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Effect of the segregation-induced potential barrier on gas/solid kinetics. Impact on corrosion kinetics of Zircaloy

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Abstract

The surface vs. bulk defect chemistry of zirconia is considered in terms of electrical properties, such as electrical conductivity (bulk) and work function (surface). The difference between the two is considered in terms of segregation-induced concentration gradients. It is postulated that the transport of charged defects through the interface layer of zirconia may be influenced strongly by the local electric field, which is formed within this layer across the segregation-induced concentration gradients. The effect of this field on the oxidation kinetics of metals and alloys, such as Zircaloy, is considered. © 1997 Elsevier Science B.V.

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1. Introduction

It has been assumed generally that equilibration processes in metal oxides are rate-controlled by the bulk mobility of point defects, such as oxygen and metal vacancies. It has also been assumed that the rate of surface reactions is very fast and, concordantly, the gas/solid equilibration rate is determined by the bulk transport kinetics [1]. The same model has been generally assumed for zirconia as well. Accordingly, it has been considered that equilibration for the oxygen/zirconia system is rate controlled by the bulk mobility of oxygen vacancies rather than by a surface reaction.

The effect of segregation-related effect on heterogeneous kinetics in nuclear materials has already been considered by Yamawaki and Yamaguchi [2]. It was shown that interface segregation of impurities has an impact on the permeation rate of deuterium through metallic membranes.

The purpose of the present work is to consider the mechanism of the equilibration in the oxygen/zirconia system. Specifically, this work considers the effect of the segregation-induced electric field, formed within the interface layer of zirconia, on the transport kinetics of charge and matter through this layer. Concordantly, it is postulated that the oxidation kinetics of Zircaloy may be substantially retarded by the segregation-induced electric fields, causing a near-surface diffusive resistance for the transport of oxygen vacancies through the zirconia scale which is the oxidation product of Zircaloy.

Discussion of the segregation-related effects is preceded by a short description of the high-temperature Kelvin probe, which has been used for ‘in situ’ surface monitoring of processes at the oxygen/zirconia interface, and defect chemistry of zirconia.

2. Kelvin probe as a method for ‘in situ’ surface monitoring

The high temperature Kelvin probe has been applied to measure the work function (WF) of oxide materials at elevated temperatures, up to 1000°C, and under controlled gas phase composition [3,4]. In this method, a contact potential difference (CPD) is measured between the studied oxide specimen and a Pt reference electrode:

$$CPD = (1/e)(\phi_2 - \phi_1), \qquad (1)$$

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where e is elementary charge and ϕ_1 and ϕ_2 are the WF values of the Pt reference electrode and the studied specimen, respectively. Thus, WF changes of the studied specimen may be determined in respect to the Pt reference level:

$$\Delta\phi_2 = e\Delta\mathrm{CPD} + \Delta\phi_1. \qquad (2)$$

Isothermal WF changes at elevated temperatures, due to changes in oxygen partial pressure, may be expressed by the following relation [3]:

$$(1/kT)\{\partial\phi/\partial\ln p(O_2)\} = 1/n. \qquad (3)$$

Knowledge of the component $\Delta\phi_1$ in Eq. (2) is required to determine the WF changes of the studied specimen as a function of $p(O_2)$. It has been shown that the parameter n in Eq. (3) for Pt at elevated temperatures is equal to 7.1 [3–5]. This value characterizes the extent of the WF changes of the Pt reference electrode as a result of changes in $p(O_2)$.

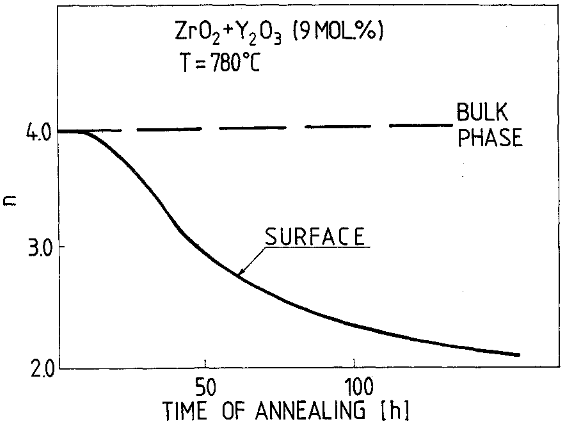

Fig. 1. Absolute value of the reciprocal of oxygen of a bulk electrical property, such as electrical conductivity, and a surface electrical property, such as work function, of yttria-doped zirconia as a function of annealing time at 780°C [5].

