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RESEARCH ARTICLE

Investigation of the interaction of material of fuel cladding for WWER-1000 reactor with steam at a temperature of accident overheatings

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Abstract: The subject of this study is the oxidation of fuel rod cladding made of material Zr1Nb(0.1% O) in steam at temperatures in the range of 660°C to 1200°C with a surface in the initial state (after manufacturing - grinding) and after additional chemical etching. The changes in the microstructure of tubes due to the interaction with steam were investigated. A comparison was made between the oxidation rate of this material (weight gain) and the data on the oxidation of other alloys for nuclear power plants. The oxidation rate of Zr1Nb(0.1% O) is close to the oxidation rate of other zirconium alloys. It is shown that after chemical treatment of the surface of the samples there is a more even growth of oxide films, and they have a smaller thickness for the same time of exposure than after mechanical grinding. Surface treatment before oxidation also affects the change of microstructure of samples when heated to high temperatures.

Keywords: high-temperature oxidation, nuclear power plants, zirconium tubes, fuel rod cladding, steam, surface treatment, alloy and oxide structure, accident overheating

1 Introduction

Investigation of high-temperature oxidation of zirconium alloys for the fuel rod cladding of WWER and PWR reactors in steam has been carried out for a long time.[1–9] There were studied as alloys already used in existing reactors for better prediction of their behavior in emergency overheats,[1–4, 7–9] and new materials that were developed to achieve better resistance to oxidation.[5, 6]

Currently, such studies have become particularly relevant in connection with the desire to prevent the release of large amounts of hydrogen due to oxidation in high-temperature steam, the explosion of which led to leakage of radiation at the accident at the nuclear power plant “Fukushima”. In addition, the oxidation of zirconium at high temperatures is accompanied by the absorption of oxygen and hydrogen by the material of the fuel rod cladding, which leads to a deterioration of their mechanical properties and embrittlement with the possible subsequent destruction of the assembly during post-accident unloading and contamination of radioactive substances of the environment. The purpose of this work is to study the high temperature oxidation of Zr1Nb(0.1% O) material obtained in Ukraine[10] .

The corrosion resistance of claddings made of zirconium alloys can depend not only on the chemical composition of the alloy itself, but also by the state of their surface[7] . Thus, additional grinding and fine polishing of the surface of the E110 alloy has led to a significant increase in the protective properties of the oxide film.

The improvement of the corrosive behavior of the E110 alloys is explained[7, 11] by the decrease in surface roughness and the removal of surface impurities, in particular fluorine interacting with the surface of E110 in industrial finishing, including etching in fluorine-containing solutions. Fluorine, known for its negative effect on the corrosion resistance of zirconium alloys, at low temperatures is in the form of compounds (fluorides), but at elevated temperatures, it can interact with the shell material due to the decomposition of fluorides and simultaneously accelerated diffusion.

Thus, it was expedient to investigate the behavior of the oxidation of Zr1Nb(0.1% O) as with the surface in the initial state and after chemical treatment in the fluorine-containing etchers, followed by neutralization

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of possible precipitation of fluorides in a solution of aluminum nitrate and compare the data obtained with data on other reactor zirconium alloys.

2 Materials and methods

Samples of tubes from Zr1Nb(0.1% O) material obtained in Ukraine by the experimental technology[10] were taken for corrosion studies, which included the following main operations: the manufacture of a Zr1Nb material (Zr+1%Nb alloy based on zirconium obtained by reduction of zirconium tetrafluoride with calcium with an oxygen content of 0.14% to 0.16% by weight) and Zr1Nb dilution with zirconium obtained according to Van Arkel method (with an oxygen content of less than 0.05% by weight). The chemical composition of the material by the alloying elements and the main impurities was as follows: 0.9% Nb; 0.08% to 0.10% O; 0.004% to 0.006% N; 0.01% to 0.02% C; 0.003% to 0.005% F. Samples of tubes from this material showed high corrosion resistance at a temperature of normal operation in the reactor (350°C) and temperature of express corrosion tests for fuel cladding (400°C)[12] .

