Oxidation and hydrogenation of zirconium alloy E110 under electron and plasma irradiation in various conditions

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Abstract. The features of oxidation and hydrogenation of zirconium alloy E110 under electron and plasma irradiation in various conditions are studied. It is revealed that irradiation intensifies both the oxide layer growth and the hydrogen absorption by zirconium. Applying the anode potential on the E110 sample in plasma allowed to achieve the maximum rates of these processes and at the same time to reproduce their characteristic features exhibited in traditional steam tests. This circumstance determines the choice of plasma anodizing as a perspective basis for the method of accelerated testing of Zr alloys.

1. Introduction
Zirconium cladding tubes and other components of a light water reactor core undergo corrosion and hydrogen embrittlement as a result of interaction with the water coolant [1]. To increase the fuel campaign duration and the fuel burnup, the attempts to improve the corrosion resistance of zirconium alloys are being actively undertaken. This activity requires numerous out-of-core tests. However, traditional tests (the exposure of samples in a high-temperature water or steam) take many thousands of hours [1-5], and, therefore, slow down the process of improving current and creating new alloys.

It is known that irradiation with low-temperature plasma or its components allows to increase the rates of oxidation [6-9] and hydrogenation [10-13] of metals. Accelerated growth of the oxide layer is achieved due to the following factors [6]: (i) chemical interaction of active oxygen-containing particles (atoms, ions, radicals) with the surface; (ii) the penetration of fast oxygen-containing particles into the near-surface region due to their kinetic energy; (iii) creation of electric field across the growing oxide layer that stimulates the transport of oxygen anions to the bulk. Accelerated hydrogenation of metals under irradiation with hydrogen atoms or ions arises from the facilitated overcoming of the surface potential barrier by these particles due to their potential or kinetic energy [10-13].

However, the optimal irradiation regime that provides intense oxidation and hydrogenation of zirconium alloys and at the same time reproduces the kinetics of these processes exhibited in traditional steam tests, has not yet been determined. The aim of this work is to study the features of oxidation and hydrogenation of zirconium alloy E110 under electron and plasma irradiation in an oxygen-containing gas ambient in various conditions.

2. Experimental
Samples with dimensions $\approx 7 \times 8 \times 1$ mm$^3$ were cut from a tube of E110 alloy (Zr-1%Nb), rinsed in an ultrasonic ethanol bath, and dried. After that, sets of experiments (from 60 to 1200 min) were carried...
out on the oxidation of the samples under the irradiation with electrons in Ar + 25% O₂ gas ambient or with plasma ignited in this ambient. For comparison, some of the samples were exposed to the gas without irradiation. The residual gas pressure (> 90% - H₂O molecules) in all experiments was \(1\times10^{-5}\) Torr, the working gas pressure \(-1\times10^{-3}\) Torr. During the experiments the samples were kept at a constant temperature of 400°C controlled by a W-Re thermocouple.

To irradiate the samples with electrons in gas, we used an electron emitter manufactured from tungsten wire (diameter 0.5 mm) in the form of a flat spiral of 25 × 25 mm². The emitter was spaced from the sample at a distance of 40 mm. The irradiation was performed with electrons of \(E = 400\) eV by a current of \(i = 0.4\) mA.

For plasma irradiation of the samples, a gas discharge with a hot cathode was applied. The experiments were carried out in two modes. One series of samples was irradiated in plasma at a floating potential, which is several eV lower than the plasma potential near the sample. Another series of samples was irradiated at the anode potential, which is \(\approx20\) eV higher than the floating one.

Before and after the experiments, the samples were weighed using AND BM-20 microbalance to determine the corrosion gain. The amount of hydrogen in the samples and the features of its retention were determined via thermal desorption spectrometry (TDS). During the TDS analysis, the sample was heated from 300 to 1500 K at a rate of 5 K/s, and the desorption flux from the sample was measured. More than 90% of hydrogen was released from the samples in the form of H₂ molecules. Therefore, of all the TDS spectra of H-containing molecules, only the spectra of molecular hydrogen were analyzed.

3. Results and discussion

3.1. Electron irradiation in gas

Figure 1 presents the corrosion weight gain of the E110 alloy as a function of time of exposure to Ar + O₂ gas mixture and electron irradiation in this ambient. It can be seen that without irradiation E110 exhibits close to parabolic oxidation kinetics (the weight gain is proportional to square root of time). This means that the rate-limiting step of the oxide film growth is the diffusion of oxygen ions through it [14]. The corrosion weight gain of the sample by 1200 min of gas exposure was equal to \(\approx10\) mg/dm².

