THE A PHYSICAL MODEL FOR THE CIRCUMFERENTIAL CRACK INITIATION IN THE OXIDE SCALE DURING ISOTHERMAL OXIDATION OF THE ZY-4 CLADDING

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ABSTRACT

The zirconium alloys oxidation and the oxidation kinetics is governed by the diffusion of oxygen in the oxide scale formed at the surface of the metal, and the oxide scale is formed normally under compression. With the increase of the oxide scale thickness the compressive stress at the oxide-metal interface increase until plastic deformation of the oxide and metal ensues, meanwhile the compressive stress at oxide-environment interface decreases and may become tensile. The kinetic curve reflects the changes of the compressive stress by changes in the rate of oxygen uptake. The volume expansion associated with this transformation is the cause of the oxide cracking. The crack initiation is the primary cause of the cyclicity of the post-transition kinetic curves at temperatures up to 700^{0}C. The purpose of the present paper is to correlate the oxide scale thickness at cracking obtained from the kinetic curves and those obtained by SEM.

Key words: oxide, crack, stress

Introduction

The oxidation of zirconium alloys was the subject of intensive studies in paste years. The kinetic of oxidation, mechanisms of oxygen uptake, diffusion mechanisms, the structural changes caused by the oxide layer development, effects of temperature, porosity development, of the oxidising media pressure, are presented in experimental works ([1], [2], [3]). A correlation of the kinetics and the stress gradient development in the oxide scale during oxidation, are presented in reference [4]. Our previous works concerned the compressive stress development at high temperatures in different oxidising media (ref. [4]), the correlation of the kinetic of oxidation with the stress, a model of damped oscillations proposed for the oxidation kinetics ([ref. [5]) and the average diffusion coefficient measurement using kinetic data (ref. [6]). The goal of the present paper is to reveal the structural changes, the effect of cracks initiation on kinetic changes and the compressive stress developed.

Experimental

The specimens cute from Zy-4 cladding were subjected to an isothermal oxidation in a SETARAM SETSYS EVOLUTION thermo-balance at 600 and 700^{0}C in a mixed Ar-steam atmosphere. Table 1. presents the data related to the samples.

In all cases the heating and the cooling rate was of 50 deg./min, in pure argon and the flow of steam at isotherms was of 28ml/min.

Tabel 1. The test grids for the oxidation isotherms

Weight m_0 (g)	Surface area S (dm^2)	Temp T (^0C)	Time t (h)	Final weight m_f (g)	Weight gain Δm (mg)
2.2523	0.17423	600	48	2.34487	96.4
2.2359	0.17243	700	20	2.52394	179.07

From the kinetic curves using the simple relation (1), the oxide scale thickness grow can be found :

$$X=\Delta m V_m/2M_0 \qquad (1)$$

Here V_m Is the molar volume of t-ZrO_2 V_m=2.10x 10^{-5} m^3mol^{-1}, and M_0 the atomic weight of the oxygen. Using the relation (2), of the stress dependence with oxide scale thickness, the average compressive stress evolution curves can be obtained (ref.[5])

$$\sigma_h = 6.9X \qquad (2)$$

Results and discussion

Figure 1 presents the weight gain and the average stress evolution during the isothermal oxidation at 600^0C.

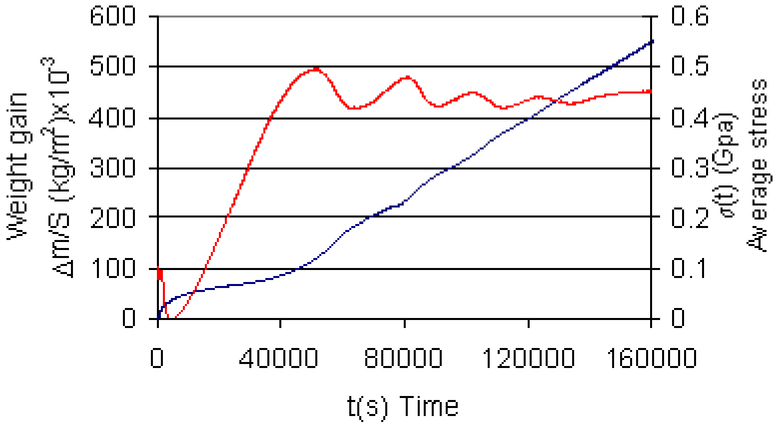

Figure 1. *The weight gain and the average compressive stress evolution at the 600^0 isotherm*

In figure 2 the same parameters for the 700^0C isotherm are showed.