In this paper, the behavior of Zr1Nb(0.1%O) cladding in steam at temperatures of 660°C to 1200°C (which may arise in case of accident overheating in nuclear power plant) was investigated.

The outer diameter of the cladding samples in the initial state was 9.13 mm, the internal 7.72 mm. The sample length was 16 mm. The specimens were tested with both a grinded surface (in the state of delivery) and after additional etching (chemical polishing) according to a special procedure in a solution of bidistilled water containing 5% HF, 45% HNO_3 (% vol), followed by neutralization in an aqueous 30% solution of aluminum nitrate at a temperature of 40°C to 45°C. The outer surface of the samples before oxidation or etching was rubbed with alcohol to remove possible contaminants. The surface of the polished samples in the initial state was light, but matte, and etched-bright and shiny. On grinded samples in the initial state it was possible to notice some marks of grinding on the inner surface of the tubes.

For corrosion tests in steam at high temperatures, the facility shown in Figure 1 was used. It is an electric furnace with alund tube, through which steam formed in a flask of boiling water passes.

3 Results

3.1 Appearance of samples

After oxidation at 660 and 770°C for 10 h, a dark glossy layer of oxide was formed on the surface of both etched and untreated samples, and on the untreated it was more dull (Figure 2).

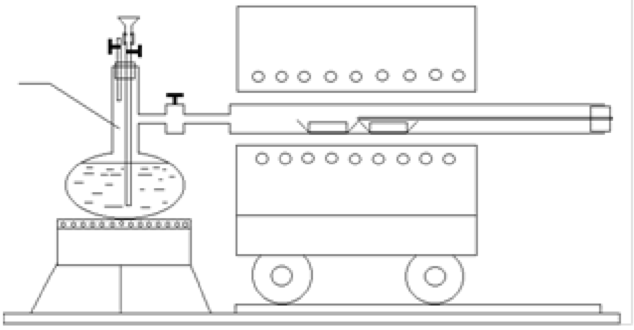

Figure 1. Facility for oxidation tests

After oxidation at 900°C during 5 h, the oxide on the pickled sample stayed dark and shiny, whereas net of cracks filled with white oxide were seen on the dark matted oxide of the non-etched sample.

After oxidation at 1000°C for 3 h, the etched sample oxide had an even, but relatively lighter color, while at the same bright surface of the untreated sample there were not only cracks, but also stains of white oxide.

After oxidation at 1200°C for 0.5 h, the surface of both samples was again quite dark, and a net of cracks with light oxides inside was observed on the untreated sample.

Practically in all samples (to a greater extent this was noticeable on samples oxidized without preliminary etching), the inner surface after oxidation had a lighter shade than the outer surface.

Despite the presence of light areas, there was no visible significant detachment of oxide on any of the test specimens, except for the end sections of the tubes.

3.2 Weight gain and thickness of formed oxide

The weight gain of untreated (grinded) samples in all cases exceeded the weight gain of the etched (Table 1).

The thickness of the oxide layer was measured on the cross-section of the cladding tubes after grinding and polishing. Before fine grinding and polishing, about 1 mm was removed using rough grinding to depart from the edge of the sample. After that, the thickness of the oxide film was measured on the outside and the inside of the sample and averaged. The average thickness of the oxide film on the untreated samples exceeded the thickness of the film on the etched, except for samples tested at 1100°C and 1200°C, for which the thickness of the film on the etched samples was close to the thickness of the untreated.

