



Effect of additives on the susceptibility of zirconium alloys to nodular corrosion

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ABSTRACT

A new approach based on a stability analysis of a uniformly growing oxide film was applied to estimate the effect of alloying additives on the susceptibility of zirconium alloys to nodular corrosion. The analytical results agree with available experimental data on effect of Fe and Ni on resistance of Zircaloy-2 and Zircaloy-4 to the growth of nodular oxide.

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1. Introduction

Zirconium alloys are among the base structural materials used in the cores of water-cooled nuclear power reactors. Service life and limitations on operating conditions of the core components are governed to high extent by the physical properties of zirconium alloys and their change in course of in-pile irradiation.

Interaction with coolant causes both oxidation of zirconium materials and hydrogen uptake during operation. One of the safety criteria for nuclear fuel is the limitation on growth of oxide films on fuel claddings. Despite the fact that corrosion in general is a destructive process it may also lead to some positive effects: while the oxide film on surface of zirconium structures is thin and dense it provides a protective barrier for further material degradation.

The oxidation of zirconium alloys was studied for a long time and a rather good understanding has been achieved concerning the phenomenology of the process for high temperature conditions in various oxidizing environments: oxygen, steam and water [1–6]. However, the debates on a role of different factors governing the transport of oxygen atoms through the oxide film, and on an effect of various chemical elements and charges (oxygen, hydrogen, electrons and conductivity vacancies, alloying additives and impurities) on the oxide film growth rate are still continued [7]. The ideas on mechanisms leading to different corrosion modes, uniform and nodular, are also widely argued (see for instance [4,8]).

Nowadays, many factors are known to influence the corrosion modes and rates [2,4,9]. First of all, they include chemical composition (concentration of alloying elements, impurities), microstructure (grain size and orientation), conditions of thermal and mechanical treatment of the alloy, mechanical stresses, temperature, heat flux, water chemistry and steam content in coolant, irradiation conditions for the oxidizing environment and the alloy (parameters of neutron spectrum, γ -dose rate).

The growth of uniform oxide films is observed usually in PWRs and WWERs, or in heavy water reactors with rather high content of dissolved hydrogen. Addition of hydrogen into coolant leads to suppression of water radiolysis and to decrease in concentrations of oxidizing radiolytic species.

Alongside with the uniform corrosion of zirconium alloys, the nodular corrosion is observed under definite conditions. Nodular corrosion (sometimes called also as pitting corrosion) is a problem in boiling-type reactors (BWR, RBMK) [4,8,10]. It is believed that nodular oxide growth in RBMK and BWRs is related, mainly, to two factors resulting in increase of oxygen content in coolant: water boiling and radiolysis. The lens-like oxide nodules are observed on the surface of zirconium components. In the case of nodular corrosion the oxide films are more subjected to spalling than in the case of uniform oxidation. The thickness of the nodules may greatly exceed the thickness of a uniformly growing film. Nodular corrosion may lead to rather quick local cladding thinning, increase in the rate of hydrogen uptake and increase in concentration of zirconium oxide particles migrating with coolant. Therefore, development of oxide nodules can restrict the operation time of fuel assemblies with zirconium structural components and even lead to more frequent fuel failures.

It should be noted that the problem of nodular corrosion of zirconium fuel claddings could become urgent also for the pressurized water reactors (PWRs and WWERs) in cases when the steam phase is formed at the oxide-coolant interface. It may take place, for instance, due to a formation of crud deposits on the cladding surface or in a case of power uprating.

1.1. Possible mechanisms of nodular corrosion

Several models with different physical mechanisms leading to a formation of oxide nodules have been proposed in the literature. Kuwae et al. [11] suggested that hydrogen gas could accumulate at the oxide/metal interface due to migration of protons being released from the water molecules and balancing the charge transport in low-conductivity ZrO_2 . When the H_2 pressure exceeds the