![Figure 1. Oxidation curves of the E110 samples exposed to Ar + O₂ gas mixture and irradiated with electrons (400 eV, 0.4 mA) in this ambient.](image)
Under the electron irradiation, the oxidation of E110 alloy occurs much faster. By 600 min of irradiation, the corrosion weight gain of the sample reaches 20 mg/dm$^2$, which is 3 times more than that of the gas-exposed sample for the same time. Besides, the rate law of E110 oxidation under electron irradiation evolves with time. During the first 120 min of irradiation, the oxide layer grows in approximately the same way as under the gas exposure, but then the accelerated linear oxidation occurs. One can believe that the reason for this acceleration is the emergence of a strong electric field across the growing oxide layer on the E110 alloy, which acts on oxygen ions in the oxide lattice and causes their transport to the bulk [6, 7]. The electric field arises from the dielectric properties of the oxide layer, due to which the flux of electrons reaching the surface charges it negatively with respect to the inner boundary of the oxide layer. The deviation of the oxidation kinetics from parabolic to linear indicates that the field-induced transport becomes much more significant than diffusion.

TDS analysis showed (Table 1) that during the gas exposure of the E110 sample, the hydrogen content in it does not change, while under the electron irradiation, hydrogen is absorbed by the sample, apparently, from the water molecules of residual gas.

|                     | Hydrogen content, $\times 10^{19}$ cm$^{-3}$ |
|---------------------|---------------------------------------------|
|                     | 120 min | 600 min |
| Before experiment   | 2.5 ± 0.2 | 2.5 ± 0.2 |
| After gas exposure  | 2.7 ± 0.2 | 2.6 ± 0.2 |
| After electron irradiation | 2.9 ± 0.2 | 3.1 ± 0.2 |

Both exposure and electron irradiation of the E110 sample in the gas changes the shape of the TDS spectrum of hydrogen from the sample (Figure 2). After 120 min of both experiments, when the corrosion weight gains of the samples were the same (≈3.5 mg/dm$^2$), the hydrogen spectra were also almost identical. In both spectra, in addition to the main peak at 1300 K, the low-temperature part (below 1200 K) appeared. Since it is known that the surface oxide (even native one) is a limiting factor for hydrogen desorption from zirconium [10, 15, 16], it is reasonable to assume that the high-temperature peak at 1300 K corresponds to the release of hydrogen from zirconium having an undisturbed oxide on the surface. Then, the emergence of low-temperature part in the TDS spectra of hydrogen indicates partial loss of the protective functions by the surface oxide layer during the experiment, presumably, due to hydroxylation of this layer upon penetration of hydrogen from metal into it.

![Figure 2. TDS spectra of hydrogen from the E110 sample before and after the exposure to Ar + O$_2$ gas mixture and electron irradiation in this ambient for 120 min (a) and 600 min (b).]()}
After 600 min of the experiments, when the weight gain of the sample irradiated with electrons (≈20 mg/dm²) significantly exceeds that of the sample exposed to gas (≈7 mg/dm²), the TDS spectra of hydrogen from these samples differ in shape. In the spectrum of hydrogen from a slowly oxidized sample, the low-temperature part continues to increase, while the peak at 1300 K decreases. In the spectrum of hydrogen from a sample with a rapidly growing oxide layer, opposite changes occur: the low-temperature part of the spectrum reduces, while the main maximum grows. It can be concluded that with the rapid growth of the oxide layer, its barrier properties are restored.

3.2. Plasma irradiation

In Figure 3 one can see the curves of the E110 oxidation in plasma at floating and anode potential in comparison with gas oxidation. It is seen that at both potentials on the sample, the oxidation rate in plasma is higher than in gas. By 600 min of plasma irradiation at floating potential, the corrosion weight gain of the sample reaches 22 mg/dm² (3 times more than in gas), at anode potential – 35 mg/dm² (5 times more than in gas).

![Figure 3](image)

Figure 3. Oxidation curves of the E110 samples exposed to Ar + O₂ gas mixture and irradiated in plasma at floating and anode potentials.

It should be noted that the kinetics of E110 oxidation in plasma (at both potentials) is close to parabolic, which is inherent for diffusion-limited growth of an oxide film. At floating potential, the acceleration of the oxide growth is achieved mainly due to the facilitated penetration of active oxygen-containing plasma particles (atoms, ions, radicals) through the surface. As a result, the oxygen diffusion through the oxide layer accelerates while remaining the rate-limiting step of the oxide growth. When the anode potential is applied to the sample, in addition to the contribution of active particles, the oxygen transport is also affected by the enhancement of electron-assisted oxygen dissociation on the surface as well as by the electric field arising across the oxide layer. As a result, the oxidation rate becomes faster than at the floating potential on the sample. However, the field-induced transport in these conditions is apparently less significant than diffusion. Therefore, the oxidation kinetics remains close to parabolic.