It was interesting to compare the data of measuring the thickness of films by the method of metallography, that

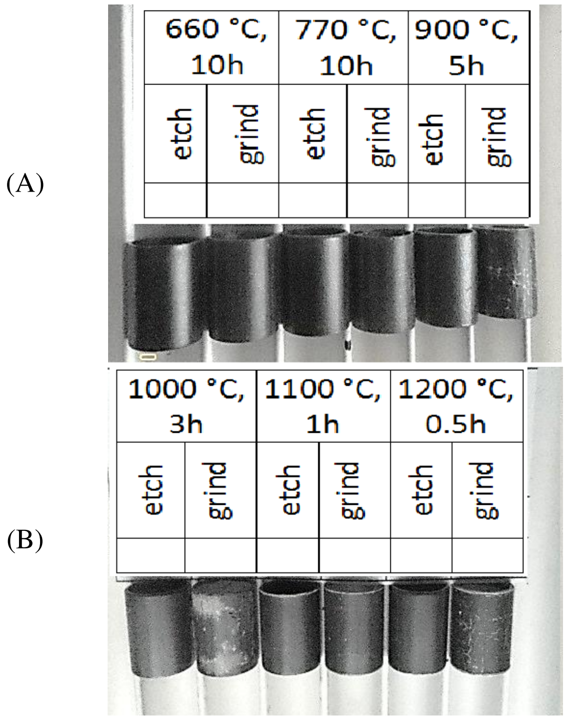

Figure 2. Appearance of samples with untreated and chemically etched surface after oxidation in steam: at 660°C to 900°C (A) and at 1000°C to 1200°C (B)

is, the direct method, and the data obtained by calculation. From the table we can see that at a temperature of 660°C to 770°C and 1100°C to 1200°C, the calculated thickness of the film in all samples is more than measured, but on samples with a surface after grinding at 900°C and 1000°C, the estimated thickness of the film is less than measured.

3.3 Oxide microstructure

The microstructure of oxide layers on untreated and chemically polished samples is presented in Figure 3. After oxidation at a temperature of 660°C to 770°C for 10 h the film was practically homogeneous. There is characteristic cracks formation, when under the crack the new oxide forms, so the crack doesn't reach the metal.

After oxidation at a temperature of 900°C for 5 h a very thick film (100 μm or more) was observed in some places on the untreated sample, which usually consisted of three approximately equal in thickness but different by color layers (each layer is lighter than the one, that under it), while the single-layered film on other sites does not exceed 35 μm to 40 μm. On the etched sample after testing under these conditions, the film is single-layered and its thickness does not exceed 40 μm to 50 μm after 5 h of exposure. After oxidation at 1000°C for 3 h a thick three-layer film on the untreated sample was observed on both sides of the tube (inner and outer). Nevertheless, there are some places with a thickness of up to 50 μm. On the etched sample, the film is single-layered, fairly uniform and its thickness does not exceed 40 μm to 50 μm.

Oxidation at 1100°C was carried out for 1 h and at 1200°C for 0.5 h. The oxide film on both samples is single-layered and reaches about 120 μm (1100°C) and 130 μm (1200 °C), with a well-defined column structure.

After exposure in steam at 900 and 1000°C, for, respectively, 3 and 5 h the microstructure of both series of samples contains the alternation of dark and light areas. You can notice that areas with small plates on the microphotographs look darker, and areas with large plates and grains are light. The proportion of such "dark" areas is to a certain degree larger on samples oxidized without preliminary etching of the surface, due to which the overall structure looks more heterogeneous.

The samples, oxidized at 1100°C and 1200°C, have a structure similar to each other, which consists of packages of large plates. Significant differences in the microstructure of samples with etched and non-etched surface at these temperatures were not detected.

In the regions under the oxide film on all samples after oxidation at 900°C to 1200°C, it is possible to see layers of a lighter structure.

4 Discussion

4.1 Comparison of the oxidation rate of Zr1Nb(0.1% O) with other zirconium alloys

The approximate comparison of the weight gain of Zr1Nb(0.1% O) and other zirconium alloys for the fuel rod claddings is given in Figure 5.

From the Figure 5 it can be seen that the weight gain of Zr1Nb(0.1% O) alloy at all temperatures is into the range of data for other reactor alloys.

