Effect of electric field on oxide layer structure at zirconium oxidation in H₂O, CO₂ and H₂O/CO₂ supercritical fluids

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Abstract. Oxidation of zirconium plates in supercritical fluids H₂O, CO₂ and H₂O/CO₂ was studied at 823 K and 24–39 MPa. An experimental cell was a flat capacitor, where the zirconium plate acted as the anode and the copper plate of the same size was the cathode. The interelectrode gap was 2 mm. The experiments were carried out in the absence of electric field and in the electric field of 300 kV m⁻¹. It has been found that in all cases the oxidized layer consists of two parts: the outer loose layer and the inner dense layer forming an interface with Zr. At oxidation in a medium containing H₂O, there is non-uniformity in distribution of oxygen near the boundary region of the loose and dense layers. When Zr is oxidized in the H₂O/CO₂ mixture, zirconium carbonate is found on the surface. In the electric field, an average specific rate of an increase in the sample mass decreases linearly with an increase in the fraction of CO₂ in the H₂O/CO₂ mixture, and without the electric field it increases. Apparently, the reason for this is formation and subsequent decomposition of zirconium carbonate, leading to additional destruction of the oxidized layer and accelerated oxidation. When Zr is oxidized in CO₂ in the presence of the electric field, a 12-fold increase in the rate of zirconium oxidation is registered, and this is associated with an increase in the surface leakage current due to formation of amorphous carbon.

1. Introduction
Zirconium alloys are widely used in nuclear power engineering as the shells of fuel elements, so their corrosion has been studied in sufficient detail [1]. After the accident at Fukushima-1 nuclear power plant, special attention was paid to the corrosion of these alloys under the conditions of a sharp increase in temperature [2]. Atomic reactors cooled by supercritical fluids (SCF) H₂O [3] and CO₂ [4] are being currently developed, which makes the study of Zr corrosion in these media relevant.

A feature of zirconium oxidation is high solubility of oxygen in it (up to 28.6% at.) [5]. At that, diffusion of O atoms and O²⁻ ions in ZrO₂ is significantly higher than that of Zr⁴⁺ ions [1, 6]. Dissolution of oxygen from already formed oxide layer occurs along the boundaries of Zr grains with formation of arrays of pores [6], which can be the sites of open porosity development [2]. Micro X-ray studies show an increased content of tetragonal β-ZrO₂ near the ZrO₂/Zr interface [7]. Due to a significant volume effect of phase transformation, the transition of β-ZrO₂ to monoclinic α-ZrO₂ contributes to oxide layer destruction and acceleration of oxidation. As a result, a layered structure of the oxide layer with cracks parallel to the interface is formed [1, 7]. In the presence of water, diffusion of hydrogen atoms [1, 2] and hydroxyl ions HO⁻ [8] becomes significant also. We have studied the kinetics of zirconium oxidation in H₂O [9], H₂O/CO₂ [10], and CO₂ SCF [11]. It was found that Zr is
oxidized forming α-ZrO\(_2\) nanoparticles with the traces of β-ZrO\(_2\). The lowest oxidation rate is observed in supercritical CO\(_2\), but a noticeable amount of amorphous carbon is formed there.

Permittivity of H\(_2\)O SCF is \(\approx 1.8\) [12] and permittivity of CO\(_2\) SCF is <1.4 [13], therefore, the effect of electrolysis on Zr oxidation under the action of an electric field can be neglected. This is also indicated by our studies [11, 14], where it was found that a constant electric field under such conditions has a significant effect only on ion transfer in the solid phase. In the electric field, oxidation of Zr in CO\(_2\) SCF is accelerated by an order due to stimulation of the directed migration of O\(^2–\) ions into Zr [11]. Without the electric field, the O\(^2–\) flow is balanced by the reverse electron flow [1, 6].

In this work, we investigated the effect of a constant electric field on the structure of oxide layer at oxidation of Zr in H\(_2\)O, H\(_2\)O/CO\(_2\) and CO\(_2\) SCF, oxidation rate, and composition of gas products.

