RESEARCH OF HIGH-TEMPERATURE OXIDATION BEHAVIOR OF E110OPT AND E110M SPONGE BASED ZIRCONIUM ALLOYS

A.G. MALGIN, V.A. MARKELOV, V.V. NOVIKOV, I.A. SHELEPOV
JSC VNIINM,
Rogova Street 5a, 123060, Moscow, Russia

V.E. Donnikov, V.I. Latunin
JSC VTI
Avtozavodskaya Street 14, 115280, Moscow, Russia

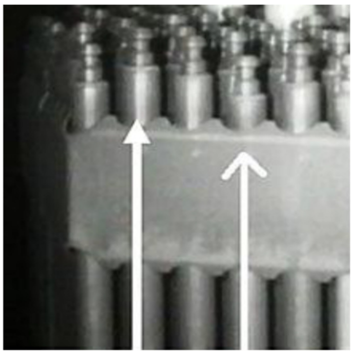
S. Linhart, J. Belac
ALVEL, a.s.,
Stefanikova 41, 602 00 Brno, Czech Republic

V. Vrtilkova, J. Krejci
UJP Praha a.s.,
Nad Kaminkou 1345, 156 10 Prague, Czech Republic

This paper presents the joint results of JSC VNIINM and JSC VTI, ALVEL, a.s. and UJP PRAHA a.s. that are part of the mutual experimental study of Kroll process sponge based E110opt and E110M zirconium alloys. The high-temperature oxidation behavior of these alloys in a water steam environment is presented.
Double-sided oxidation experiments were carried out in the temperature range of 900 – 1250°C on cladding tube samples in their as-fabricated state according to the ASTM standard and NRC LOCA test methodology.
The presented paper contains high-temperature kinetics of E110opt and E110M cladding tubes, results of the metallographic analysis, hydrogen content evaluation, as well as the results of residual ductility evaluation after ring compression tests performed at 20 and 135°C. In addition to the above mentioned, a detailed discussion of these materials' high-temperature behavior compared to NRC LOCA requirements and other oxidation criteria is presented.

1. Introduction

A most important part of the current nuclear power and LWR reactors development tendency is an increase of fuel operation effectivity which is achieved by nuclear fuel cycle improvement, an increase of fuel volume loaded into the core and using the NPP power maneuvering regimes. Because of that, requirements for fuel cladding material properties are getting more strict, as well as requirements for its radiation creep caused deformation resistance.
E110 alloy is mostly used as a nuclear fuel cladding material for VVER reactors. Its material properties meet the NRC LOCA requirements and other oxidation criteria. To improve the deformation resistance of E110 alloy with keeping its corrosion resistance, some certain alloying elements are used, especially oxygen and iron.
As a result of E110 design improvements, two advanced alloys have been developed: E110opt with optimized oxygen (700-990 ppm) and iron (400-700 ppm) content, and E110M with higher oxygen (1000-1400 ppm) and iron (750-1350 ppm) content.
The results of material research and test operation in the VVER reactor core have shown, that fuel rods with E110M cladding have higher resistance against elongation by creep in comparison with fuel rods using "ordinary" cladding from E110 (Fig 1a). In addition, the increase of Fe content in the E110 alloy favorably affects its corrosion resistance in water with lithium (Fig 1b).



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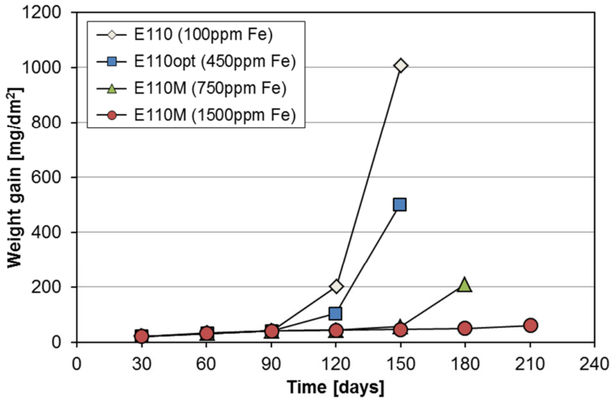

b

Fig 1. An appearance of fuel rod upper plugs from E110 and E110M alloy on a fuel loaded into Balakovo NPP unit 2 (a) and the results of autoclave tests in a water at 360℃ with 70ppm Li of E110, E110opt, E110M sponge-based alloys depending on iron content (b)

Using the E110M alloy as a fuel cladding material requires a complex and deep research, including high-temperature transient tests simulating the LOCA accident. First results of this kind research were presented in [1, 2]. According to NRC requirements and methodologies, a series of various tests have been performed [3-5] with results showing a very good resistance of E110opt sponge based alloy against high-temperature oxidation in a water steam.