4.2 Influence of surface treatment on corrosion resistance and change of microstructure of samples

It is known that the black shiny protective oxide film on zirconium alloys has a lack of oxygen relative to the stoichiometric composition of ZrO_2, and the light color of oxide is associated with an increase in its stoichiometry and a decrease in protective properties.

In our experiments on samples oxidized at 660 and 770°C after surface grinding, the oxide was not as shiny as in the chemically polished, and after the oxidation of

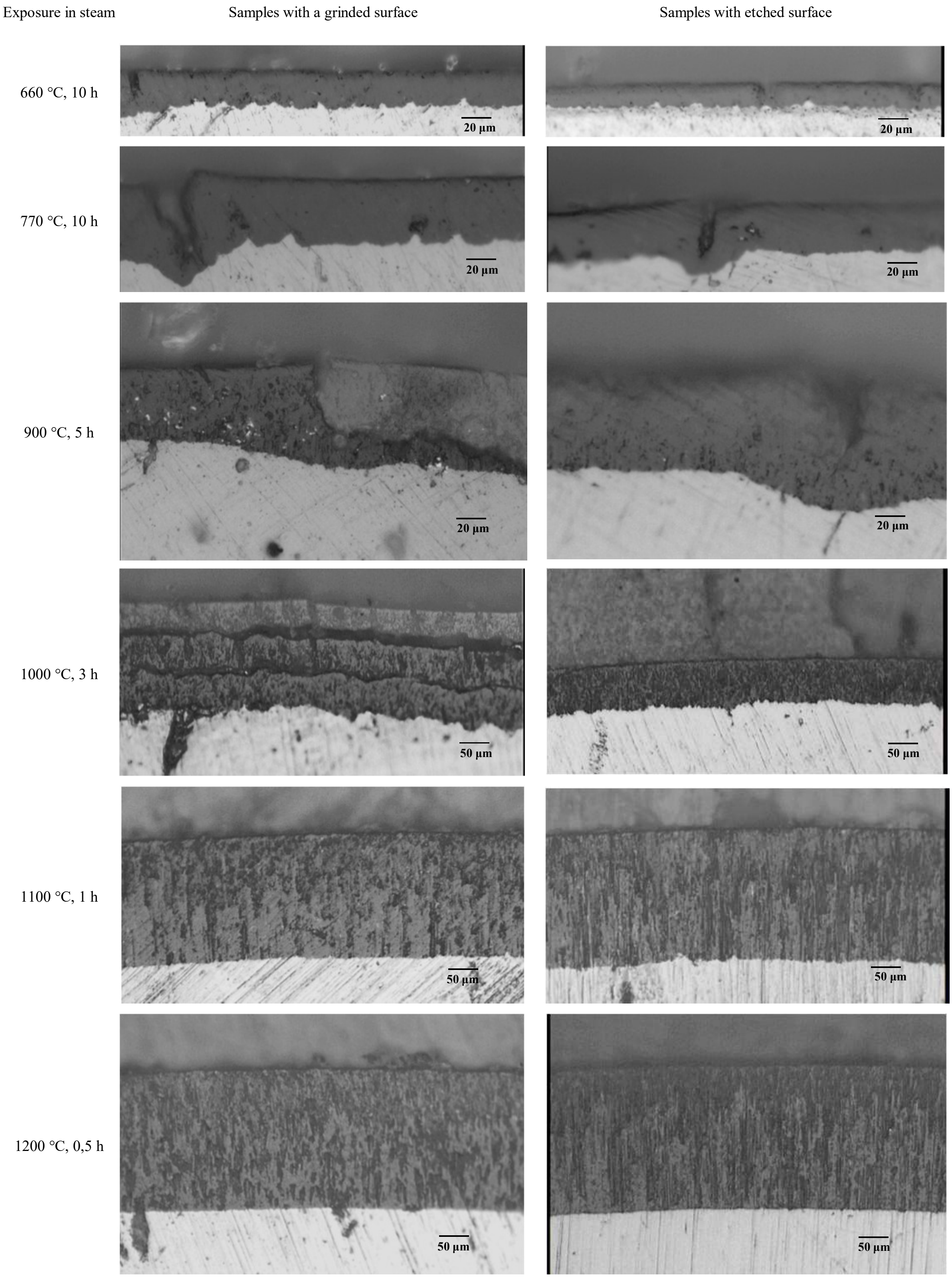

Figure 3. The structure of oxide films formed on the Zr1Nb alloy (0.1% O) after oxidation in steam