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Nomenclature

$A_{i,m}$	coefficient characterizing how the drift in field of mechanical stresses contributes to redistribution of alloying atoms in the metal in the vicinity of disturbed oxide/metal interface, see Eqs. (7) and (8)	$\vec{u}_{dr,i}$	drift velocity of atom 'i' in field of mechanical stresses
$C_{a,m}(\xi)$	distribution of alloying additive in the metal subjected to oxidation	u_0	velocity of oxidation front
$\tilde{C}_{a,m}$	perturbations of additive concentration in the metal	V_m	specific volume of the metal
$C_{a,m\infty}$	initial concentration of alloying additive in the metal (prior to oxidation)	V_{ox}	specific volume of the oxide
$C_{a,ox}$	concentration of alloying additive in the oxide	t	time
$C_{b,o}$	oxygen concentration in the metal near interface with the oxide	T	temperature, K
C_i	concentration of additive atoms in the metal	x	coordinate in direction of propagation of corrosion front, fixed coordinate system
$C_o(\xi)$	distribution of oxygen concentration in the metal	X_f	oxidation front position
$C_{o,ox}$	concentration of oxygen atoms in the oxide near oxide/metal interface	<i>Greek symbols</i>	
$C_{\infty,o}$	oxygen concentration in the metal far from oxidation front	α	ratio of solubility coefficients of alloying atoms in the metal and in the oxide in the vicinity of interface
$D_{a,m}$	diffusivity of alloying atoms in the metal	γ	instability increment
D_i	diffusivity of atom 'i' in the metal	η	parameter characterizing relative change in specific volume due to metal oxidation
$D_{o,m}$	oxygen diffusivity in the metal	λ	perturbation wavelength
E	Young's modulus of the metal	ξ	coordinate in direction of propagation of corrosion front, moving coordinate system
J_{ox}	flux of oxygen atoms (per unit area of oxide/metal interface) coming through oxide layer from outer surface	σ	mechanical stress
k	Boltzmann constant	τ	time
$\tilde{\ell}$	perturbation amplitude of corrosion front	τ_0	time of perturbation development
r_{\perp}	vector in the plane of metal/oxide interface	$\varphi_{a,m}$	potential of alloying atom in the field of mechanical stresses in the metal
		χ_{\perp}	wave number of perturbation
		$\Omega_{d,a}$	dilatation volume of alloying atoms in the metal

mechanical strength of zirconia, the film breaks and nodular corrosion is initiated. Urquhart et al. [12] related the local enhancement of proton migration to the sites with a lower concentration of intermetallic precipitates.

According to Cheng and Adamson [8], the formation of nodules in the Zircalloys is due to local inhomogeneities in the concentration of alloying additives (Fe, Ni, Cr). Replacement of Zr^{4+} by cations (Fe^{2+} , Fe^{3+} , Cr^{3+} and Ni^{2+}) produces more oxygen vacancies in the ZrO_{2-x} lattice. In areas with lower additive concentrations (e.g. at sites with no precipitates) a near-stoichiometric oxide is expected. Such oxide is unstable in a corrosive environment and is thought to transform with time into a highly porous granular ZrO_2 layer giving direct access of H_2O to the underlying metal.

Rudling and Wikmark [13] suggested that large intermetallics or clusters of small precipitates could form the sites of high hydrogen flux through the oxide film. If diffusion in the metal is not sufficient to disperse the incoming hydrogen, precipitation of hydrides occurs close to the interface. Nodules are formed due to accelerated corrosion resulting from the hydride formation.

Development of oxide nodules can be also related to the instability of the uniform oxidation front with respect to small transverse perturbations. There are different factors which may cause small perturbations at the propagating oxidation front. These factors include nonuniform conditions at the interface between the oxide film and the environment, nonuniform mechanical stresses in the metal and/or in the oxide, presence of intermetallics (second phase particles) or hydride precipitates and so on. The oxide nodules may form if some mechanisms are available to enhance the transverse inhomogeneities of the oxide/metal interface. But if there is a mechanism to stabilize these transverse inhomogeneities then its control and intensification may give opportunity to suppress the development of nodules. The possibility to predict the optimal modification to the chemical composition of the base alloy leading to a material with better resistance to nodular corrosion is of practical interest.

1.2. A way to estimate the effect of additives on nodular oxidation

The following approach is applied below for theoretical solution of the problem. Numerous experiments (e.g. [8]) have demonstrated that oxide nodules develop from 'nuclei' of small size. Such nuclei lead to transverse perturbations of the oxide/metal interface. These interface perturbations can be expanded into Fourier series in terms of space harmonics.