This paper presents the results of research and tests of cladding tubes made from E110M alloy under LOCA conditions in comparison with those results of tests performed on samples made from E110opt alloy.

2. Materials and methods

The research was performed on tube samples with a diameter of Ø 9.5×8.33 mm (E110opt) and Ø 9.1×7.73 mm (E110M) sponge based alloys. The chemical composition of both alloys is presented in Table 1. In the as-fabricated state, the outer layer of tubes was polished (Ra=0.2-0.3) and the inner surface was etched (Ra=0.4-0.5).

Alloy/Element	Zr, wt.%	Nb, wt.%	O, ppm	Fe, ppm	Impurities, wt.%
E110opt	balance	1.0	850	550	<0.01
E110M	balance	1.0	1200	950	<0.01

Tab 1: Chemical composition of E110opt and E110M alloys

2.1. High-temperature oxidation behavior

Double-sided oxidation tests of tube samples in a water steam were performed in the temperature ranging from 900 to 1250℃ in special equipment and they were carried out according to NRC LOCA methodologies [6, 7] and ASTM standard [8]. Fig 2 shows the schemes of the experimental setups in VNIINM/VTI and ALVEL/UJP.

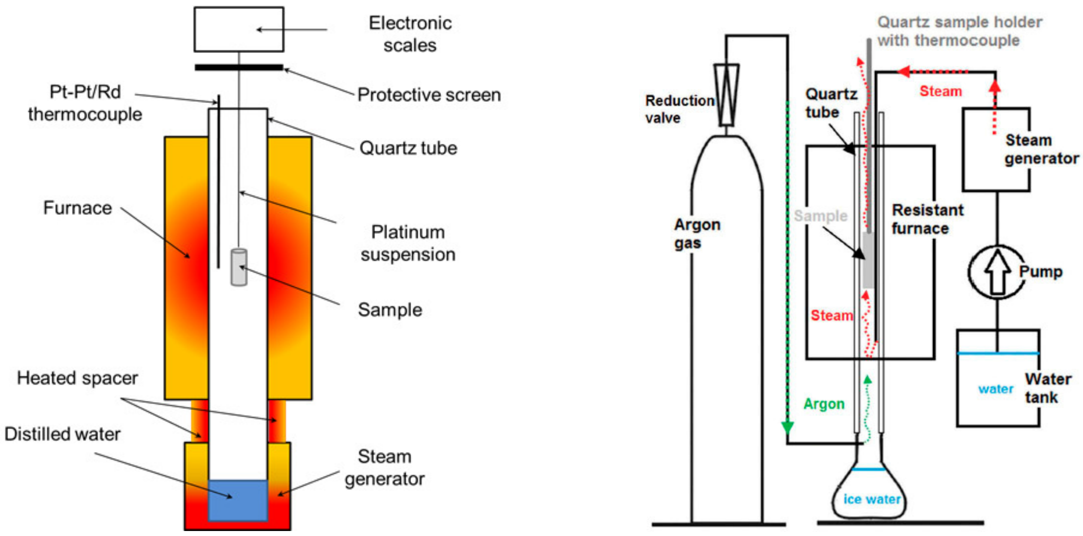

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Fig 2. The schemes of the experimental setups in VNIINM/VTI (a) and ALVEL/UJP (b)

High-temperature oxidation experiments were carried out in a water steam on samples with a length of 30 and 45 mm. Before the experiments, all samples were placed into the ultrasound pool with an ethylic alcohol solution, after that they were washed in ethylic alcohol and then dried for at least 24 hours in a drying box, and then weighed on a laboratory scale with an accuracy of 0.1 mg.

The experiments in VNIINM/VTI were carried out in 100 % water steam. The steam flow rate was 1.5 – 2.0 mg/cm^2/s at 1000℃ and 1100℃ and 5.0 – 5.5 mg/cm^2/s at 1200℃. The experiments in ALVEL/UJP were carried out in a mixture of water steam and argon, the steam flow rate during all experiments was 8.0 – 10.0 mg/cm^2/s.