2. Experimental procedures

The experiments were carried out on the setup and according to the method described previously in [14]. The scheme of experimental setup is shown in figure 1.

The electrical circuit of experimental cell is shown in insert (a). Samples of zirconium with the purity of 99.7% were produced in the form of plates \(1\) with a size of \(\approx 2 \times 10 \times 49\) mm. Similarly shaped plate \(2\) was made of copper with the purity of 99.9%. Copper wire guides (diameter of 1.2 mm) \(3\) were pressed-in at the ends of the plates; these guides were electrically isolated from the reactor walls \(4\) by quartz tubes. Immediately before the experiment, the sample was mechanically cleaned of the oxide film; its geometrical dimensions and mass were determined. The plates were placed in quartz cell \(5\) so that they formed a flat electrical capacitor, where the zirconium plate acted as the anode and the copper one was the cathode. The quartz cell ensured electrical insulation of plates from each other and from the reactor walls. To control the distance between plates \(1\) and \(2\), narrow quartz plates \(6\) with a thickness of 2 mm were used. The assembled cell was placed in tubular reactor \(7\) and blown out with nitrogen until the reactor was sealed to prevent oxidation of Zr.

The temperature was measured with chromel-alumel thermocouples \(8\) (figure 1) and regulated using TERMODAT-25E5 programmable thermostat, the pressure was controlled with SDV-I membrane strain-gauges \(9\). All experimental parameters were registered with a frequency of 10 Hz through ADC LA-2USB-14 \(10\).

Spatial distribution of electric field strength \(E\) with actual configuration and dimensions of the experimental cell was analyzed with ANSYS software. Uniform distribution of \(E\) in the interelectrode...
space was obtained with the exception of plate edges (a band with a width about 0.2 mm), where the field strength increases by 2–3 times. On the reverse side of the plates, the value of $E$ is an order of magnitude lower [14].

The supercritical fluid of a given composition was prepared in high pressure vessel $I I$ (figure 1) with a volume of 355 cm$^3$ and heated to operating temperature by ohmic heaters $I 2$. The reactor, vessel for SCF preparation and collector (13) were electrically isolated from other parts of equipment and evacuated using forevacuum pump $I 4$. The reactor with a sample (volume occupied by SCF is 57 cm$^3$) was heated to 823 K, thermostated, and voltage of 600 V (measured by V1 voltmeter) was set there using TV2 constant voltage source $I 5$. Then, the supercritical fluid was injected through a heated capillary into the reactor using control valve $I 6$. The optimal exposure time ($t_e$), when a noticeable oxidation took place, but no significant changes in the sample shape occurred, was selected on the basis of data on kinetics of Zr oxidation in H$_2$O [9], H$_2$O/CO$_2$ [10] and CO$_2$ [11] SCF. After time $t_e$, volatile reactants were discharged from the reactor into a vacuum collector, and this stopped the reaction in the cell. After the reactor cooling, the sample was removed and its mass was determined.

The composition of volatile reactants in the collector was investigated using MS 7303 mass spectrometer by the procedure described in [15]. The phase composition of the oxide layer was determined using Bruker D8 ADVANCE X-ray powder diffractometer (vertical goniometer of $\theta$/2$\theta$ geometry, $\lambda$ (Cu-K$\alpha$) = 0.15418 nm). To identify the phases, the PDF base is used [16]. The morphology of the oxidized surface of sample was studied using Hitachi S – 3400N scanning (SEM) and transmission (TEM) JEM-2200FS electron microscopes equipped with EDX spectrometers.