If addition of some alloying element promotes the increase in amplitudes of space harmonics (i.e. leads to rise the instability of the corrosion front) it can be supposed that this particular additive makes the alloy more susceptible to nodular corrosion. On the contrary, the alloying elements promoting the attenuation of transverse perturbations at the oxide/metal interface should improve the alloy resistance to growth of nodular oxide.

The present paper deals with theoretical analysis of conditions under which the addition of alloying elements into zirconium alloy improves the corrosion front stability with respect to development of its transverse structure.

It is worth noting that a wavy structure of the oxide/metal interface was observed experimentally. During oxidation of Zircaloy-4 specimens at 415 °C [14] in steam, the amplitude and periodicity of the interface roughness grew gradually in time and reached values of 0.1 and 1 μm , correspondingly. The undulation amplitudes of 0.05–0.2 μm with a period of about 1 μm for Zircaloy-4 were estimated from SEM photographs in Ref. [15]. The period and the amplitude of the undulations were reported to evolve during the oxide growth [15]. Calculations in Ref. [15] have shown that the revealed undulated (or 'egg-carton') structure of the interface was associated with high local tensile stresses both in the oxide and in the metal (in direction normal to the plane of the corrosion front). These stresses were evaluated to be sufficient to cause the observed cracking of the oxide in parallel to the interface, [15]. Finally, the wavy interface structure with $\sim 1 \mu m$ amplitude and $\sim 10 \mu m$ spac-

ing was observed for Zr–0.7Nb–0.1Fe alloy after 330 day corrosion tests at 360 °C [16].

The experimental data [14–16] provide evidence that a development of a transverse structure of the corrosion front may play an important role in the process of oxidation and produce a significant effect on the oxide characteristics.

2. Basic equations. Theoretical analysis

Several stages are distinguished in the oxidation of zirconium alloys [1–4]. One of them, the so-called ‘pre-transition’ stage of oxidation, takes place at temperatures ~ 200 °C and above. At this stage oxide films grow according to cubic or parabolic laws up to the oxide thickness of 2–3 μm . The inner part of the film is sub-stoichiometric and its outer part is close to stoichiometric composition. Such film is a protective barrier against oxidation and hydrogen uptake. However, the increase in mechanical stresses at the oxide/metal interface eventually leads to a formation of cracks, cavities and other defects in the growing oxide film. For oxide films thicker than 2–3 μm , the ‘post-transition’ oxidation kinetics obeys the quasi-linear law and the corrosion front propagates with quasi-stationary velocity.

To estimate the effect of additives on the susceptibility of zirconium alloys to the nodular oxidation in the present paper we consider the problem of the corrosion front stability with the following simplifications taken into account.

First, the steady state oxidation mode with a constant velocity of the corrosion front is considered. Second, it is assumed that diffusivity of alloying atoms in the metal is much higher than that in the oxide. Third, the analytical results are given for concentrations of additives in the alloy below the saturation values. Fourth, the role of second phase precipitates and irradiation effects are not considered. Finally, the metal layer is assumed to be much thicker than the dense (protective) oxide film on metal surface.

In the analysis of the mechanism of the additive influence on the susceptibility of zirconium alloys to nodular corrosion we will focus only on the contribution of the alloying atoms to the change of instability increment (or decrement) value.

To model the redistribution of oxygen and alloying atoms caused by transverse perturbations of the corrosion front we will use the diffusion equations taking into account the two-dimensional geometry and a possible drift of atoms in the nonuniform field of mechanical stresses. In a fixed coordinate system equation for the concentration of atoms C_i in the metal has the form:

$$\frac{\partial C_i}{\partial t} + [\bar{u}_{dr,i} C_i - D_i \nabla C_i] = 0. \quad (1)$$

Here $\bar{u}_{dr,i}$ is the drift velocity of atom ‘i’ in the nonuniform field of mechanical stresses. In the absence of transverse perturbations of the corrosion front, the mechanical stresses in the metal can be assumed homogeneous, so that the drift transport of atoms can be neglected.