The experimental procedure was as follows: a sample was heated up with a rate of >20℃/s to a nominal temperature, then exposed at this temperature for a certain time, and then cooled. In VNIINM/VTI experiments the exposed samples were cooled to 800℃ with an average rate of 8 – 11 ℃/s with consequent quenching into the water (Fig 3, A-type cooling). During the heating stage, temperature overshoot was possible, its maximum value was observed at 1200℃ tests and it didn't exceed 20℃ for less than 20 seconds.

The samples of E110opt alloy exposed in ALVEL/UJP experiments were cooled to 800℃ with a rate of 11℃/s with consequent quenching into water with ice (Fig 3, B-type cooling); the experiments on samples from E110M alloy were quenched directly from the nominal temperature into water with ice (Fig 3, C-type cooling). The C type cooling was chosen for an academic study.

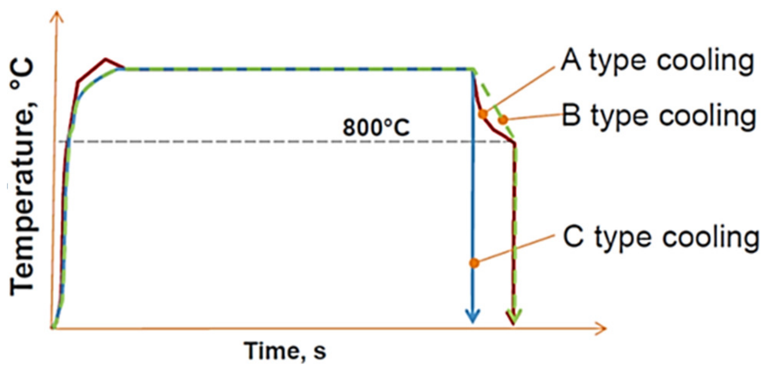

Fig 3. The scheme of high-temperature experiments of samples from E110opt and E110M alloys in VNIINM/VTI (a) and ALVEL/UJP (b, c)

After the high-temperature oxidation, the samples were inspected visually and then weighed on a laboratory scale to obtain the mass gain.
Afterward, the equipment Struers “Accutom-5” (VNIINM) or Buehler (ALVEL/UJP) was used for cutting into ring segments, which were later used for hydrogen content evaluation, metallographic analysis and ring compression tests (Fig 4).

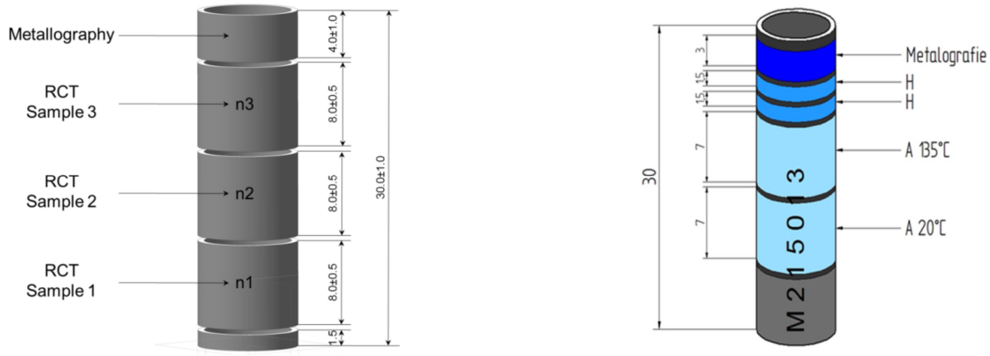

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Fig 4. The scheme of cutting the samples for their further evaluation after high-temperature oxidation in VNIINM (a) and ALVEL/UJP (b)

2.2 Metallographic analysis

The metallographic analysis of the cross-section of the oxidized tube samples with consequent evaluation of reaction layers thickness (ZrO_2, α-Zr(O), prior β) was carried out on the optical microscope Leica DM IRM with AxioVision v4.9 software (VNIINM) and on optical microscope Nikon Neophot 3 with LUCIE Image analyzer (ALVEL/UJP).
A typical microstructure of samples from E110opt and E110M alloys after high-temperature oxidation in water steam is shown in Fig 5.

