ELSEVIER

Journal of Nuclear Materials 264 (1999) 327–332

journal of nuclear materials

Influence of stress developed due to oxide layer formation on the oxidation kinetics of Zr–2.5%Nb alloy

A.P. Zhilyaev *,[1], J.A. Szpunar

Department of Metallurgical Engineering, McGill University, 3610 University Street, Montreal, PQ, Canada H3A 2B2

Received 9 March 1998; accepted 30 June 1998

Abstract

Knowledge of oxidation kinetics of Zr alloys is extremely important because it helps to evaluate the lifetime of pressure tubes, which constitute an integral part of the heat transfer system of many nuclear power stations. The presented diffusion model describes oxidation kinetics of zirconium alloy (Zr–2.5%Nb) under stress at the oxide/metal interface. A major assumption of this model is that the gas/oxide interface moves inwards into the oxide scale by creating a continuous network of internal defects (cracks, voids, etc.). A linear relation coupling the equations describing the evolution in the movement of the gas/oxide and oxide/metal interfaces was used as a first approach. After a certain period of time, the diffusion process obeys a pseudo-steady-state solution. A distance between gas/oxide and oxide/metal represents a thickness of the non-porous layer that remains constant during the pseudo-steady-state growth. An explanation of a possible transition between the parabolic and the cubic character of the oxidation kinetics is presented.

Keywords: Diffusion model; Oxidation kinetics; Zirconium alloy

1. Introduction

The importance of zirconium alloys in the nuclear power industry is attributed to a high corrosion resistance during the operation of a reactor. Zirconium oxide serves as a diffusion barrier, limiting the rate of oxidation and reducing the hydrogen uptake by the substrate metal [1–3]. Knowledge of the kinetics of the oxidation process and of hydrogen permeation is extremely important because it permits the evaluation of the lifetime of the pressure tubes.

Due to several causes such as lattice mismatch, different thermal expansion coefficient, etc., a growth stress is built up in the oxide scale. This stress has only in-plane component $\sigma_{yz}(x)$ and it is a function of x-axis, the normal to a substrate plane. Further we assign a symbol $\sigma(x)$ for it. The maximum value of the compressive stress measured by different methods [4–6] at the oxide/metal (O/M) interface is about 1 GPa. Stress vanishes at the gas/oxide (G/O) interface. The compressive stress built up has to be relieved at some stage of the oxide growth into the zirconium.

Elastic failure (cracking) is the main mechanism of stress relief in the oxide scale formed on the Zr–Nb alloy. This view is supported by ac-impedance experiments [7], which determined that the oxide film consists of two layers: the external layer, which is porous, and the internal one which is dense. The dense layer serves as a protecting film for the zirconium metal against hydrogen diffusion. Experiments [8] show that the oxide film may consist of a mixture of two phases: metastable tetragonal and a stable monoclinic phase. The tetragonal phase is stabilized by a high stress that exists in the vicinity of the O/M interface. One of the ways of relieving stress can be a transformation of the tetragonal phase by twinning,

---

* Corresponding author. Present address: Department of Chem. Eng. and Materials Science, UCD, One Shields Avenue, Davis, 95616-5294 CA, USA.

[1] On leave from Institute for Metals Superplasticity, Problems, Russian Academy of Science, 450001 Ufa, Russia.

0022-3115/99/$ – see front matter © 1999 Published by Elsevier Science B.V. All rights reserved.
PII: S0022-3115(98)00478-4

which is accompanied by extensive cracking. There is some evidence that this mechanism of transformation really exists. A large area of microstructure with a very high fraction of twin boundaries has been observed in Zr oxide films [9]. Other authors [10] tried to theoretically evaluate the stress gradient in the metal/oxide composite using the Bollman's method [11]. Their calculations gave approximately the same magnitude of stress as measured in [4–6].

A model of oxidation has been presented in [12–14] where authors describe a possible relation between the change in the oxide microstructure with the rate of oxide growth during isothermal oxidation of polycrystalline Zr. The main assumption of this model is that the diffusion coefficient of the oxide scale is a function of distance from the G/O interface for the static model. In addition, it may be a function of time for dynamic model. This change of the diffusion coefficient is related to grain growth in the oxide scale. Under certain conditions (radiation damage, for example), it can happen in spite of low service temperature, which is lower than $0.5T_m$ (Melting point for zirconium oxide, T_m, equals 2715°C).