3. Defect chemistry of zirconia

The predominant defects in zirconia are oxygen vacancies, which react with oxygen according to the following reaction:

$$1/2O_2 + V_{\ddot{O}} + 2e' \leftrightharpoons O_O. \qquad (4)$$

The charge neutrality condition for yttria-doped zirconia requires that

$$[V_{\ddot{O}}] = 1/2[Y'_{Zr}]. \qquad (5)$$

The reciprocal of the $p(O_2)$ exponent, n, of WF above 1400 K is equal to four [6] what is in agreement with the above defect disorder model.

It was shown, however, that segregation of impurities, such as Ca, may result in the formation of concentration gradients within the surface layer. Then the parameter n in Eq. (3) assumes different values than that predicted by the above ideal defect model.

Evaluation of defect disorders at the surface is only possible using a surface sensitive method, such as WF. So far WF is the unique surface sensitive technique which can be applied for 'in situ' study of surface properties of oxide materials.

4. Surface electrical properties of zirconia

Loup and Odier [6] have found that, in the range 1400–1600 K, the $p(O_2)$ WF dependence of yttria-doped zirconia is in agreement with Eq. (3). A more complicated picture was obtained from studies of zirconia during long annealing at 780°C [5]. It was shown that the parameter n in Eq. (3) is equal to four, as predicted by defect chemistry, only during a short period of time, while longer annealing resulted in a substantial change in the parameter n, which took place over 250 h. As seen from Fig. 1, the parameter n in Eq. (3), which corresponds to the defect structure at the surface, exhibits variations between $n = 4$, at the beginning, to $n = 2$ after 200 h. At the same time, the bulk electrical properties, monitored by, for example, electrical conductivity, results in the $p(O_2)$ exponent equal to four which is independent of the annealing time. This study indicates that the crystalline bulk reaches an equilibrium state (which should be defined as a quasi-equilibrium) very quickly while the equilibration process at the surface layer is much slower. It was shown that this slow process involves Ca segregation, which is present in the bulk at the level of several ppm's and, after segregation equilibrium is reached, assumes several percent at the surface. At the same time the bulk concentration of Ca remains virtually unchanged. In consequence, segregation results in the formation of a strong concentration gradient and related electrical potential gradient within the boundary layer, as it is schematically illustrated in Fig. 2.

Equilibrium within an oxygen/metal oxide system requires that chemical activity, μ_i, of all components within the system is constant where μ_i is defined as

$$\mu_i = f_i a_i, \qquad (6)$$

where f_i is activity coefficient and a_i is activity. The formation of the segregation-induced chemical potential gradient in equilibrium thus requires to assume that also the activity coefficient exhibits a gradient within the boundary layer.

It was postulated that the electric field, which is formed

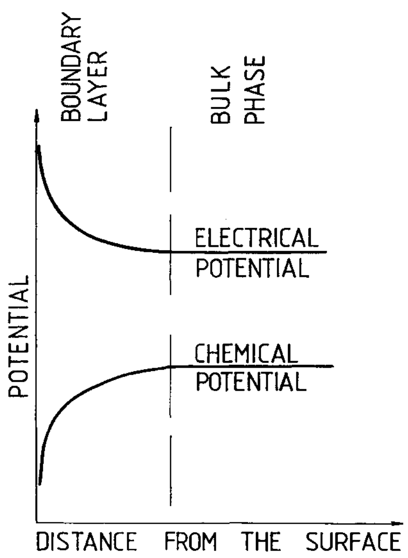

Fig. 2. Schematic illustration of both chemical and electrical potential barriers within the boundary layer and the bulk phase of zirconia [7].

along the segregation-induced concentration gradient, has a substantial effect on the transport of charge defects through this layer [7]. Concordantly, the segregation-induced potential barrier has an effect on the gas/solid heterogeneous kinetics [7]. This barrier assumes significant values even at high temperatures. Accordingly, oxidation of metals and alloys may be efficiently retarded by appropriately engineered segregation-induced diffusive resistance within the boundary layer of oxide scales. Fig. 3 illustrates schematically a retarding effect of an electrical potential barrier on chemical diffusion coefficient, D_{chem}, in oxides where D_{chem} is defined as a rate constant of the equilibration process for a metal oxide/oxygen system.

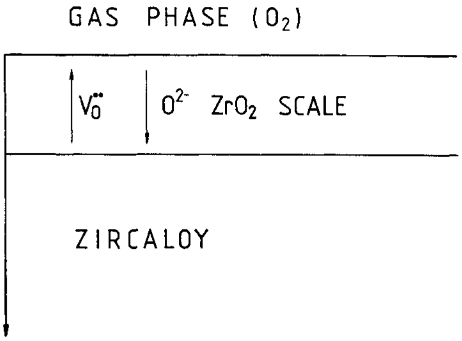

Fig. 3. Schematic illustration of the oxidation corrosion of zircaloy involving the transport of oxygen, and equivalent transport of oxygen vacancies, through the zirconia scale.