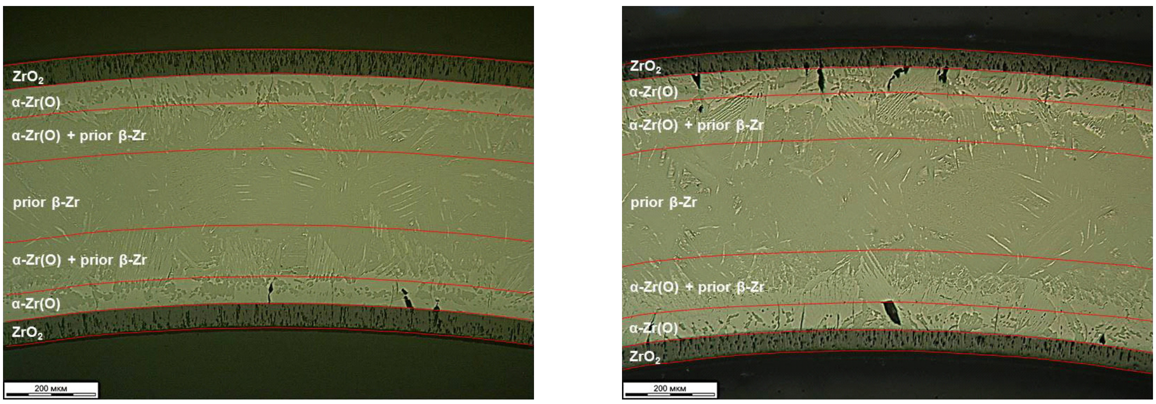

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Fig 5. A typical microstructure of tube samples from E110opt and E110M alloys after high-temperature oxidation in water steam (Tox=1200℃, 17% $ECR_{C\text{-}P}$)

2.3 Hydrogen content evaluation

Hydrogen content was determined according to ASTM standard [9] on a LECO TCH-600 analyzer on ring segments of samples after ring compression tests (VNIINM) or on Exhalograph BA-1 / Bruker Galileo G8 on ring samples with the height of 1.5 mm (ALVEL/UJP).

2.4 Mechanical testing – ring compression tests

Ring compression tests (RCT) were performed according to [7] at 20 and 135°C temperatures at the following equipment: INSTRON 8861 with a temperature chamber INSTRON 3119-408 (VNIINM) and INSTRON 1185 with a temperature chamber INSTRON SFL (ALVEL/UJP). These ring compression tests were performed on samples with the height of 7-8 mm, which were prepared from the samples after high-temperature oxidation. The deformation rate during the mechanical testing was invariable – 0.55 mm/min or 1.0 mm/min. Based on evaluated deformation diagrams, a value of residual ductility of the oxidized sample was determined at the moment of through-wall crack creation (Fig 6).

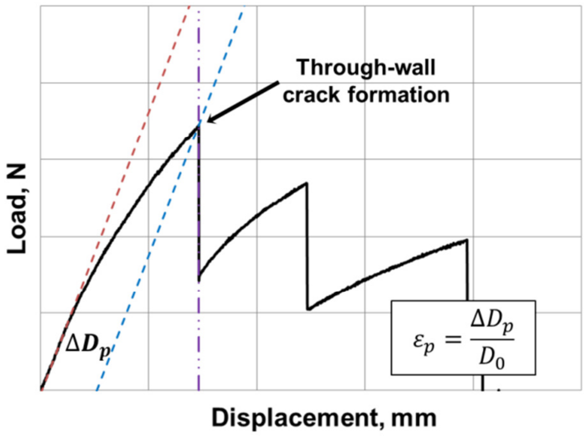

Fig 6. Deformation diagram of the oxidized sample

3. Results of the research

3.1 Oxidation kinetics

The results of the high-temperature oxidation experiments have shown that oxidation kinetics of E110opt and E110M alloys is similar in the temperature range of 900-1250°C and no breakaway effect was observed (Fig 7). It was found a good agreement with E110 sponge based alloy oxidation kinetics data obtained by other investigators [4, 10].