Consider the oxidation stage when the oxide film thickness is increased at a constant rate without any transverse inhomogeneity. In a coordinate system moving with the velocity of the oxidation front (u_0), $\xi = x - u_0 t$, $\tau = t$ the transformed operators are:

$$\frac{\partial}{\partial t} = \frac{\partial}{\partial \tau} - u_0 \frac{\partial}{\partial \xi}; \quad \frac{\partial^2}{\partial x^2} = \frac{\partial^2}{\partial \xi^2}. \quad (2)$$

Assuming the absence of transverse perturbations and drift of atoms, Eq. (1) can be written as:

$$\frac{\partial C_i}{\partial \tau} - u_0 \frac{\partial C_i}{\partial \xi} = D_i \frac{\partial^2 C_i}{\partial \xi^2}. \quad (3)$$

While in one dimension the solution of the diffusion problem with a fixed oxide/metal interface takes the form of the error function, in the case when the oxide/metal interface moves with the constant velocity there are exponential-type solutions to the diffusion equation (relative to coordinate ξ).

The steady state solution for spatial distribution of oxygen in the metal is as follows:

$$C_o(\xi) = C_{\infty,o} + (C_{b,o} - C_{\infty,o}) \exp\left(-\frac{u_0}{D_{o,m}} \xi\right). \quad (4)$$

Here $C_{b,o}$ is the value of an oxygen concentration in the metal near the interface with the oxide (to be found from the metal–oxygen phase diagram), $C_{\infty,o}$ is the value of an oxygen concentration in the metal far from the oxidation front, $D_{o,m}$ is an oxygen diffusivity in the metal. The coordinate x is directed perpendicularly to the plane of the oxide/metal interface.

The steady state velocity of the corrosion front is proportional to the difference between two fluxes of oxygen atoms at the oxide/metal interface: the flux from the side of the oxide film and the flux into metal. Taking into account Eq. (4) we come to:

$$u_0 = J_{ox} / (C_{o,ox} - C_{\infty,o}). \quad (5)$$

Here J_{ox} is the flux of oxygen atoms per unit area of the oxide/metal interface from the side of the oxide film, $C_{o,ox}$ is the concentration of oxygen atoms in the oxide near the oxide/metal interface.

For the linear law of oxidation, in the coordinate system moving at a constant velocity of the corrosion front there are also steady state solutions for spatial distribution of alloying additives in the metal:

$$C_{a,m}(\xi) = C_{a,m\infty} - C_{a,m\infty}(1 - \alpha) \exp\left(-\frac{u_0}{D_{a,m}} \xi\right). \quad (6)$$

Here $C_{a,m}(\xi)$ is the distribution of alloying additive in the metal, $C_{a,m\infty}$ is the initial concentration of alloying additive in the metal (prior to the onset of oxidation), $D_{a,m}$ is the diffusivity of alloying atoms in the metal. The values of additive concentrations in the metal and in the oxide (in the vicinity of the interface) can be correlated by means of the ratio of solubility coefficients, α . For many additives, for example Ni and Fe, the solubility in zirconium oxide is higher than that in metallic Zr. For such additives $\alpha < 1$.

The question is the following. How the alloying additives may influence the evolution of small transverse perturbations of the oxidation front? We have to determine, first, the effect of the transverse modulation of the corrosion front on redistribution of alloying atoms in the vicinity of the oxide/metal interface to answer this question. If redistribution of the additive results in enhancement of the transverse structuring, then such additive makes the alloy more susceptible to nodular corrosion. Otherwise, the additive will provide better resistance of the alloy to nodular oxidation.

Let the oxidation front, X_f , be modulated in transverse direction with a small amplitude ℓ and wavelength $\lambda = 2\pi/\chi_{\perp}$, so that $X_f = u_0 t + \ell \sin(\chi_{\perp} r_{\perp})$. The ‘small amplitude’ implies that the following conditions are matched $\ell \ll \max(\lambda, D_{o,m}/u_0, D_{a,m}/u_0)$.

Due to a difference in specific volumes between the oxide V_{ox} and the metal V_m , the spatial modulation of mechanical stresses occurs near the oxide/metal interface, Fig. 1. For alloying atoms dissolved in the metal the mechanical stresses create a potential which can be estimated as:

$$\tilde{\varphi}_{a,m} \approx A_{im} \ell \chi_{\perp} \sin(\chi_{\perp} r_{\perp}) \exp(-\chi_{\perp} \xi). \quad (7)$$

Here A_{im} is of the order of $\Omega_{d,a} E \eta$, where $\Omega_{d,a}$ is the dilatation volume of alloying atoms in the metal, E is the Young’s modulus of the alloy and $\eta = (V_{ox}/V_m - 1) > 0$.