Plasma irradiation, like the previously considered electron irradiation in gas, leads to the trapping of hydrogen in the E110 sample from the water molecules of residual gas (Table 2). Besides, under the irradiation at anode potential, the hydrogen uptake occurs more intensely.
Table 2. Hydrogen content of the E110 samples before and after the exposure to Ar + O\textsubscript{2} gas mixture and plasma irradiation in this ambient.

|                        | Hydrogen content, ×10\textsuperscript{19} cm\textsuperscript{-3} |
|------------------------|---------------------------------------------------------------|
|                        | 120 min            | 600 min            |
| Before experiment      | 2.5 ± 0.2          | 2.5 ± 0.2          |
| After gas exposure     | 2.7 ± 0.2          | 2.6 ± 0.2          |
| After plasma irradiation (floating potential) | 3.1 ± 0.2          | 3.1 ± 0.2          |
| After plasma irradiation (anode potential)  | 3.2 ± 0.2          | 3.8 ± 0.2          |

In contrast to gas exposure and electron irradiation (Figure 2), plasma irradiation for 120 min does not cause the appearance of a low-temperature part (<1200 K) in the TDS spectrum of hydrogen (Figure 4). Moreover, the temperature of the main peak of hydrogen desorption from the sample irradiated at anode potential and characterized by the maximum weight gain becomes higher by 50 K. By 600 min of plasma irradiation, in the TDS spectrum of hydrogen from the more slowly oxidized sample (irradiated at floating potential), the low-temperature part (<1200 K) is added to the main peak at 1300 K. At the same time, the maximum of hydrogen desorption from a more rapidly oxidized sample (irradiated at anode potential) shifts further to higher temperatures. Thus, one can conclude that the barrier properties of the oxide layer depend on the oxidation rate. With a relatively slow growth of the oxide layer, its barrier properties reduce, and thermal desorption of hydrogen from the E110 sample begins at lower temperatures. With the rapid oxidation of the alloy, its surface oxide layer remains a barrier for hydrogen, and as it thickens, the time of hydrogen diffusion through it during TDS increases.

Figure 4. TDS spectra of hydrogen from the E110 sample before and after the exposure to Ar + O\textsubscript{2} gas mixture and plasma irradiation in this ambient for 120 min (a) and 600 min (b).

Figure 5 shows a comparison of the E110 oxidation kinetics in Ar + O\textsubscript{2} plasma at anode potential at 400°C and in atmospheric-pressure water steam at the same temperature [10], while in Figure 6 the TDS spectra of hydrogen from the samples tested under these two conditions are compared. It can be seen that the plasma and steam oxidation perform almost the identical kinetics. At the same time, in plasma the oxide layer grows more than 30 times faster. The evolution of the TDS spectra during testing in plasma and in steam is also similar (Figure 6): the main maximum of hydrogen desorption shifts to higher temperatures. Thereby, plasma anodizing seems to be a promising basis for developing a method of accelerated testing of zirconium alloys for corrosion and hydrogenation resistance.
4. Conclusion
The features of oxidation and hydrogenation of zirconium alloy E110 under electron and plasma irradiation in Ar + O₂ gas mixture in various conditions were studied. The experiments revealed that in plasma E110 alloy exhibits parabolic oxidation kinetics ($\Delta m \sim t^{1/2}$), as in traditional steam tests. At the same time, oxidation in plasma occurs up to 30 times faster than in steam. Maximum acceleration of E110 oxidation was achieved when the anode potential was applied to the irradiated sample. Under electron irradiation in gas the rate of E110 oxidation also increases, but the kinetics of this process evolves from parabolic to linear due to the strong influence of the electric field arising across the growing oxide layer.

It was established that under both electron and plasma irradiation, hydrogen is absorbed by E110 alloy from water molecules, which are the main component of the residual gas. The largest hydrogenation rate was observed upon plasma irradiation at anode potential.

The barrier properties of the surface oxide layer of E110 alloy were found to be dependent on the oxidation rate. When the oxidation proceeds relatively slow, the barrier properties of the oxide layer gradually reduce, presumably, due to hydroxylation of the layer upon penetration of hydrogen from metal into it. This decreases the temperature of hydrogen desorption from E110 alloy. When the surface is rapidly oxidized (as in plasma at anode potential on the sample), the barrier properties of the oxide layer are retained, and the hydrogen desorption maximum shifts towards higher temperatures with thickening of the oxide layer. The latter scenario is usually observed in steam tests.

Thus, applying the anode potential on the E110 sample in plasma allowed to achieve the maximum rates of oxidation and hydrogenation and at the same time to reproduce their characteristic features exhibited in traditional steam tests. This circumstance determines the choice of plasma anodizing as a perspective basis for the method of accelerated testing of Zr alloys.

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