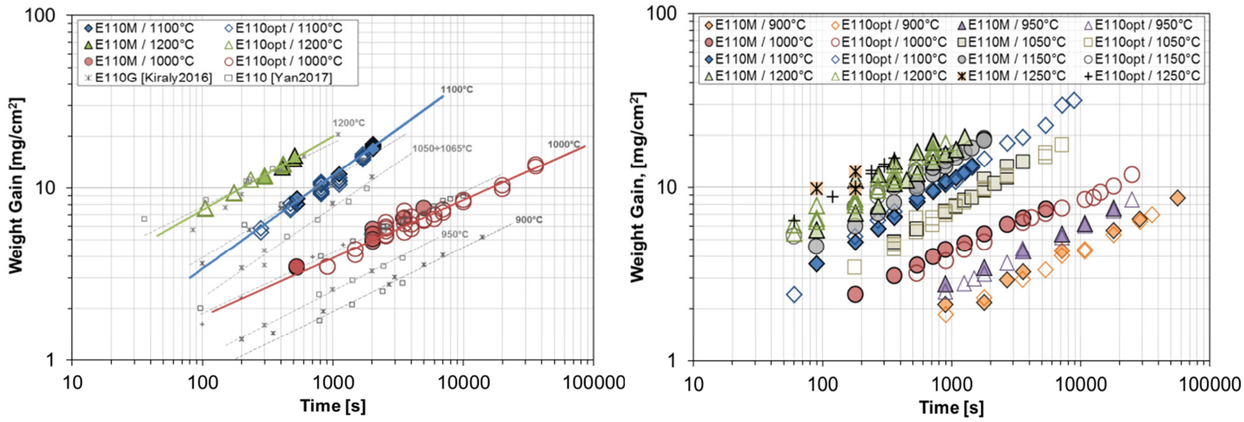

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Fig 7. Oxidation kinetics of E110opt and E110M alloys based on VNIINM/VTI (a) and ALVEL/UJP (b) experimental data

All the samples after high-temperature oxidation were covered by a lustrous-black oxide film well bonded with a metal. A typical appearance of samples after high-temperature oxidation at 1000, 1100 and 1200°C is shown in Fig 8.

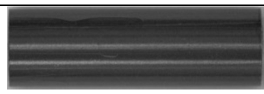
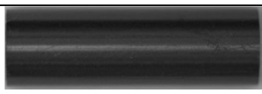
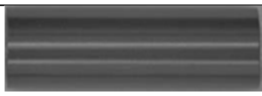
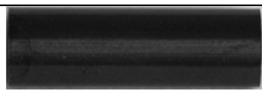
T, °C / Alloy	E110opt	E110M
1000		
1100		
1200		

Fig 8. An appearance of tube samples from E110opt and E110M alloys after high-temperature oxidation in water steam at 1000, 1100 and 1200°C to 17 % ECR_{C-P}

3.2 Metallographic analysis

The results of metallographic analysis have shown, that the kinetics of oxide layer and α-Zr(O) layer growth is mostly similar for both alloys in the temperature range of 1000 – 1200°C (Fig 9). It was also observed, that after high-temperature oxidation at 1000°C, the thickness of the oxide and α-Zr(O) layers of samples from E110M alloy is 20-25% higher than it was observed on samples from E110opt alloy. There was no difference in the oxidation of the inner and outer surface of samples.