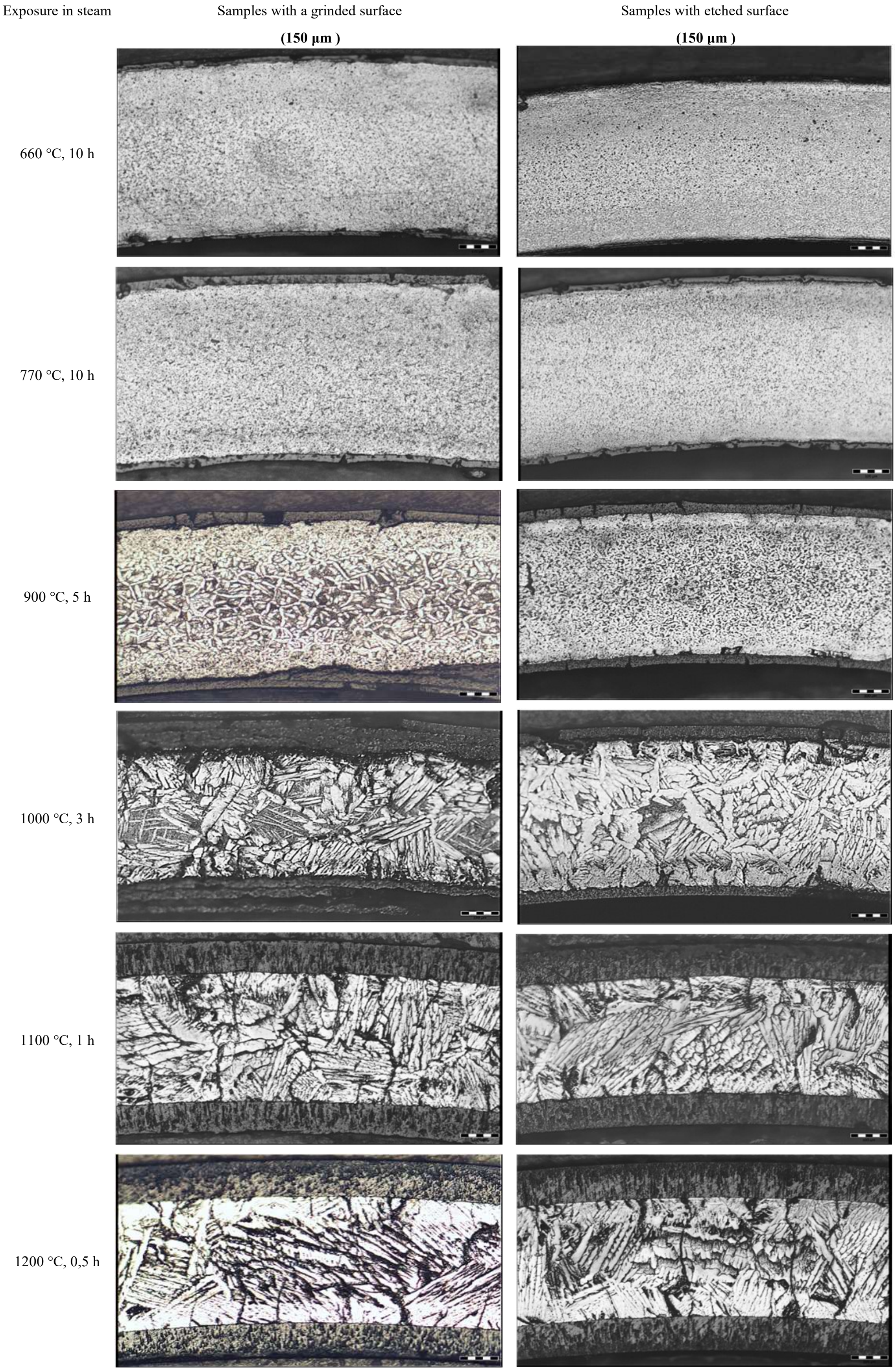

Figure 4. The microstructure of the samples after high temperature oxidation in steam

