mechanical fields. Experimental results obtained by Raman spectroscopy give the growth stress evolution in ZrO_2 films. Using a modelling of the system, both asymptotic forms and an optimization procedure are developed to determine the mechanical characteristic parameters of the system.

1. Introduction

Surface Mechanical Attrition Treatment (SMAT) is a recent process that enables to nanocrystallise the surface of metallic alloys. It can thus enhance mechanical properties of the treated material by inducing a grain refinement down to the nanometre scale, in the top surface layer. This nanocrystallisation process leads to different effects that were successively studied on several metallic materials (on pure metals such as copper; but also on steels or other alloys [1–4]). In the present work, investigations on mechanico-physico-chemical effects are carried out on a M5 zirconium alloy. This material is of great interest for example in nuclear industry thanks to its neutron resistance [5]. Technological applications in high temperature environments are thus of particular interest. However, the present paper is focused on modelling the first stages of the high temperature oxidation of this specific Zr alloy, independently of any particular applications, to show the influence of the SMAT process. The latter should change some surface properties of zirconium alloys. From a general point of view, an increase of grain boundary fraction from the bulk to the top surface of the sample can modify the value of diffusion parameters. Moreover, it is now well established that the surface reactivity can also be modified by nanocrystallisation treatments. As a matter of fact, oxidation properties are supposed to be affected by SMAT, and possibly improved by this surface treatment. Some studies have been purchased to show the influence of SMAT on corrosion and oxidation on different materials [6–9]. The different authors have proved that the nanocrystallisation process generally improved its resistance, but some mechanisms need yet to be investigated.

Moreover, the presence of residual stresses in thermal oxide layers has been recognized for a long time [9–11]. In particular, the growth stresses evolution occurring during the isothermal oxidation process may influence the protective properties of the oxide layers. Irrespective of the particular alloy being oxidised or the oxide type formed, the growing oxide film is usually under stress (compressive and/or tensile). Thus, it is important to determine the strain and stress fields associated to the growth of oxide films on metallic substrates. On one hand, determination of the residual stresses of oxidised materials has often been performed experimentally after cooling, thus allowing the determination of both thermal and growth stresses only by calculation. On the other hand, the direct experimental determination of growth stresses is less common, because of its complexity.

Oxidation mechanisms occurring in metal/oxide systems and including phase evolution are briefly presented in the first section of the present paper. This synthesis shows how these mechanisms can influence the stress fields developed in the growing oxide. The main aim of the present study is to determine the lateral compressive stress evolution in the growing oxide film. Then, both mathematical asymptotical forms at short and long oxidation times are used to extract some characteristic mechanical parameters. An optimization process is also performed on the whole data, giving

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additional important features. Eventually, the results are discussed with respect to the surface treatment used.

2. Material and surface treatment conditions

The studied material is a M5 zirconium alloy containing a zirconium base with niobium (1% in mass) and 1000 ppm of oxygen. Half of the samples were treated with the nanocrystallisation process (SMAT). Steel balls of 3 mm diameter were used with a sonotrode frequency of 20 kHz. Fig. 1 shows simple geometrical representation of such a process. The surface nanocrystallization of these specimens was obtained by ultrasonic-assisted SMAT in air and at room temperature during 15 min on each main surface (symmetric treatment) [8]. Moreover, after nanocrystallisation treatment, oxidation under different temperatures has been investigated. However, only the case at 550 °C in a furnace with ambient air during an oxidation time of 20 h is considered in the present paper, in order to present the methodology. This temperature was chosen and carefully investigated, according to common solicitations of zirconium alloys [9], but also to keep benefits of the SMAT technique [8,12]. Indeed, if oxidation temperature reaches too high values, then grains recrystallisation occurs so that the nanocrystals can disappear [8,12].

3. SMAT chemical effects on oxidation at 550 °C

3.1. Experimental procedure

Oxidation of the zirconium alloy has been studied using several techniques. First, the problem has been considered from a chemical and macroscopic point of view. A classical thermogravimetric analysis in a Setaram TGA 92 thermobalance has thus been used. The sensitivity of the balance is 1 μg. Samples were heated at 50 °C/min up to the desired oxidation temperature of 550 °C under an argon atmosphere. The selected temperature is thought to be stable after 1000s within the range ±0.1 °C. Oxidation was then performed under artificial air at 1 bar (20% O_2; 80% N_2) and at a gas flow in the thermobalance of 0.6 l/h.