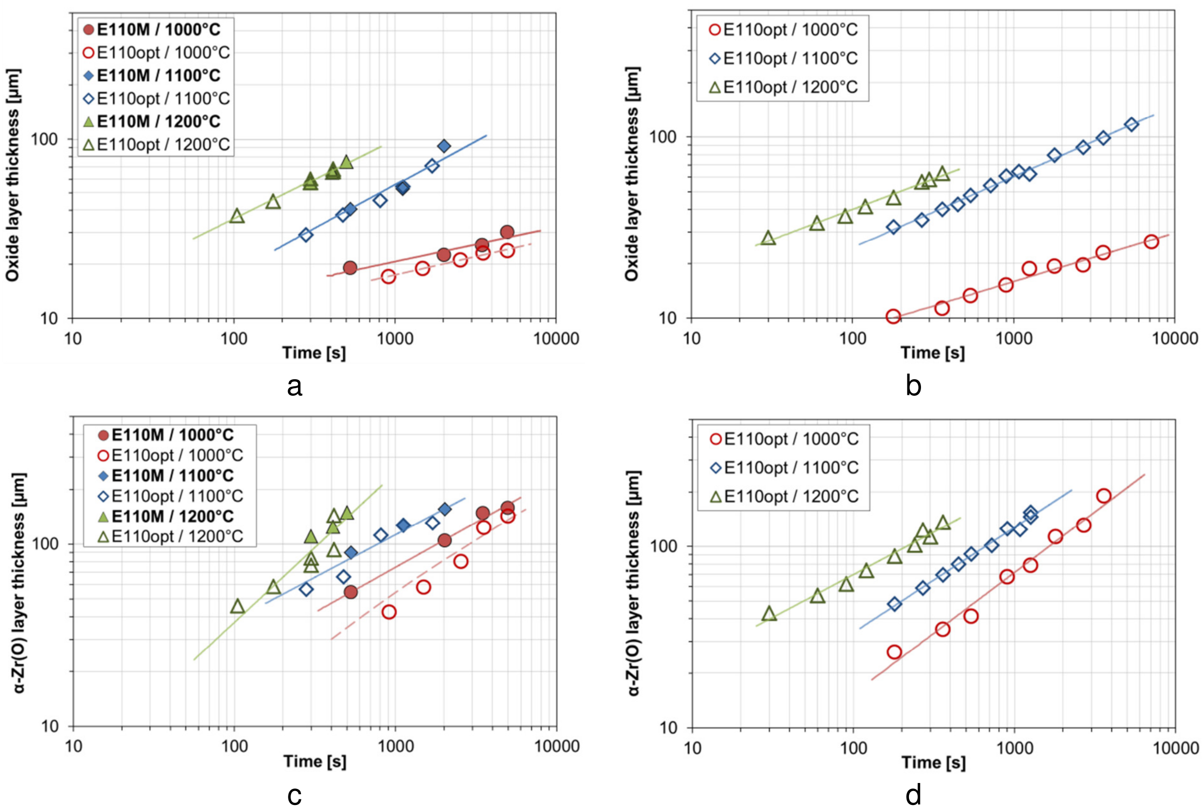


Fig 9. Kinetics of ZrO_2 and α-Zr(O) layers growth of samples made from E110opt and E110M alloys after high-temperature oxidation performed in VNIINM (a, c) and ALVEL/UJP (b, d)

3.3 Hydrogen content

Fig 10 shows the hydrogen content in oxidized samples from the researched alloys after high-temperature oxidation at 1000, 1100 and 1200℃. Hydrogen content in all samples does not exceed 50 ppm, which additionally shows, that there is no breakaway oxidation of E110opt and E110M alloys.

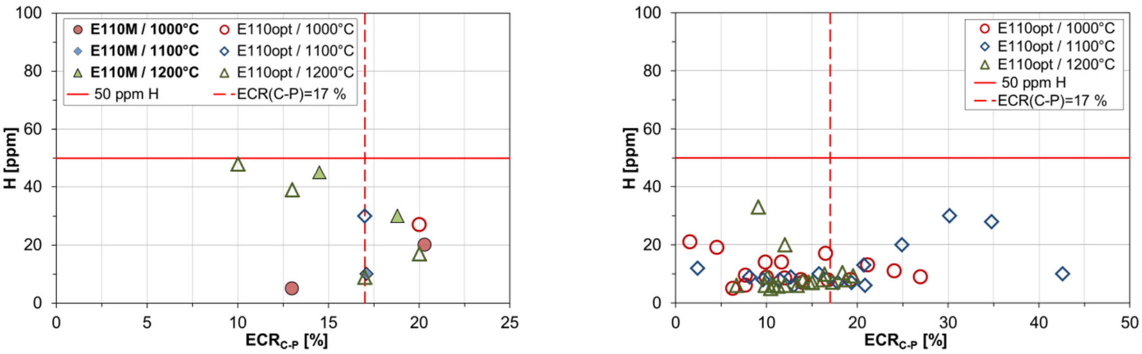


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Fig 10. Hydrogen content of samples from E110opt and E110M after high – temperature oxidation observed at VNIINM (a) and ALVEL/UJP (b)

3.4 Residual ductility

The results of ring compression tests have shown, that the residual ductility of samples from E110opt alloy after oxidation in a steam at the temperature of 900–1200℃ to 17% $ECR_{C\text{-}P}$ is higher than 2% when tested at 135℃ (Fig 11).