Table 1. Conditions and results of tests.

| Test | $x_{CO_2}$ | $E$ (kV m$^{-1}$) | $m$ (g) | $S_0$ (cm$^2$) | $P_0$ (MPa) | $t_e$ (min) | $\Delta m$ (mg) | $v$ (g m$^{-2}$ hr$^{-1}$) |
|------|-------------|------------------|--------|---------------|-------------|-------------|-----------------|-----------------|
| 1    | 0.0         | 0                | 6.5782 | 11.74         | 26.71       | 61          | 3.3             | 2.77            |
| 2    | 0.0         | 300              | 6.4222 | 11.63         | 23.77       | 60          | 4.0             | 3.44            |
| 3    | 0.5         | 0                | 6.5336 | 11.64         | 37.61       | 81          | 4.4             | 2.80            |
| 4    | 0.5         | 300              | 6.7088 | 12.09         | 38.43       | 81          | 3.9             | 2.39            |
| 5    | 0.9         | 0                | 6.2335 | 11.35         | 35.97       | 120         | 7.5             | 3.30            |
| 6    | 0.9         | 300              | 6.6345 | 11.90         | 37.11       | 123         | 4.3             | 1.76            |
| 7    | 0.9         | 0                | 6.5139 | 11.63         | 37.77       | 120         | 22.4            | 9.63            |
| 8    | 0.9         | 300              | 5.8134 | 11.15         | 39.00       | 120         | 4.3             | 1.93            |
| 9$^a$| 1.0         | 0                | 6.0388 | 11.25         | 20.17       | 240         | 0.6             | 0.13            |
| 10$^a$| 1.0       | 300              | 6.3865 | 11.67         | 14.09       | 240         | 7.5             | 1.59            |

$^a$ From [11].

The conditions and results of experiments: number of experiment, molar fraction of CO$_2$ in the initial SCF $x_{CO_2}$, electric field strength $E$, sample mass $m$, initial sample area $S_0$, initial pressure of SCF in the reactor after injection $P_0$, exposure time $t_e$, sample mass increase $\Delta m$, and average specific rate of mass increase $v$ are presented in table 1.

3. Results and discussion

Diffraecy studies have shown that in all experiments $\alpha$-ZrO$_2$ with small additions of $\beta$-ZrO$_2$ is the basis of the oxide layer. A typical example of such a study is presented in figure 2. The minimal size of ZrO$_2$ grain was estimated by the Scherrer equation [17] using the half width of the main peak: $d_{\alpha-ZrO_2} = 18.2$ nm, $d_{\beta-ZrO_2} = 13.3$ nm.
The electron microscopic study of sample cross-sections revealed that the oxidized layer of zirconium electrode facing the cathode consists of two parts: the outer loose layer and the inner dense layer, forming the interface with Zr. A typical example of such a layer is shown in figure 3. In all cases, formation of a double-layer structure is associated with formation of pores and cracks at $\beta \rightarrow \alpha$ transition of ZrO$_2$ due to the volume effect of phase transformation, making up to 5.4% at room temperature (PDF Card 00-037-1484 and 00-050-1089). According to the results of EDX-spectrometric study of the oxide layer, it was found that layer composition is inhomogeneous over the thickness and in the general case it corresponds to ZrO$_{2-x}$. Near the boundary region of the loose and dense layer, there are the areas with lower oxygen concentration, usually corresponding to the composition of solid solution based on Zr$_3$O or its mixture with ZrO$_2$. The minimal concentration of oxygen found in the oxide layer corresponds to an ordered solid solution based on Zr$_6$O [2, 5]. The diffusion ZrO$_2$/Zr interface is clearly visible in figure 3b, c and it is continuous, i.e., it is not determined by structure macro-heterogeneity of the original Zr sample (figure 3a). A change in oxygen concentration in the boundary region can be associated with a release of H$_2$ during oxidation.
of Zr in a medium containing H₂O. Accumulation of H₂ in the pores and cracks formed during the β → α transition of ZrO₂ can lead to partial restoration of some regions of the oxide layer at the boundaries of pores and cracks. It should be noted that the maximum of H₂ solubility in Zr corresponds exactly to the temperature of our experiments of 823 K (5.93% at. H₂) [18]. Therefore, accumulation of H₂ could also occur during sample cooling, which is promoted by acceleration of hydrogen diffusion with an increase in oxygen concentration in the oxidized zirconium layer [2].