In this paper we are going to investigate the influence of stress generated at the O/M interface on oxidation kinetics. Despite intensive research devoted to describing the oxidation kinetics in zirconium alloys, the quantitative influence of stress built up near the oxide/metal interface on the growth of oxide scale has not yet been investigated. Our aim is to use a continuum model as a first approach to evaluate the thickness of the oxide film as a function of time and stress. Details of the model are presented in the next section.

2. Model of oxygen diffusion through oxide scale

Physical processes, on which this mathematical model is based, are described elsewhere [12]. Oxygen decomposes at the G/O interface. Thereafter O^{2-} ions diffuse through the scale, preferentially along two-dimensional defects (triple junctions, grain boundaries, pores and cracks). The oxidation progresses when the oxygen is transported to the O/M interface, where it produces new oxide. Mismatch of lattice parameters and differences in thermal expansion create stress gradient in the oxide scale, which slows down the oxidation process. This stress is maximal at the O/M interface and it vanishes at the G/O interface. The G/O interface moves towards the metal substrate as the continuous network of two-dimensional defects is developed as a result of the process of stress relieving.

The physical processes that take place are simplified in the proposed mathematical model using the following assumptions:

- For simplicity, a semi-infinite sample with a plane interface between ZrO_2 film and substrate of zirconium alloy has been taken.
- Oxide scale consists of two sub-layers: the first made of a connected network of cracks and micro defects; the second is a dense film that slows down the oxidation process and ingress of hydrogen into metal.
- There are two interfaces: G/O interface and O/M interface that move inwards into the zirconium substrate.
- Growth stress is created at the O/M interface and it vanishes at the G/O interface.
- Oxygen diffusion process that occurs in the dense layer is governed by a gradient of oxygen concentration and a gradient of stress built up at the O/M interface.

During the oxide growth process, the stress may be relieved through various mechanisms [15]: (i) plastic deformation of oxide scale; (ii) deformation (elastic and plastic) of the substrate of Zr–2.5%Nb alloy; (iii) detachment at the O/M interface; (iv) recrystallization of the oxide; and (v) elastic failure (cracking) of the ZrO_2 film. We have chosen the fifth as the main mechanism of stress relief in the proposed model.

An important assumption of our model is that movements of both interfaces (G/O and O/M) are coupled by a relationship between their rate constants. This assumption allows us to present the model as a feedback machine shown in Fig. 1. Our IU (input unit) is the G/O interface and OU (output unit) is the oxide/substrate interface. The CU (control unit) represents chemical composition, microstructure, texture of the oxide scale, and also grain boundary statistics. It is known [16] that the control unit has a strong impact on behavior of the whole system. Specifically, the grain boundary misorientation distribution as a component of the CU can change the rate constant of diffusion up to one order of magnitude [17,18]. However, in the present paper we are not going to investigate this problem. This will be the aim of future work that will be devoted to study the role of the grain boundaries as one of the control parameters of our model.

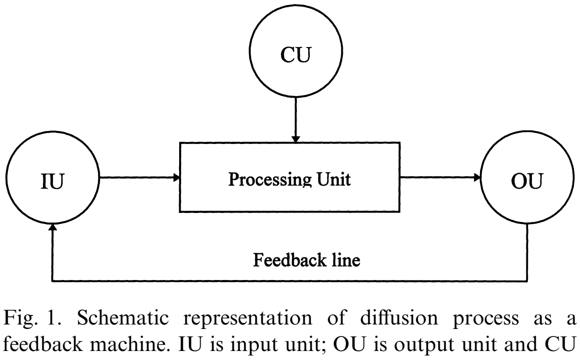

Fig. 1. Schematic representation of diffusion process as a feedback machine. IU is input unit; OU is output unit and CU is control unit (see the text).

3. Mathematical model and analytical solution

A schematic representation of the diffusion of oxygen through the oxide film is shown in Fig. 2. Mathematically, we have defined a one-dimensional diffusion problem from an infinite source for a semi-infinite region with two moving boundaries. We can neglect diffusion through the metal substrate because the diffusion coefficient of oxygen for the $\alpha + \beta$ phase of the alloy is rather small with respect to the effective oxygen diffusion coefficient of zirconia film. Therefore, for a non-porous layer diffusion equation is