The Eq. (7) is derived with taking into account the following reasons. In any elastic deformation of an isotropic body (the simplified

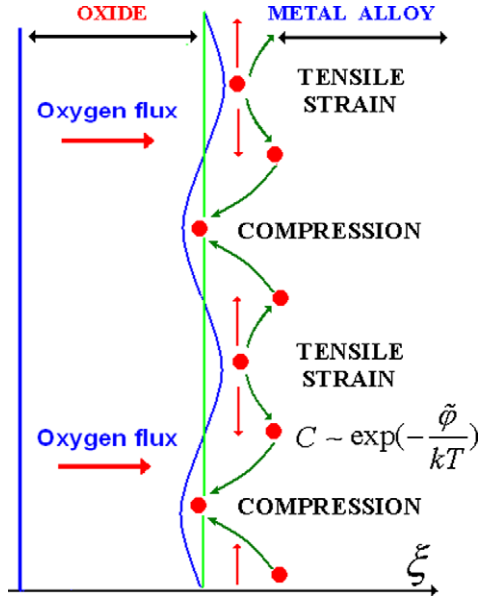


Fig. 1. Mechanical stresses and redistribution of alloying atoms near the disturbed oxide–metal interface.

case under consideration) the relative change in volume θ is proportional to the sum of diagonal components of the stress tensor $\Sigma\sigma_{ii}$ [17]. The energy of alloying atoms in the field of mechanical stresses can be written as $\varepsilon \propto \Omega_{d,a}\Sigma\sigma_{ii}$, [18]. For two-dimensional deformations the relative change in volume is a harmonic function, i.e. $\Delta\theta = 0$, [19]. The harmonic deformations corresponding to Fig. 1 and decreasing at infinity should have the form $\theta \propto \sin(\chi_{\perp}r_{\perp}) \exp(-\chi_{\perp}\xi)$. Due to the relationship $\Sigma\sigma_{ii} \propto \theta$ this form is used in Eq. (7).

The level of mechanical stresses in the metal estimated from Eq. (7) is consistent with the results of the sophisticated computations, Ref. [15]. Assuming the perturbation amplitude and the wavelength to be ~ 0.1 and ~ 1 μm and the Young's modulus of the metal to be ~ 70 GPa the stress is estimated as $\sigma \sim (\tilde{\ell}/\lambda)E\eta/3 \sim 1$ GPa. Stresses of about several hundred MPa in the metal in the vicinity of the undulated oxide/metal interface were calculated in Ref. [15].

The sign of A_{im} in Eq. (7) depends on the sign of dilatation volume of alloying atoms in the metal, $\Omega_{d,a}$. For some additives, for example Ni and Fe, the volume occupied by one alloying atom in the alloy is less than the volume per one atom of zirconium. In this case the sign of A_{im} is positive.

Under thermodynamic equilibrium, for alloying atoms with $A_{im} > 0$ the concentration of additive in the metal will decrease in the field of tensile stresses; in the field of compressive stresses the concentration will increase (compared to the case of no stresses). Vice versa, for alloying atoms with $A_{im} < 0$ the concentration of additive in the metal will be higher in the field of tensile stresses and lower in the field of compressive stresses. Taking into account diffusion and drift of atoms in the field of mechanical stresses, perturbations of additive concentration in the alloy can be described with the following equation:

$$\begin{aligned} \frac{\partial \tilde{C}_{a,m}}{\partial \tau} - u_0 \frac{\partial \tilde{C}_{a,m}}{\partial \xi} + D_{a,m} \cdot \frac{A_{im}}{kT} \tilde{\ell} \chi_{\perp}^2 \cdot e^{-\chi_{\perp}\xi} \cdot \frac{\partial \tilde{C}_{a,m}}{\partial \xi} \\ = -\chi_{\perp}^2 D_{a,m} \tilde{C}_{a,m} + D_{a,m} \frac{\partial^2 \tilde{C}_{a,m}}{\partial \xi^2}. \end{aligned} \quad (8)$$

The Eq. (8) comprises only linear terms with respect to small perturbations. The third left-hand term describes redistribution of alloying atoms due to drift in the field of mechanical stresses.

