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On the evolution of wave structure at the metal/oxide interface during oxidation of Zr alloys

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ABSTRACT

Undulations of metal/oxide interface were determined in experiments during oxidation. Such structure can cause cracking near metal/oxide interface when a critical thickness of oxide film has been achieved. Cracking of the oxide leads to increase of metal oxidation rate and changes the oxide growth kinetics. In this paper conditions of the periodic structure parameters evolution have been determined based on minimization of mechanical stress energy appearing in the oxide film and the metal during oxidation. It has been shown that the process leading to increase of the wavelength near metal/oxide interface during oxidation can be the effect of period doubling bifurcation.

1. Introduction

Zirconium alloys are widely used as a constructional material for production of fuel rods and fuel assemblies for pressurized water reactors. Oxide film grows on the surface of fuel rods during operation. Restriction of the oxide film thickness on the fuel cladding is one of the criteria for the safe operation. Modes of oxide growth can be different significantly depending on the alloy chemical composition, thermomechanical treatment and operating conditions.

Oxide growth on the surface of zirconium alloy can be characterized by several successive stages [1–6]. Formation of thin dense oxide film strongly bonded to metal occurs at the initial stage of oxidation. Oxide film growth rate at this stage obeys mainly cubic or parabolic law up to thickness around 1.5–3 μm. Such film acts like a protecting barrier against later oxidation and hydrogen penetration. This stage is called pre-transition. Cracking of the oxide occurs with further growth of the film. Oxide growth rate becomes quasi-linear for the thick oxide film. This stage is called post-transition and is characterized by a large number of defects in the oxide film such as cracks and pores [7,8]. Cracks develop along metal/oxide interface, as it was shown in experiments [9,10]. Cracking provides fast access of the oxidant to the surface of the metal which leads to faster growth of oxide.

Therefore, growth rate of the oxide film (quasi-linear stage) is determined by parameters of the transition, [11,12]. Later transition leads to lower oxidation rate. Transition in the oxidation kinetics can be associated with growth of mechanical stresses near the metal/oxide interface, [13,14]. Mechanical stresses increase with the growth of oxide film thickness due to significant Pilling–Bedworth ratio values for Zr and ZrO_2. Formation of a wavy structure is often observed in corrosion experiments near metal/oxide interface, [9–11,14–18]. In some publications it has been suggested, that the development of the wavy structure can precede the transition in the oxide growth kinetics. To optimize experimental efforts it is desirable to have parametric dependencies relating the oxide growth rate and chemical composition, mechanical properties and microstructure parameters of the alloy and the oxide film.

Publications [19,20] were based on an assumption that the oxide film growth will lead to the metal/oxide interface deformation that will minimize total mechanical energy of the metal and the oxide. In [19,20] a theory which determines conditions of the wavy structure formation and the dependence of its wavelength on mechanical properties of the alloy and the oxide was developed. Analysis of theoretical results [19,20] and experiments [12,21–25] indicates that the phenomenon of transition is caused by evolution of mechanical stresses in oxide film and metal and is linked to the wavy structure formation in metal/oxide system. According to [19,20] the wavelength and amplitude that minimize mechanical energy are uniquely defined for the given oxide thickness. Large values of the wavelength and the amplitude are optimal for a large thickness of the oxide film. But the question how the wavelength is changing with the growth of the oxide is still not clear.

This work is dedicated to the development of transition model. Analysis of experiments has shown that one of possible scenarios leading to growth of wavy structure wavelength near metal/oxide interface can be period doubling bifurcation effect.

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2. Theoretical analysis

As it was shown in [19,20], the process that decreases mechanical energy in oxide film/zirconium alloy system is conversion to wavy-structure state near metal/oxide interface. Let's find the elastic energy change of wave structure compare to flat metal/oxide interface. If the wavelength of the wave structure is $2\pi/k$, the amplitude is a and the oxide thickness is h, the elastic energy change is given by:

$$\Delta U_{m,ox} = -\frac{(ka)^2}{8\varepsilon}\frac{hE_{ox}}{(1-\nu^2)}\left(\frac{2(\varepsilon-1)}{\varepsilon}-\frac{(ka)^2}{4\varepsilon}\right)+\frac{E_{ox}(kh)^3ka^2}{48(1-\nu^2)}\beta + \frac{E_m ka^2}{8(1-\nu_m^2)}. \quad (1)$$

In (1) E_{ox} – is Young's modulus of oxide, E_m – is Young's modulus of metal, ν, ν_m – are Poisson ratios for oxide and metal, ε – is the coefficient of linear expansion during oxidation in plane of the interface. The first term of (1) describes the decrease of elastic energy in the oxide film due to increase of its length during wavy structure formation. The second term in (1) describes bending strain energy in the oxide film. The third term in (1) describes elastic stress energy in metal.

The oxide film consists of columnar grains of oxide monoclinic phase. The columnar grains are elongated in direction which is perpendicular to the metal/oxide interface. The binding energy of the grain interface is significantly lower than binding strain energy in a single oxide crystal. This microstructure is characterized by lower bending strain energy. This fact is taken into account with the introduction of parameter $\beta \ll 1$, [19].

Minimum of elastic energy (1) is obtained if the following relationships (2) between the oxide thickness h, the modulus of wavy structure wave vector k and the wave amplitude a hold true:

$$ka = 2\sqrt{(\varepsilon-1)-\frac{3\varepsilon^2}{4}\left(\frac{\beta}{3}\frac{E_m^2}{E_{ox}^2}\right)^{\frac{1}{3}}},\; kh = (3E_m/\beta E_{ox})^{1/3} \quad (2)$$

If wavy structure formation was determined only by elastic deformation, the wavelength and the amplitude would grow simultaneously. But in experiments plastic deformations were found in the vicinity of corrosion front. As a result, additional work spent on plastic deformations in material is required for conversion to the structure with a larger wavelength. Therefore with small increase of the oxide film thickness wave structure amplitude can change when wavelength is constant.