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{V}{RT}\frac{\partial C}{\partial x}\frac{\partial \sigma}{\partial x}\right), \qquad S_0(t) \leqslant x \leqslant S(t).$$

$$C(S_0(t), t) = C_0, \qquad C(S(t), t) = C_{01}. \tag{1}$$

The Stefan condition for the O/M interface at $x = S(t)$ is as follows:

$$-D\frac{\partial C}{\partial x}\bigg|_{x=S(t)} = C_{01}\frac{\mathrm{d}S}{\mathrm{d}t}. \tag{2}$$

Two assumptions essentially simplify our problem. A linear relationship between two moving surfaces $S_0(t) = \beta S(t)$ is chosen as a first approach. Here β is coefficient proportionality. The stress is a linear function of the distance between S and S_0, $\sigma(x) = \sigma_0(x - S_0)/(S - S_0)$. Using dimensionless variables the system of equations is

$$\frac{\partial \overline{C}}{\partial \tau} = D\left(\frac{\partial^2 \overline{C}}{\partial \overline{x}^2} + \frac{\delta}{\overline{S} - \overline{S_0}}\cdot\frac{\partial \overline{C}}{\partial \overline{x}}\right), \quad \overline{S_0}(\tau) \leqslant \overline{x} \leqslant \overline{S}(\tau).$$

$$\overline{C}(\overline{S_0}, \tau) = 1, \ \overline{C}(\overline{S}, \tau) = 0, \tag{3}$$

and the Stefan condition,

$$-\frac{\partial \overline{C}}{\partial \overline{x}}\bigg|_{\overline{x}=\overline{S}(t)} = \alpha\frac{\mathrm{d}\overline{S}}{\mathrm{d}\tau}, \tag{4}$$

where

$$\overline{x} = \tfrac{x}{a}, \quad \tau = \tfrac{Dt}{a^2}, \quad \overline{S_0} = \tfrac{S_0}{a}, \quad \overline{S} = \tfrac{S}{a}, \quad \overline{C} = \tfrac{C - C_{01}}{C_0 - C_{01}}, \quad \alpha = \tfrac{C_{01}}{C_0 - C_{01}}, \quad \delta = \tfrac{\Omega\sigma_0}{RT} \tag{5}$$

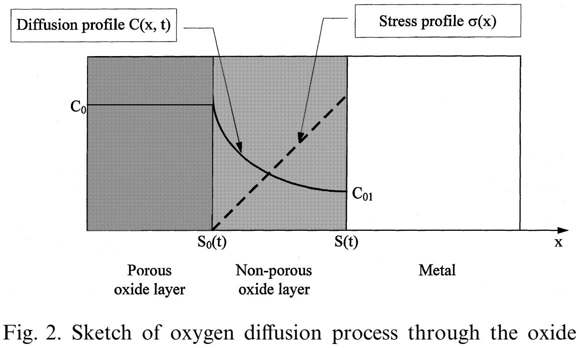

Fig. 2. Sketch of oxygen diffusion process through the oxide film.

and a is some characteristic length. R and T are molar gas constant and temperature, respectively. An analytical solution is presented in the next section. Other parameters used here are shown in the table below.

Parameter	Value or/and meaning
C_0	Concentration at the G/O interface (1511 kg m^{-1}) [12]
C_{01}	Concentration at the O/M interface (1417.1 kg m^{-1}) [12]
Ω	Molar volume of ZrO_2 (282.2×10^{-7} m^3 mol^{-1})
σ_0	Maximum of stress at the O/M interface (~1 GPa) [13,19]

Others (α, β, δ and γ) are described in the text.

3.1. Non steady-state solution

Assuming that the solution of variable $\overline{C}$ has the following form: $\overline{C} = \Psi(\overline{x}/\sqrt{\tau})$, $\overline{S} = \sqrt{2\gamma\tau}$, $\overline{S_0} = \beta\overline{S}$, where $0 \leqslant \beta \leqslant 1$, we obtain the solution for the diffusion profile,

$$\overline{C} = \frac{\operatorname{erf}(\sqrt{\gamma/2} + A) - \operatorname{erf}(\overline{x}/(2\sqrt{\tau}) + A)}{\operatorname{erf}(\sqrt{\gamma/2} + A) - \operatorname{erf}(\beta\sqrt{\gamma/2} + A)},$$

$$\text{where } A = \frac{\delta}{\sqrt{2\gamma}(1-\beta)}. \tag{6}$$

In Eq. (6), γ is the rate constant of oxidation kinetics and may be determined from the transcendental equation

$$\alpha\sqrt{\frac{\pi\gamma}{2}}\exp\left[(\sqrt{\gamma/2} + A)^2\right]\Big[\operatorname{erf}(\sqrt{\gamma/2} + A) - \operatorname{erf}(\beta\sqrt{\gamma/2} + A)\Big] = 1. \tag{7}$$