The first right-hand term corresponds to damping of small concentration perturbations due to diffusion in the metal. The second right-hand term in Eq. (8) describes diffusional transport of concentration perturbations in a direction of the corrosion front propagation.

Two boundary conditions were set for Eq. (8). First, the perturbations of additive concentration in depth of metal shall be zero:

$$\tilde{C}_{a,m}(\xi \rightarrow \infty) = 0. \quad (9)$$

The second boundary condition is for changes of additive concentration in the metal at the oxide/metal interface due to spatial modulation of energy of mechanical stresses and due to spatial shifts of the disturbed oxidation front:

$$\begin{aligned} \tilde{C}_{a,m}(\xi)|_{\xi=0} = C_{a,m\infty}(1 - \alpha) \frac{u_0}{D_{a,m}} \tilde{\ell} \sin(\chi_{\perp}r_{\perp}) - \alpha C_{a,m\infty} \frac{A_{im}}{kT} \tilde{\ell} \chi_{\perp} \\ \times \sin(\chi_{\perp}r_{\perp}). \end{aligned} \quad (10)$$

After solution of Eq. (8) with boundary conditions (9,10) we can find the changes in a balance of oxygen fluxes: the one coming from the side of the oxide and the one transferred into the metal through the disturbed oxide/metal interface. The solution of Eq. (8) is assumed to exponentially depend on time, i.e. $\sim \exp(\gamma\tau)$. The changes between the incoming and outgoing oxygen fluxes at the disturbed oxide/metal interface govern the process of whether the modulation of the corrosion front will grow in amplitude or fall down.

Simplified solutions can be obtained for the long-wave perturbations (with accuracy to the squared terms by χ_{\perp}) and near the threshold of stability (small γ). For this case the analysis gives the following expression for the effect of additive concentration on stability of oxidation front with respect to development of small transverse perturbations:

$$\frac{\partial \tilde{\ell}}{\partial \tau} \sim -\frac{\tilde{\ell}}{u_0} \left(\frac{\partial u_0}{\partial C_{a,ox}} \right) C_{a,m\infty}(1 - \alpha) \cdot D_{a,m} \chi_{\perp}^2 \cdot \left(1 + \frac{A_{im}}{kT} \right). \quad (11)$$

Within the long-wave limit, if $A_{im} > 0$ then the additive concentration in the oxide increases in regions where the oxidation front lags behind the plane boundary (region of delayed oxidation), and decreases in regions at antiphase. If (under the specified environment conditions) the growth rate of the uniform oxide film is higher for higher concentration of alloying additive, $\partial u_0 / \partial C_{a,ox} > 0$, then according to Eq. (11) such alloying leads to stabilization of the corrosion front (see Fig. 2).

On the contrary, if the volume of alloying atoms exceeds the volume of the base metal atoms ($A_{im} < 0$), the concentration of additive in the oxide film increases in regions where the disturbed oxidation front is ahead of the plane boundary, and decreases in regions where it lags behind. In this case the stabilizing properties of alloying atoms also depend on the sign of $\partial u_0 / \partial C_{a,ox}$ derivative, i.e. whether the alloying additive enhances or decelerates the growth of the uniform oxide film.

Actually, Eq. (11) shows what kind of perturbations in the oxide film can be stabilized with one or another alloying element. Assume that some external factors lead to enhancement of perturbations of the oxide/metal interface at a rate higher than decrements in Eq. (11) for basic additives in the alloy. Then for the given alloy composition and under the specified conditions of oxidation the nodular corrosion is possible. Otherwise, formation of oxide nodules will be suppressed due to stabilizing effect of the alloying elements.