3.2. Kinetics results

The weight change curves (per unit of surface) as a function of the exposure time are shown in Fig. 2, for both treated (full line) and untreated (dashed-dotted line) specimens. In this figure, the numerical scheme is based on an improved Crank–Nicholson method. This theoretical curve does not include SMAT effect. Kinetics constants were also extracted. Transformation curves, not shown in the present paper, lead to parabolic laws (at first approximation). Such parabolic results are coherent with other works for untreated zirconium based materials [13,14]. In the zirconium alloys and in the range of studied temperature, two stages are frequently observed: it starts with a more or less parabolic stage, then after a breakaway a linear stage is found. The critical oxidation time of the breakaway depends on the alloy. In our study, such breakaways have not been observed during the 20 h of oxidation. Other authors have presented the oxidation of Zr alloys as a subparabolic kinetics, or as a succession of parabolic steps with a moving k_p constant. Mechanical effects sometimes explain such specific laws. It depends on the alloy contents and on the considered temperature. In our case, no such oxidation behaviour has been observed even if mechanical effect can occur in the samples as detailed further. For SMATed samples, a parabolic rate constant k_{MP} of 1.677 μg/m^2 is obtained, whereas for untreated ones k_{MP} is 2.134 μg/m^2, corresponding to a relative increase of 21% (more than experimental uncertainties). However, transformation curves present some small differences between linear fit and experimental points, meaning that oxidation kinetics are not completely due to diffusional mechanisms. Therefore, a complete law has been used according to the successful approach of Huntz-Aubriot and Pieraggi [15] with the following equation:

$$t = \frac{1}{k_1}\frac{\Delta M}{S} + \frac{1}{k_{MP}}\left(\frac{\Delta M}{S}\right)^2 \quad (1)$$

where t is the oxidation time, $\frac{\Delta M}{S}$ is the weight gain per unit of surface, k_{MP} is the parabolic rate constant and k_1 is the linear constant correlated to a pure chemical reaction mechanism. With this model, the fit process leads to more accurate kinetics parameter values (corresponding curves are not shown in the present paper but can be found in [16]). For SMATed samples, a value for k_{MP} of 1.402 μg/m^2 is obtained, whereas for untreated ones k_{MP} is 1.872 μg/m^2, corresponding to a relative increase of 25% (more than experimental uncertainties). Consequently and whatever the data treatment, experiments show that SMAT can induce a decrease of the degradation for the studied materials during high temperature oxidation at 550 °C, after 20 h when SMAT process is used. It can be emphasized that the SMAT process has an impact on the oxygen diffusion in the metal, as studied in [16], and then influence the weight gain. In this case the comparison of weight gain curves between SMATed and untreated samples cannot be directly performed. However, because SMAT leads to a weaker kinetics and

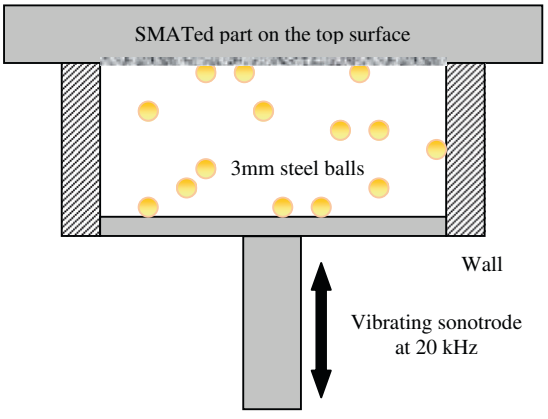

Fig. 1. Geometric representation of the SMAT process.

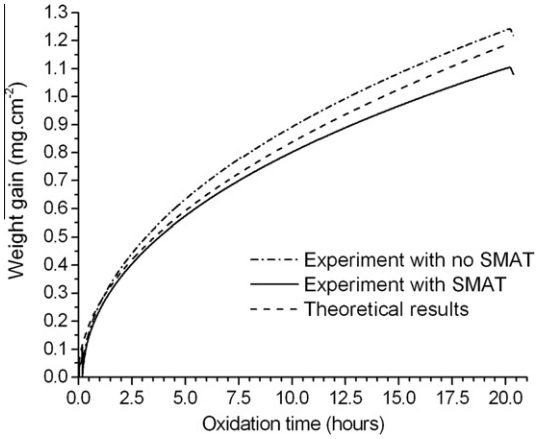

Fig. 2. Weight gain Δm per unit of surface of untreated (dashed-dotted line) and treated (full line) samples of a M5 zirconium alloy due to oxidation at 550 °C in artificial air, as a function of the oxidation time. Experimental values and theoretical values (dashed line) obtained from a diffusion model in ZrO_2 oxide growing on Zr metal are superimposed.