With $\delta = \beta = 0$ this equation is reduced to the known equation used for description of heat conduction or diffusion process with moving boundary,

$$\alpha\sqrt{\frac{\pi\gamma}{2}}\exp(\gamma/2)\operatorname{erf}(\sqrt{\gamma/2}) = 1.$$

Analysis of the transcendental equation for large and small values of the parameter α is described elsewhere [19]. We are going to analyze it for different values of two other parameters: β and δ. For large δ, one can use the approximation

$$\operatorname{erf}(x) \approx 1 - \frac{\exp(-x^2)}{x\sqrt{\pi}},$$

then the rate constant can be determined from

$$\gamma = \frac{\delta\exp(-\delta)}{\alpha(1-\beta)}. \tag{8}$$

3.2. Pseudo- steady-state solution

From our recent experiments where the thickness of the porous layer was measured by means of the ac-impedance technique [8], it is shown that after a certain period of time, both the G/O and O/M interfaces start to move self-consistently while the distance between them is kept constant. Therefore, we can use the relationship $\overline{S} = \overline{S}_0 + \overline{h}$. In this case, the diffusion process can be considered as a pseudo-steady-state stage and diffusion equations are transformed into

$$\frac{\partial^2 \overline{C}}{\partial \overline{x}^2} + \frac{\delta}{h}\frac{\partial \overline{C}}{\partial \overline{x}} = 0, \quad \overline{S_0}(\tau) \leqslant \overline{x} \leqslant \overline{S}(\tau),$$
$$\overline{C}(\overline{S}_0, \tau) = 1, \quad \overline{C}(\overline{S}, \tau) = 0. \tag{9}$$

This equation has a trivial solution

$$\overline{C} = \frac{\exp(-\delta(\overline{x} - \overline{S_0})/h) - \exp(-\delta)}{1 - \exp(-\delta)}. \tag{10}$$

During a pseudo-steady-state process, diffusion obeys the kinetics of a G/O interface moving towards the metal. At the crossover point where diffusion becomes a pseudo-steady state, the difference between the O/M and G/O interfaces equals $\overline{h}$, which can be measured in ac-impedance experiment. We can thus calculate the crossover time,

$$\tau_{\mathrm{cr}} = \frac{\overline{h^2}}{2\gamma(1 - \beta)^2}. \tag{11}$$

At this point, a profile of concentration (given by Eq. (6)) has to be the same as the one given by Eq. (10).

4. Results and discussion

The purpose of the diffusion model is to predict kinetics of the process. In our case, it is assumed that we have a parabolic law of kinetics and that we need to calculate a rate constant. This depends on the system parameters such as β and δ.

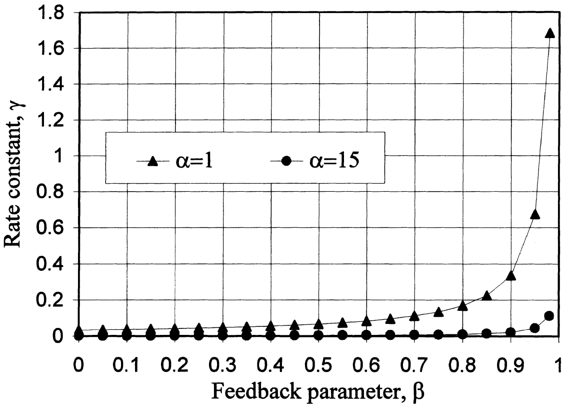

Fig. 3. Rate constant vs. feedback parameter for two different values of α.

In Fig. 3, the dependence of the rate constant in moving the O/M interface on the feedback parameter β is depicted. The other parameters (α and δ) are presented on the same picture. From Eq. (8), it can be seen that for $\beta = 1$, the rate constant becomes infinity. The parameter β can be named "system responding coefficient" because it shows us how fast the stress built up at the O/M interface can be relieved. It is clear that the rate constant must decrease with the increasing stress generated at the moving interface between the metal substrate and the oxide scale.

Fig. 4 shows the influence of stress on the rate constant. The transcendental equation (7) has been solved numerically for values of δ less than 3. For δ larger than 3, we used approximating equation (8). With increasing stress, the rate constant decreases exponentially.