As a result of mechanical testing, an impact of the cooling regime on residual ductility was observed. The residual ductility of samples made from E110opt alloy and quenched into water+ice from the nominal temperature (C-type cooling) was slightly lower than the residual ductility of samples cooled to 800℃ and then quenched (A and B-type cooling), when tested at 135℃.

The results of RCT at 20 and 135 °C performed on samples made of E110M alloy after high-temperature oxidation at 1000 and 1100 ℃ have shown, that their residual ductility is still 2% higher ($ECR_{C\text{-}P} \leq 17\%$) and comparable with the results for the E110opt alloy. After high – temperature oxidation at 1200℃, the residual ductility was higher than 1 and 2%, respectively.

It was also observed that the E110M alloy has slightly lower residual ductility than the E110opt alloy. This is clearly visible from the results for 1200℃ (Fig 11e).

A most probable cause of this decrease of residual ductility at 1200℃ is the higher content of iron in the E110M alloy. During the oxidation process, iron and niobium diffuse into β-phase and becoming a “β-stabilizer” they have an impact on oxygen solubility at high temperature, which leads to the additional decrease of material ductility [11, 12]. A similar effect of iron was earlier observed on Zr-Nb-Sn-Fe alloys [13].

The results of WDS analysis, performed on samples from E110opt and E110M after their oxidation at 1200℃ confirm the change of Fe and Nb distribution in the samples (Fig 12).