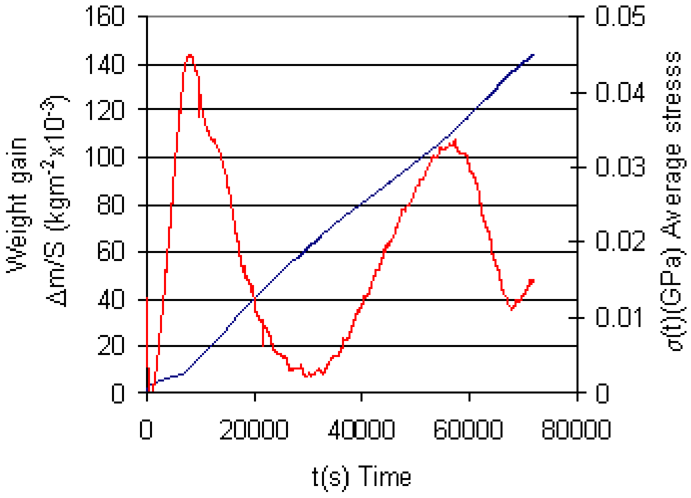

Figure 2. *The weight gain and the average stress vs. time for the 700^{0}C isotherm*

In figure 3, the average stress vs. the oxide scale thickness at 600^{0}C are presented. It can be see the damped oscillator behaviour of the stress (ref. [6]).

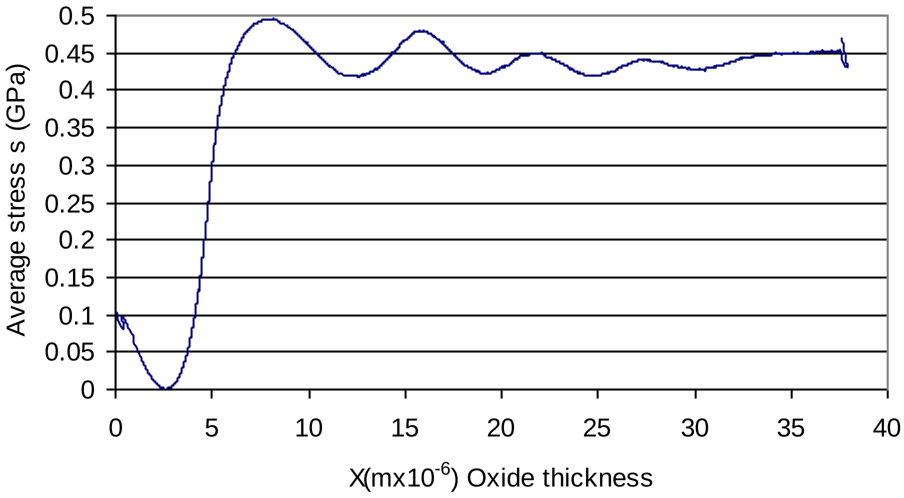

Figure 3. *The average stress vs. oxide scale thickness at 600^{0}C*

On this graph, the thickness corresponding to the maximum values of the stress give the distance from the surface at which the cracks are initiating. In the table 2 we present the results obtained for the critical distances at each temperature.

Table 2. *The critical distances ant the corresponding stress measured*

600^0C		700^0C	
Critical distance X (μm)	Average stress σ_h (Gpa)	Critical distance X (μm)	Average stress σ_h (Gpa)
5.7721	0.4329	7.6042	0.04558
8.1961	0.3444	10.2222	0.04037
12.0616	0.4118	18.6506	0.04756
15.9178	0.3405	27.6387	0.04108
19.0522	0.3950	36.9758	0.04506
22.0374	0.3657	45.2105	0.04234
25.0198	0.3941	56.67245	0.4431
27.17	0.3727	-	-
30.466	0.3872	-	-
33.423	0.3733	-	-

As can be seen with increase of temperature the critical distance (or volume) increase and the average tensile stress decrease with an order of magnitude. With increasing step of cracking the critical distance between cracks, shortened. The shape of the average compressive stress and the results obtained confirm the phenomenological model given in the literature. This explain the formation of the cracks in the compressive region of the oxide near to the oxide –metal interface, by the transformation of t-ZrO_2 to m-ZrO_2.This martensitic shears are able to produce small cracks at crystallite boundaries (ref. [2]). Interlinking of this cracks will produce a network of cracks near to oxide metal interface. The network of cracks is used to explain the cyclic posttransition rate of oxidation.

