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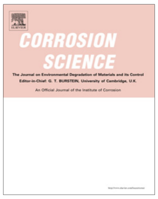

Review

Review of stress fields in Zirconium alloys corrosion scales

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ABSTRACT

A review of the data available in the literature on the residual stress determination in zirconia scales has been undertaken. Deflexion method and curvature measurement as well as Raman spectroscopy and X-ray diffraction have been used. Stress magnitudes obtained by different authors vary between a few hundred of MPa and more than 5 Gpa, depending on the parameters investigated such as oxidized alloy, oxidation atmosphere and temperature. The influence of the later on both the average stress magnitudes and also on its evolution has been determined, and the stress release processes have been discussed.

1. Introduction

The oxidation resistance of Zirconium alloys is one of the main issues for their use as fuel cladding material in nuclear plants. During Zr alloys oxidation, it is generally accepted that a dense and protective oxide layer first forms on the metal, giving rise to a reaction kinetics decreasing with time with a parabolic to cubic law. However, after a certain time period, a kinetic acceleration occurs, corresponding to the so-called breakaway phenomenon, which is due to the loss of protectiveness of the first formed oxide layer [1]. This phenomenon can repeat several times, at least for temperatures relevant to in-service pressure, temperature and atmosphere conditions, giving rise to a corrosion kinetics having a more or less cyclic behaviour in nature [2]. Severe breakaway phenomena are also observed at temperature relevant to accidental situations up to 1050 °C, either in steam [3,4] oxygen or air atmospheres [5–7]. The oxidation resistance of a given alloy, in normal operation as well as in accidental situations, is mostly controlled by the resistance to breakaway of the zirconia scale. Loss of protectiveness of the oxide is likely due to formation of diffusion shortcuts, for example micro-cracks or interlinked pore arrays, which were evidenced both for temperatures relevant to in-service conditions [6] and to accidental situations [7]. Although the breakaway phenomenon can be explained by purely mechanical considerations [8], failure of the protective oxide leading to the breakaway transition is a complex phenomenon involving strongly coupled mechanical, microstructural, crystallographic and even chemical aspects. Specifically, it has been early proposed that the transition from a protective to a more pervious oxide would be associated to a phase transitions, tetragonal ($t\text{-}ZrO_2$) to monoclinic ($m\text{-}ZrO_2$), at the metal/oxide interface [9]. Actually, it has been shown many times by X-ray diffraction (XRD) [2,10,11–14], Raman spectroscopy [15–18] or transmission electron microscopy (TEM) [19,20] that $t\text{-}ZrO_2$ can be found in significant amounts at the metal/oxide interface in pre-transition scales while it is hardly detected in the post-transition regime. Various factors or a combination of factors as a nanometric grain size, deviation from stoichiometry, chemical doping, compressive stresses … can explain the stabilization of the $t\text{-}ZrO_2$ form for temperatures far below its thermodynamic stability domain. A high concentration of $t\text{-}ZrO_2$ at the metal/oxide interface is often correlated with the presence of high local compressive stresses [2,11,13,15,16,18]. Thermodynamic calculations have confirmed that compressive stresses can effectively stabilize the $t\text{-}ZrO_2$ form of zirconia [21], and it is now widely accepted that an important factor for $t\text{-}ZrO_2$ stabilization in Zr alloys corrosion films is the high compressive stress field, generated, among other things, by the high Pilling–Bedworth ratio of the Zr/ZrO_2 system. It is generally observed that zirconia scales exhibiting the highest compressive stresses and thus a better stability of the $t\text{-}ZrO_2$ compound exhibit a better corrosion resistance [11–13,19]. It has been proposed that not only the stress intensity but also its distribution in the scale is important in determining the corrosion resistance of the alloy, a stepper stress

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gradient leading to a weaker resistance to breakdown of the oxide [21]. The t-ZrO_2 to m-ZrO_2 transformation is considered by most of the authors to have a detrimental effect on the corrosion resistance. On the contrary, El Kadiri and co-workers [17] suggest that this phase transformation has a beneficial effect: due to the lattice expansion that accompanies the transformation, it contributes to maintain a compressive stress state in the scale and thus delays the oxide breakdown, which occurs when the stress sign change from compressive to tensile. Whatever is the exact role of the m-ZrO_2 to t-ZrO_2 transformation on the breakaway phenomenon, the local stress field that develops in oxide scales formed on Zr alloys appears to be a first order factor for the understanding of their oxidation resistance. This easily explains why stress development in zirconia scales has been a widely studied issue in the past.

In this paper, we review the available literature on the measurements of stress fields in zirconia scales formed on Zr and Zr alloys. Various methods have been used for stress determination (Deflexion-based methods, XRD, Raman spectroscopy, to name a few) and this review points out the high data variability, regarding both the stresses magnitude and also their spatial distribution in the scale. Effects of the measurement method, but also temperature, the oxidizing media and the alloy composition are examined and discussed. Some of the available results are considered taking into account possible stress relaxation mechanisms.