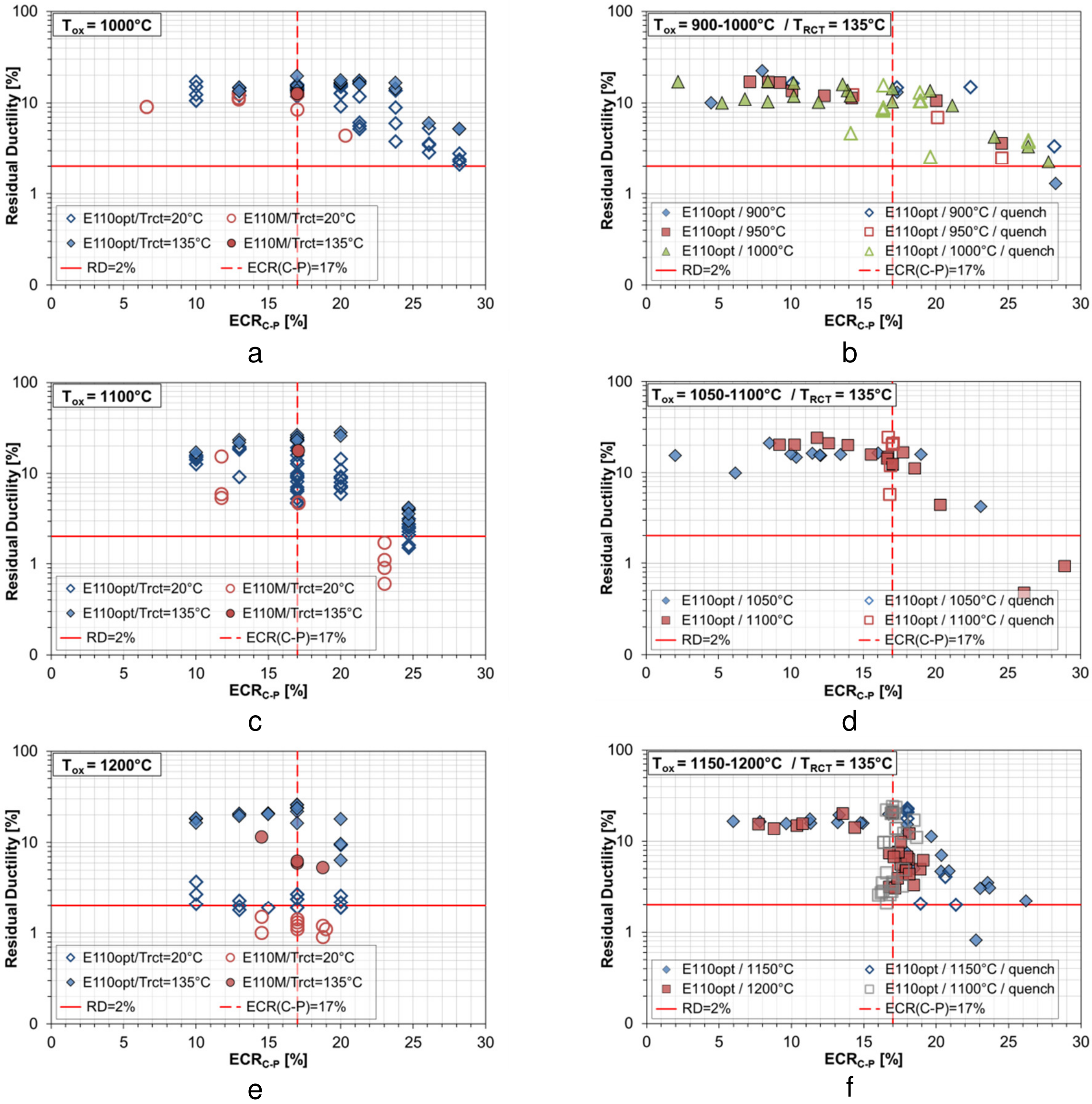

Fig 11. Dependence of residual ductility on ECR$_{C-P}$ after high-temperature oxidation within the temperature range of 900 – 1200℃ (samples made from E110opt and E110M alloys).

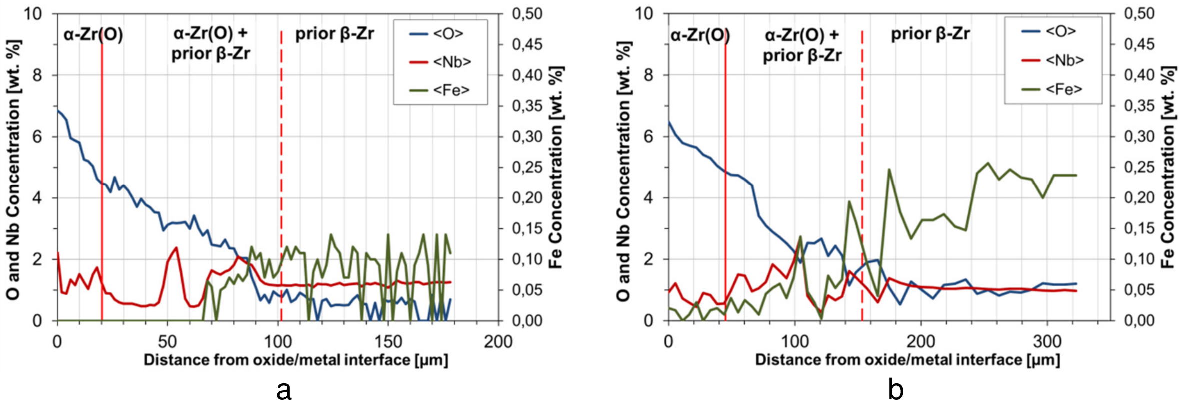

Fig 12. Distribution profiles of Nb, O and Fe along the wall thickness of samples from E110opt (a) and E110M (b) alloys after the oxidation at 1200℃ to 17% ECR$_{C-P}$

Therefore, based on the experimental results, a conclusion can be made, that after high-temperature oxidation of samples made from E110opt and E110M alloys within the temperature range of 900-1200°C to 17% ECR_{C-P}, both these materials keep their residual ductility higher than 2% when tested at 135°C, which meets the NRC LOCA requirements.

6. Conclusions

1. High-temperature oxidation tests performed in VNIINM/VTI and ALVEL/UJP in a water steam within the temperature range from 900 to 1250°C have shown, that no breakaway oxidation was observed during the oxidation of E110opt and E110M alloys on sponge based. All the samples were covered by a black and bright oxide film, well bonded to the metal. The high-temperature oxidation resistance of E110M is comparable with the E110opt alloy.
2. The residual ductility of oxidized samples from E110M and E110opt alloy (900 – 1200°C, $ECR_{C-P} \leq 17\%$) and tested at 135°C is higher than 2%, which meets the NRC LOCA requirements.
3. Hydrogen content of samples from E110opt and E110M alloys after their oxidation to 17% ECR_{C-P} within the temperature range of 900 to 1200°C does not exceed 50 ppm.
4. The results of metallographic analysis of the oxidized samples from E110M and E110opt alloys have shown the difference in oxide and α-Zr(O) layers growth for the temperature of 1000°C. The kinetics of growth of both layers is similar for temperatures 1100 and 1200°C.

7. References

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