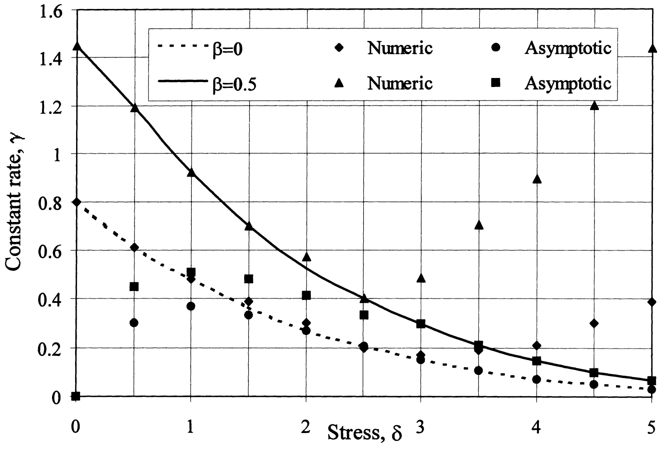

Fig. 4. Rate constant vs. stress for two different feed back parameters.

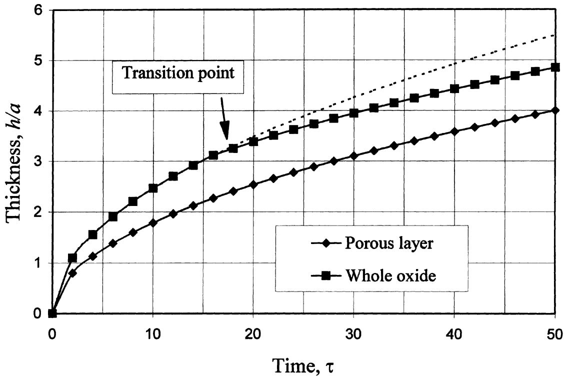

Fig. 5. Oxidation kinetics for porous and whole oxide.

Experimental data was used to represent the oxidation kinetics for porous and dense oxide scales in ZrO_2 film, in order to evaluate the order of the rate constant. For given parameters (see the table for details) α is $\sim$15 and δ is about 15 if maximal stress at the O/M substrate σ_0 equal 1 GPa. Temperature was taken as used in the oxidation experiments in [19], $T = 673$ K. Parameter β can be calculated using experimental data [19] for thickness of the non-porous (h) and the whole (w) oxide layers $\beta = 1 - h/w \sim 0.733$. Knowing β it is possible to evaluate the rate constant $\gamma \sim 0.297$ from Eq. (11) and the crossover time, $\tau_{cr} \sim 15$ from Eq. (10). The diffusion coefficient of oxygen in ZrO_2 was taken from [20]. Fig. 5 represents the oxidation kinetics for a porous oxide layer and an entire oxide thickness. For the time less than τ_{cr} we have plotted $S(t)$ and $S_0(t)$ as function of time $S(t) = \sqrt{2\gamma t}$ *and* $S_0(t) = \beta S(t)$. For the time larger than τ_{cr}, the rate constant of the entire whole oxide thickness becomes the same as the rate constant of the G/O interface. The solid line in this figure represents the kinetics if there is no transition in kinetics at the crossover time.

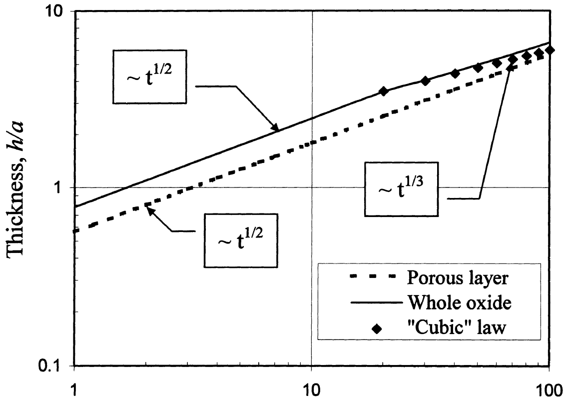

Fig. 6. Schematic log–log plot of oxidation kinetics.

There is some reasonable speculation supporting this idea. We re-plotted the data from Fig. 5 in log–log axes (Fig. 6) and put on the same plot a curve that actually describes cubic law kinetics. One can see for the time close to crossover time (τ_{cr}), there is not much difference between 'cubic law' kinetics and power law kinetics. On the experimental plot it is impossible to distinguish them at all. Thus, it is more likely that switching in constant rate of oxidation kinetics at the crossover point is a possible explanation of this phenomenon.