2. Origins of residual stress in zirconia scales

Residual stress, determined in zirconia scale after cooling down to room temperature can be defined as:

$$\sigma_{res} = \sigma_{gr} + \sigma_{th} + \sigma_{rel} \tag{1}$$

where

- σ_{res} is the residual stress in the scale.
- σ_{gr} is the growth stress, occurring during oxidation. It is in part due to the molar volume difference between the oxide and the metal. Assuming a fully dense monoclinic zirconia, growth stresses are usually discussed taking into account the Pilling and Bedworth ratio (PBR), the oxide to metal molar volume ratio. It is positive for the Zr/ZrO_2 system (PBR = 1.56), resulting in formation of compressive stress in the oxide scale, at least at the beginning of the corrosion process. Other causes, often overlooked, can also induce growth stresses. In particular, epitaxial relationships between the oxide and the metal at the very beginning of oxidation can be raised. However, such epitaxial relationships are rarely discussed, and, as a rule, require extensive studies.
- σ_{th} is the thermal stress associated with the heating/cooling of the system. In particular, it is proportional to the difference between the expansion coefficients of the oxide and the metal. It also depends on the Young's modulus of both the metal and the oxide film. Within the approximation of thin films, thermal stresses can be approximated by:

$$\sigma_{th} = -\frac{E_{ox}(\alpha_{ox} - \alpha_m)(T_f - T_i)}{1 + 2\frac{e_{ox}E_{ox}}{e_m E_m}} \tag{2}$$

T_f is the final temperature after cooling (usually room temperature), and T_i the initial temperature for which oxidation occurred. E_{ox}, E_m, e_{ox} and e_m, α_{ox} (2.1×10^{-6}) and α_m (5.8×10^{-6}) are the Young's modulus, the thicknesses and the thermal expansion coefficients of the oxide scale and metal respectively.

For the Zr_{alloy}/ZrO_2 system, the thermal expansion coefficient of the metal is higher than the oxide scale one. Thus, thermal stress is expected to be compressive in nature and is added to the growth stresses in the oxide.

- σ_{rel} is a relaxation term of opposite sign to σ_{gr} and σ_{th}. Stress relaxation can be destructive (mainly by buckling or cracking of the oxide scale in the case of zirconia), or non-destructive (visco-elastic strains). It occurs during oxidation and/or cooling. Metal creep mechanism and cracking of zirconia scale are regularly mentioned in the literature [22]. Recently, thanks to in-situ determinations of growth stresses and corresponding modelling, the work of Panicaud et al. [23] suggests that diffusion creep mechanism also occur in zirconia scale. It leads to stress relaxation in zirconia, while dislocation-assisted creep mechanisms lead to stress relaxation in the metal, in the vicinity of the metal/oxide interface.

3. Stress determination methods

Four different methods are mainly used to determine stress fields in zirconia scales. Among other, these methods are also commonly used to determine the stresses in other simple oxides scales (chromia, alumina, iron oxides) or in metals. Each of these methods is briefly presented below.

3.1. Deflexion methods and curvature measurement

Methods based on the deflection and/or curvature radius measurements were very early used for the estimation of stresses in the Zr corrosion scales. Concerning the deflection method, one of the faces of a Zr foil is protected from oxidation. Then, only the unprotected face is oxidized. The growth stresses which occur in the scale during the oxidation lead to the bending of the foil. The deflection can then be measured with an in-situ optical monitoring of the foil position [24]. A rigid wire suspended at the extremities of the foil can also be used [25] for such a purpose.

In the elastic regime, stresses in the oxide scale can be calculated using relation (3) [25]:

$$\sigma = \frac{E_{met}e_{met}^3}{6R(1-\nu_{met})e_{ox}(e_{met}+e_{ox})} - \frac{E_{ox}e_{ox}^2}{6R(1-\nu_{ox})(e_{met}+e_{ox})} \tag{3}$$

E_{met}, $E_{ox,}$ ν_{met}, ν_{ox}, e_{met} and e_{ox} are the Young's modulus, the Poisson ratio and the thicknesses of the metal and the oxide respectively... R is the foil curvature radius extracted from L, the length of the foil and D its deflexion:

$$R = \frac{L^2 + D^2}{2D}$$

In most cases, the thickness of the metal foil is by far higher than that of the oxide scale, relation (3) simplifies according to:

$$\sigma = \frac{E_{met}e_{met}^2}{6R(1-\nu_{met})e_{ox}} \tag{4}$$

The main advantage of this method is that it makes it easy to perform in situ measurements which give access to the growth stresses.

The curvature measurement method, which principle is similar to that of the deflection method, also gives access to the residual stress in the sample. At room temperature after oxidation and cooling, the oxide is removed on one side. Again, compression stresses in the oxide scale on the other side induce a curvature of the sample. The radius is then evaluated and provides stress magnitudes in the oxide scale.

3.2. X-ray diffraction

Stress magnitude may also be determined using X-ray diffraction, according to the well-known "$\sin^2 \Psi$" method. The d_{hkl} lattice interplane distance is used as a strain gauge. The technique