The theoretical analysis performed in the present work did not include the similar consideration of the effect of oxygen redistribution in the metal on stability of the corrosion front. The problem in such formulation is more complicated. It should be solved consistently accounting for a transport of oxygen ions and electrons

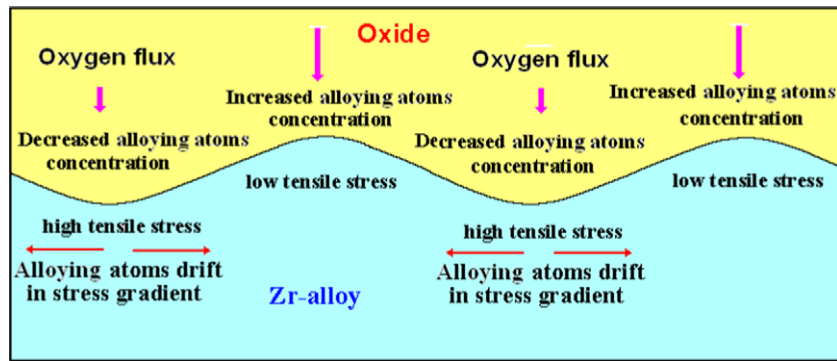


Fig. 2. Schematic view of the oxidation front stabilization effect at $A_{im} > 0$.

through the oxide film and also for processes at the outer boundary of the dense oxide film being in contact with the oxidizing environment.

However, the results gained from the above analysis may be used to predict how the certain alloying additives affect the susceptibility to nodular corrosion of some zirconium alloy. It is possible if there is information on parameters which characterize the corrosion regime for given oxidation conditions. It is necessary to measure the nucleation time and the size of nucleating nodules to make predictions.

It follows from Eq. (11) that the damping time for perturbation with the wavelength $\lambda = 2\pi/\chi_{\perp}$ can be assessed by the order of magnitude from the expressions $1/\tau_0 \sim D_{a,m}\chi_{\perp}^2 \cdot (1 + A_{im}/kT)$, $A_{im} = 0,15 \cdot \Omega_{d,a}E$. For example, if we use diffusivities of the order of $10^{-15} \text{ cm}^2/\text{s}$ (iron diffusivity in Zircaloy-2 at $T = 510 \text{ }^{\circ}\text{C}$ [1]) then the damping time of perturbation (for a typical size of secondary phase precipitate $\sim 10^{-5} \text{ cm}$)¹ is less than one hour. If the measured nucleation time of nodules exceeds the calculated value τ_0 then the additive under consideration is able to suppress the development of nodules under the specified conditions of oxidation.

3. Discussion of results

Let us compare the obtained results with experimental data available for the effect of some alloying additives on susceptibility of zirconium alloys to nodular corrosion.

Detailed studies of the effect of iron and nickel additions and heat treatment modes for Zircaloy-2 and Zircaloy-4 (Zry-2 and Zry-4) on their susceptibility to nodular corrosion were reported by Cheng and Adamson, [8]. The behavior of Zry-2, Zry-4 and the alloyed specimens of crystal bar and sponge zirconium was studied out-of-pile. The resistance of specimens to formation of oxide nodules was tested in steam atmosphere with two-step method: first, heating up to 410 C with 8 h duration and then heating up to 510°C with the subsequent exposure under isothermal conditions during 4, 8, 12 or 16 h (see details in Ref. [20]). It was demonstrated that for Zry-2 and Zry-4 nucleation of oxide nodules occurred inside grains and was not related directly to presence of intermetallic precipitates. Based on the data analysis the authors came to a conclusion that the key factor governing development of nodular corrosion was the content of dissolved chemical elements in the Zr crystal matrix [8].

An addition of iron and nickel into pure zirconium in amount exceeding some threshold value led in experiments [8] to substantial – 2 orders of magnitude – decrease in the specimen weight

gain during oxidation. Further increase in concentration of Fe and Ni in specimens resulted in slow, approximately linear, increase in the growth rate of uniform (black) oxide film. The stabilizing effect of Fe and Ni additions into zirconium alloys is consistent with the above analysis of the corrosion front stability. Since for iron and nickel atoms in zirconium $A_{im} > 0$, then, according to Eq. (11), at positive derivative $\partial u_0/\partial C_{a,ox}$ these additives have to stabilize development of oxide nodules.

The experiments [8] also demonstrated that it was possible to avoid development of nodules under definite modes of preliminary heat treatment of Zircaloys due to addition of Fe in Zry-4 and addition of Fe and Ni in Zry-2.

Microstructure analysis of Zry-2, Zry-4 specimens, used in [8], showed that the initial number density of secondary phase precipitates was about 10^7 per cm^2 . Before two-step oxidation tests (using technique described in Ref. [20]) the specimens were annealed under different conditions. Various heat treatments were used to study an effect of redistribution of the additives between intermetallic particles and the crystal matrix on the alloy susceptibility to nodular corrosion.