5. Concluding remarks

The model describing oxidation kinetics in the zirconia film under stress at the O/M interface is presented. The main assumption is that the stress relief proceeds by creating a continuous network of cracks and voids. The G/O interface moves inwards into the metal substrate through the process of stress relief and this movement affects the kinetics of the oxidation process. Oxidation kinetics is divided into two stages: a non-steady stage and a pseudo-steady-state stage. During the second stage, the oxidation process is controlled by the kinetics of generation of the porous network. The influence of the stress and the system responding coefficient on the rate constant for the non-steady state process is presented. As expected, an increase in the stress leads to a decrease of the rate constant. It is possible to use an asymptotic equation to calculate the rate constant of the oxidation process.

In this paper, we had solved coupled equations describing the diffusion process and stress evolution in the oxide scale. Such a simplified approach may give us a good evaluation of a material's lifetime, if we properly use some experimental data as phenomenological parameters of our system. One has to include the hydrogen swelling that might decrease stress levels in the oxide film. This depends on how fast the hydrogen can permeate through the oxide film. At the same time, the effective coefficient of hydrogen diffusion is linked to the evolution of the network of internal defects in the oxide film. Clearly, this is a connected system of three processes that need to be considered as an entity.

Acknowledgements

The authors would like to acknowledge the support of Ontario Hydro Technologies and the National Science and Research Council of Canada.

References

[1] V.R. Urbanic, D. Khatamian, O.-T.T. Woo, in: Zirconium in the Nuclear Industry, Tenth International Symposium, ASTM STP, vol. 1245, 1994, p. 116.

[2] Y.P. Lin, T.O. Woo, D.J. Lockwood, in: Polycrystalline Thin Films: Structure, Texture, Properties and Applications, MRS Symposium Proceedings, vol. 343, 1994, p. 487.
[3] G. Wilkmark, P. Rudling, B. Lehtinen, B. Hutchison, A. Oscarson, E. Ahlberg, in: Zirconium in the Nuclear Industry: Eleventh International Symposium, ASTM STP, vol. 1295, 1996, p. 53.
[4] J. Godlewski, in: Zirconium in the Nuclear Industry, Tenth International Symposium, ASTM STP, vol. 1245, 1994, p. 663.
[5] M.G. Glavicic, J.A. Szpunar, Y.P. Lin, A method for the determination of stress in ZrO_2 film grown on Zr–2.5% Nb pressure tubes, submitted.
[6] H.J. Beie, A. Mitwalski, F. Garzarolli, H. Ruhman, H.J. Sell, in: Zirconium in the Nuclear Industry, Tenth International Symposium, ASTM STP, 1994, p. 615.
[7] M.G. Glavicic, unpublished.
[8] M.G. Glavicic, J.A. Szpunar, Y.P. Lin, J. Nucl. Mater. 245 (1997) 147.
[9] V.Y. Gertsman, Y.P. Lin, A.P. Zhilyaev, J.A. Szpunar, Special grain boundaries in zirconia corrosion films (1997), submitted to Philos. Mag.
[10] T. Montesin, H. Sabar, G. Bertrand, M. Berveiller, Def. Diffus. Forum 143–147 (1997) 1631.
[11] W. Bollman, Crystal Defects in Crystalline Interfaces, Springer, Berlin, 1970.
[12] E.A. Garcia, J. Nucl. Mater. 224 (1995) 299.
[13] E.A. Garcia, J. Kovacs, J. Nucl. Mater. 210 (1994) 78.
[14] R. Piotrkowski, A. Denis, J. Kovacs, E.A. Garcia, J. Nucl. Mater. 202 (1993) 252.
[15] P. Kofstad, High Temperature Corrosion, Elsevier, New York, 1988.
[16] H.-O. Peitgen, H. Jöurgen, D. Sauoe, Chaos and Fractals: New Frontiers of Science, Springer, New York, 1992, p. 984.
[17] V.Y. Gertsman, A.P. Zhilyaev, J.A. Szpunar, Modelling Simul. Mater. Sci. Eng. 5 (1997) 35.
[18] A.P. Jiliaev (Zhilyaev), V.Y. Gertsman, J.A. Szpunar, in: Interfacial Engineering for Optimized Properties, MRS Symposium Proceedings, vol. 458, 1997.
[19] M.G. Glavicic, private communication.
[20] Zirconium: Physico-Chemical Properties of its Compounds and Alloys, Atomic Energy Review, International Atomic Energy Agency, Vienna, 1976.