5. Corrosion of Zircaloy

5.1. Corrosion mechanism

Oxidation of Zircaloy has a substantial economical and environmental impact. Therefore, there have been many attempts to inhibit its corrosion [8–13].

Corrosion of zirconium alloys, including Zircaloy, in high temperature aqueous environments has been usually considered to be controlled by the growth of a protective surface oxide layer. The corrosion process includes several interfering phenomena, such as dissolution and precipitation of ZrO_2 [8], radiation-induced corrosion acceleration [9], thermal or radiation-induced transformations of ZrO_2 [10], acceleration of corrosion by hydrides precipitates and lithium addition in the water coolant [11]. The problems related with corrosion of Zircaloy have been extensively overviewed in Refs. [8,12,13].

5.2. Corrosion inhibition

Amongst several phenomena interfering with the corrosion of Zircaloy, the corrosion rate has been considered to be controlled by the transport of oxygen through the zirconia scale, which is the product of Zircaloy oxidation (Fig. 4). One should expect that oxygen transport through the zirconia scale occurs predominantly via doubly ionized oxygen vacancies, which are the predominant defects of zirconia and which are known to have a high mobility. Consequently, inhibition of Zircaloy corrosion requires to retard or to block the transport of oxygen through the zirconia scale. Possible way of tackling this problem may involve interface engineering aiming at imposition of a segregation-induced electric field at the zirconia/Zircaloy

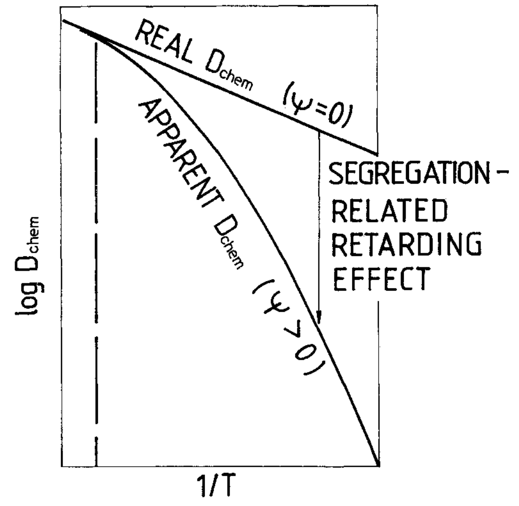

Fig. 4. Illustration of the effect of the segregation-induced potential barrier on chemical diffusion coefficient in metal oxides.

interface. This field may be generated by segregation-induced concentration gradients of aliovalent ions within the boundary layer of the zirconia scale. Thus generated potential barrier may retard corrosion if its polarity and height result in the formation of a diffusive resistance [6] which effectively retards or blocks the transport of oxygen vacancies through the scale. One should, therefore, expect that the most efficient retarding effect will be imposed by a negative electric charge in the space charge layer which will result in a substantial reduction of the concentration of oxygen positively charged defects, such as oxygen vacancies. Then the transport will occur via substantially less mobile cation vacancies.

The electric field, required for corrosion inhibition, may be imposed by segregation of the defects which result in the formation of required space charge. Stability of the barrier may be achieved when the segregation-induced concentration gradient correspond to segregation equilibrium. In this case interface engineering would require adding traces of these elements whose segregation is desired to form a barrier which remains stable in the operational or storage conditions of the cladding material.

6. Conclusions

Rate of oxidation corrosion of Zircaloy is determined by the transport kinetics of oxygen vacancies, which are the predominant defects in the zirconia scale formed as an oxidation product of Zircaloy. This oxidation rate may, therefore, be retarded be reduction of the concentration of the oxygen vacancies. This may be achieved by imposition of a segregation-induced electric field formed within the boundary layer of the zirconia scale. This field may be generated by segregation-induced concentration gradients of aliovalent ions at gas/solid or solid/solid interfaces. Imposition of the potential barrier of appropriate polarity and height requires knowledge of segregation equilibria in the zirconia scale.

Zirconia is known as an oxygen conductor with a wide range of applications to electrochemical devices, such as solid oxide fuel cells and chemical gas sensors. From the viewpoint of these applications of zirconia, intensive studies aim at increasing oxygen conductivity of zirconia. On the other hand corrosion inhibition of Zircaloy requires one to produce a zirconia scale of reduced oxygen conduction. Accordingly, studies on corrosion inhibition of Zircaloy should aim at decreasing the concentration of oxygen vacancies in zirconia and, therefore, at reduction of its oxygen conduction. A possible way in tackling this problem may involve imposition of a segregation-induced electric field at the Zircaloy/zirconia interface which may retard the overall transport across the interface.

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