In Zry-4 and Zry-2 specimens heat treated at temperatures in α -phase field the changes in concentration and sizes of intermetallic precipitates were insignificant. Due to relatively low mobility of Fe atoms at temperatures 650–800 °C there was no noticeable dispersion of iron from precipitates into the Zircaloy matrix during the time of annealing. As a result, the resistance of Zry-4 specimens to nodular corrosion did not change according to two-step testing technique [20]. After estimating the decrement for iron from Eq. (11) by the value of Fe diffusivity in Zircaloys [1], we come to $\gamma\tau \sim 0.2$ for time of ~ 4 h and the given number density of secondary phase precipitates (the distance between precipitates was assumed to be the typical scale of perturbations $\sim 1/\chi_{\perp}$).

Mobility of Ni atoms in Zry-2 is considerably higher compared to that of Fe atoms. Therefore, during the preliminary annealing of Zry-2 specimens, nickel atoms from $\text{Zr}_2(\text{Ni}, \text{Fe})$ precipitates migrated into matrix in appreciable amounts (concentration and sizes of inclusions varied weakly). The effect increased for higher annealing temperatures. Zry-2 specimens heat treated at higher temperatures were more resistant to nodular corrosion (according to the technique [20]). It is in agreement with the conclusions of the corrosion front stability analysis. Indeed, for nickel under conditions of these experiments we have $\gamma\tau > 1$, and increase in concentration of Ni in solid solution, according to Eq. (11), should enhance the effect of stabilization of the corrosion front perturbations.

Finally, the concentration of secondary phase precipitates increased considerably in Zry-2 and Zry-4 specimens quenched after annealing at temperatures above the point of α - β transition. For such modes of heat treatment Zry-2 and Zry-4 became more resis-

¹ If data are available on size of nucleating nodules the wavelength of perturbation should be assessed on the basis of these data.

tant to a development of nodules. This result is also consistent with Eq. (11), because higher concentrations of precipitates (higher χ_{\perp}) and higher additive (Fe, Ni) concentrations in the metal lead to higher values of the stabilization parameter $\gamma\tau$, which exceeds the unity both for nickel and iron.

The stabilizing effect of Fe addition into zirconium was also shown experimentally by Kim et al. [16]. In the experiments [16] the formation of wavy structure was observed on the oxide/metal interface during oxidation of Zr–Nb alloy with small Fe content. The tests were carried out in autoclaves in water at 360 °C. An increase of the iron concentration in the alloy led to decrease of the weight gain rates and to the stabilization of the oxidation front.

Experiments [12] showed that the development of the transverse structure at the oxide/metal interface caused increase of Fe, Ni and Cr concentrations in areas which lagged behind the corrosion front. At sites of nodule growth concentrations of these additives in the metal were found to be lower than in space between the neighboring growing nodules [12]. The observed redistribution of additives is in agreement with the analytical results obtained in the present work. Data by Urquhart et al. [12] indicate a possible role of additive redistribution in the process of transverse structuring of the corrosion front.

The results of stability analysis, Eq. (11), were obtained from the general (rather cumbersome) expression with some simplifying assumptions listed in Section 2. In spite of a number of noticeable limitations the qualitative agreement between the results of the simplified analysis and the experimental data counts in favor of the approach developed.

4. Conclusions

The present paper outlines the approach to evaluate the effect of alloying additives on susceptibility of zirconium alloys to nodular corrosion. The approach is based on a stability analysis of the oxidation front. Results of the simplified analysis for Fe and Ni additives in the Zircalloys are in good agreement with the available experimental data. The described approach can be also applied to Zr–Nb alloys. However, for this purpose the interference between Nb atoms and other alloying additives has to be considered. For more detailed quantitative evaluations of the effect of alloying ele-

ments on susceptibility of zirconium alloys to nodular corrosion it is necessary to include the extended stability analysis, in particular, for the case when additive concentrations are above the saturation values. Such analysis is planned in the near future. In addition it is planned to carry out a self-consistent numerical modelling with account for irradiation effects and oxygen transfer through the oxide film.

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