However, the SEM images obtained on the oxide layers show a slightly different situation. The critical distances obtained for the cracks near to the oxide surface are smaller then those obtained from the kinetic curves (around 3~3.5μm) and in the bulk of the oxide they become even smaller (~2μm). It seems that the cracks don’t initiate at the oxide –metal interface but slightly fare for this. Certainly, the stress development in each region of the oxide is a local effect but it has an influence an vicinity even at the positions of cracks.

Figure 4 presents a SEM image of the oxide scale obtained at 600^0C during a 48H isotherm.

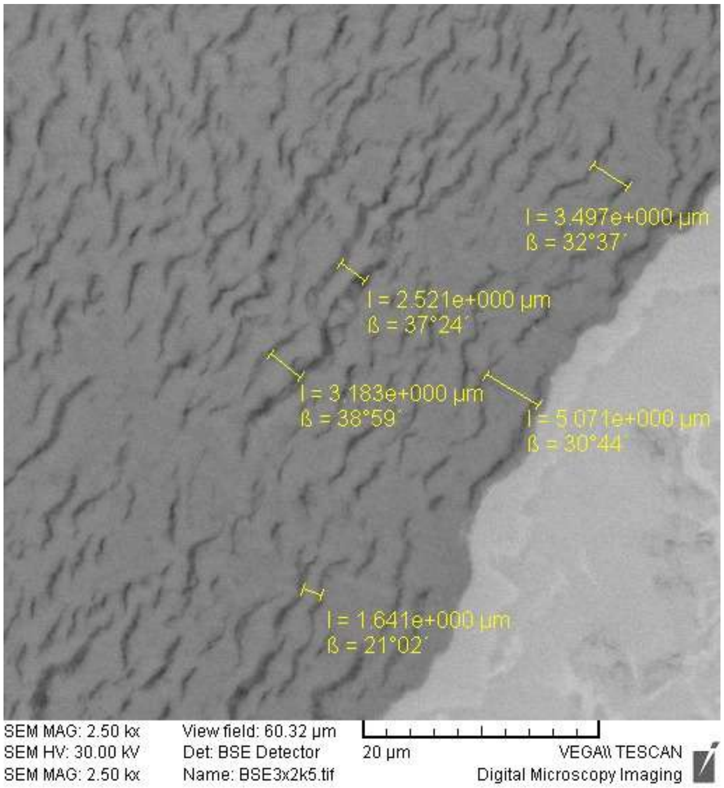

Figure 4. *The SEM image of the oxide scale obtained at 600^{0}C*

A model of crack initiation proposed is presented in the figure 5. The distance of crack initiation will be different from the critical thickness of the oxide scale and will be given by the pressure acting on the external surface and the compressive stress acting at the oxide –metal interface. This can explain why the distances revealed by kinetic curves and those from SEM images are different.

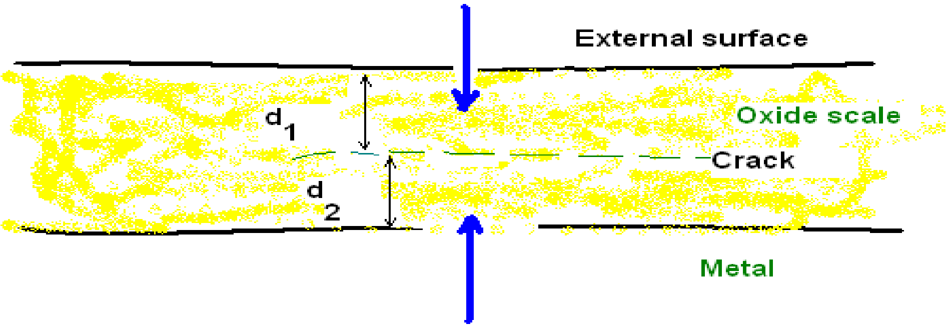

Figure 5. *A physical model for the distance of crack initiation*

Conclusions

The critical distances obtained for the cracks near to the oxide surface are smaller then those obtained from the kinetic curves. The distance of crack initiation will be different from the critical thickness of the oxide scale.

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