How do the wave structure parameters change during oxide film growth? We assume that the oxide thickness has increased on a small value $\mathrm{d}h \ll h_0$. The system has to transform to a new equilibrium with parameters different from (2). Using the elastic approach let's determine the change of amplitude $\mathrm{d}a$ when the oxide film thickness is increased by $\mathrm{d}h$ assuming that the wavelength is constant.

From the relations (1), (2) it follows that the wave amplitude is decreasing and the reduction has a parabolic dependence on $\mathrm{d}h$.

$$k_0\cdot \mathrm{d}a \sim -\frac{3\varepsilon^2}{2ka}\left(\frac{\beta}{3}\frac{E_m^2}{E_{ox}^2}\right)^{\frac{1}{3}}\left(\frac{\mathrm{d}h}{h_0}\right)^2 = -\frac{C}{\sqrt{(\varepsilon-1)-C}}\cdot\left(\frac{\mathrm{d}h}{h_0}\right)^2. \quad (3)$$

here $C=\frac{3\varepsilon^2}{4}\left(\frac{\beta}{3}\frac{E_m^2}{E_{ox}^2}\right)^{\frac{1}{3}}$.

Dependence of metal and oxide mechanical energy on the wave amplitude is shown in Fig. 1 for different oxide film thickness and constant wavelength. The following parameters are used here and for further calculations: $E_{ox}/E_m = 3$, $\nu = 1/3$, $\varepsilon = 1.02$, $\beta = 10^{-4}$. Mechanical stresses and mechanical energy increase with the oxide thickness growth. This occurs because wavelength is fixed for all thicknesses (according to our assumption) but it is optimal only for one oxide film thickness (h_0). Note that optimal amplitude changes (the amplitude with the minimum mechanical energy in Fig. 1) are negative and depend on $\mathrm{d}h$ quadratically form according to (3).

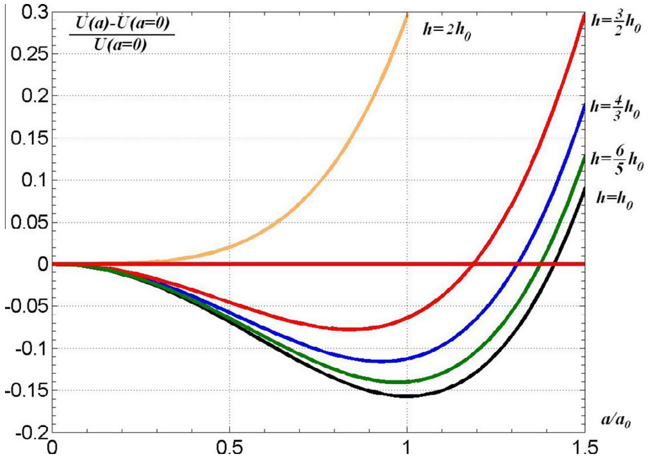

Fig. 1. Dependence of elastic energy change on wave amplitude (a_0 – optimal wave amplitude corresponding to oxide thickness h_0). Lower curve is for thickness h_0, others are for thickness $h_0 + \mathrm{d}h$.

If the oxide thickness was increased significantly (for example, $h = 2h_0$), the wave existence with the initial wavelength is energetically "disadvantageously", as it can be seen in Fig. 1.

What process can increase the period of the wave structure at the metal/oxide interface? Let's assume that wavelength can increase with the oxide film growth by a factor of 2, 3, 4 or another integer factor from time to time as it is observed in many physical processes [26,27]. Let's find mechanical energy change in the presence of two waves to determine what kind of wavelength increase is most energetically favorable. We assume that in addition to the wave with initial wavelength the perturbation wave with small amplitude δ and the wavelength n times larger than the initial wavelength is formed. So we can write interface equation as:

$$A = (a_0 + \mathrm{d}a)\sin(k_0x) + \delta\sin\left(\frac{k_0x}{n}+\varphi\right) \quad (4)$$

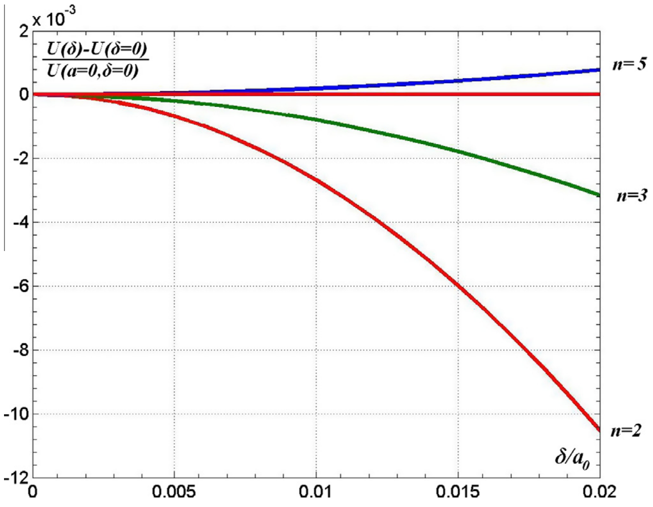

Fig. 2. Energy change vs. amplitude δ of the second wave with different n, $dh = 0.9h_0$. Horizontal axis is δ/a_0 value, vertical – $(U(\delta) - U(\delta = 0))/U(\delta = 0, a = 0)$.