An increase in x_CO₂ in SCF leads to an increase in the thickness of the loose layer. The thickness of the loose layer is as follows: in experiments 1–4 and 6–8, it is 2–4 μm (for example, figure 3 b, c); in experiment 5, it is ≈4 μm (figure 3 d), in experiment 7, it is 4–10 μm (figure 3 e), and in experiments 9 and 10 (for example, figure 3 f), almost the entire oxidized layer is loose. At that, in experiments 5–10, the ZrO₂/Zr boundary becomes invisible in SEM images (figure 3 d, e, f), and carbon appears in the EDX spectra due to participation of CO₂ in oxidation of Zr [10]. Blurring of the ZrO₂/Zr boundary can be explained by the fact that with an increase in x_CO₂, the fraction of HO⁻ decreases and the fraction of O²⁻, diffusing into Zr, increases. The ionic radius of HO⁻ is 97 pm [19], and ionic radius of O²⁻ is 132 pm [20]; therefore, at significant concentration of H₂O in SCF, diffusion of HO⁻, accompanied by release of H during Zr oxidation, dominates. Atomic hydrogen diffuses into both ZrO₂ and Zr. Increased concentration of H in Zr can prevent oxidation of zirconium by HO⁻ ions and contribute to formation of a distinguished ZrO₂/Zr boundary.

The SEM and EDX-spectrometric study of the surface oxidized in H₂O/CO₂ facing the cathode showed the presence of a phase containing ZrO₂, as well as an excess of oxygen and carbon with an average atomic ratio [O]/[C] ≈ 2. The only compound, which can be formed under the conditions of our experiments is zirconium carbonate nZrO₂·CO₂·mH₂O (n = 1–3). It can stay stable up to 823 K [21]. The remains of zirconium carbonate found on the sample surface could have been preserved due to sample cooling in the reactor after the release of reactants. It can be seen that in the electric field, v decreases linearly (with a coefficient of approximation confidence R² = 0.984) with increasing x_CO₂, and at E = 0, it increases (figure 4). The extreme values of v at E = 0 (table 1) are not shown in Figure 4 in order to mark out the result for E = 300 kV m⁻¹. Formation and subsequent decomposition of zirconium carbonate during Zr oxidation in H₂O/CO₂ can lead to destruction of the oxide layer and acceleration of oxidation. It follows that the electric field prevents formation of zirconium carbonate, thereby reducing the destruction of oxide layer and an access of the oxidizing agent to metal.

According to mass-spectrometry analysis of gases obtained at oxidation of Zr in H₂O/CO₂ SCF, the main volatile products are H₂, CO and CH₄. The trace amounts of C₂H₄, C₂H₆, C₃H₈, CH₃OH are also detected. Formation of methane and other hydrocarbons is associated with the Fischer-Tropsch synthesis in a medium containing H₂ and CO [10].

![Figure 4](image-url)  
**Figure 4.** The average specific rate of mass increase of the sample vs CO₂ fraction in initial mixture: (1) E = 0; (2) E = 300 kV m⁻¹ (according to table 1).
of Zr oxidation in H$_2$O/CO$_2$ mixture is ambiguous: as water concentration decreases, the rate of oxidation increases by an order (table 1).

**Conclusion**

In this work, we studied the effect of electric field in a gap of capacitor, made of zirconium (anode) and copper (cathode) plates, on the structure of oxide layer and rate of zirconium oxidation in supercritical fluids H$_2$O, CO$_2$ and H$_2$O/CO$_2$ at 823 K. It is found out that the oxide layer of ZrO$_{2-x}$ composition consists of two parts: the upper loose layer and the lower dense layer, forming a boundary with Zr. At Zr oxidation with participation of water, reduced concentration of oxygen was found at the boundary of the loose and dense layers, apparently, due to accumulation of H$_2$ in the pores and cracks of the oxidized layer. The electric field accelerates oxidation of Zr in supercritical H$_2$O and CO$_2$. In the absence of electric field, the rate of Zr oxidation in supercritical H$_2$O/CO$_2$ increases with increasing CO$_2$ concentration, which is explained by formation of zirconium carbonate. The electric field in this case reduces the rate of oxidation, preventing formation of zirconium carbonate. Oxidation of Zr in supercritical CO$_2$ is accompanied by formation of a significant amount of amorphous carbon.

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