Table 1. Weight gain, measured and estimated thickness of the oxide layer on samples of Zr1Nb(0.1% O)

Exposure in steam	Samples with a grinded surface			Samples after chemical etching of the surface		
	Weight gain (mg/dm^2)	Measured thickness of the film (μm)	Calculated thickness* (μm)	Weight gain (mg/dm^2)	Measured thickness of the film (μm)	Calculated thickness* (μm)
660 °C, 10 h	205	13,25	13,85	133	6,69	8,99
770 °C, 10 h	352	20,75	23,79	349	18,38	23,6
900 °C, 5 h	836	61,25	56,51	647	33,25	43,7
1000 °C, 3 h	1233	87,5	83,55	873	36,52	59,01
1100 °C, 1 h	1901	116,67	128,5	1899	116,88	128,37
1200 °C, 0.5 h	2104	123,13	142,2	2088	126,25	141,15

Note: *Calculation is made by the ratio: the weight gain of 15 mg/dm^2 corresponds to 1 μm thickness of the oxide film[14]

the polished samples at other experimental temperatures, more light and white portions were observed on the surface. This may mean reducing the protective properties of oxide on samples with a polished surface, which is also confirmed by the fact that for the grinded samples weight gain after oxidation at all oxidation temperatures is higher than that of chemically polished.

The most significant differences in the corrosion behavior of samples with a grinded and chemically polished surface are observed in the range of temperatures 900°C to 1000°C. Thus, the thickness of the oxide on the grinded samples substantially exceeds the thickness of the samples with the chemically treated surface, while on the grinded sometimes there is a layered structure of oxide.

It should also be noted that at a temperature of 660°C to 770°C and 1100°C to 1200 °C, the calculated thickness of the film in all samples is more than measured, which indicates the absorption of oxygen by a metal, but on samples with a surface after grinding at temperatures of 900 and 1000°C, the calculated thickness of the film is less than measured, which may indicate defects in the microstructure of oxide films (loosening), which leads to a decrease in their density.As for the microstructure of the metal after the exposure in steam at elevated temperatures, the microstructure of the Zr-1%Nb alloy samples after the oxidation at 660°C still has the appearance of the initial low-temperature α-phase of zirconium. Differences in the structure of the samples begin after exposure in steam at a temperature of 770°C. Thus, in the structure of the untreated specimen, the precipitates similar in morphology with hydrides were quite distinct, which were not observed on the sample oxidized after the preliminary treatment of the surface.

The samples oxidized at 900°C to 1200°C have a structure typical of the former high-temperature β-phase of zirconium converted by cooling to the lamellar α-phase. In areas under the oxide film, you can see a lighter layer, such like as the so-called oxygen-stabilized α-layer on Zy-4.

On samples oxidized without prior chemical treatment, after oxidation at 900°C and 1000°C, a greater heterogeneity of the metal structure is observed (Figure 4). This is possible if when cooled, the first plates of the α-phase are first formed in places enriched in oxygen and begin to grow. This is due to the fact that oxygen is better dissolved in the α-phase of zirconium than in the β-phase, and therefore begins to further diffuse into the α-phase. In places where the amount of oxygen is lowered, the α-phase plates begin to grow later and will be smaller. As far as hydrogen is concerned, it has opposite properties for α- and β-phases of zirconium than oxygen. Thus, the heterogeneity of the metal microstructure of samples oxidized without prior chemical treatment can be explained by the redistribution of the increased amount of oxygen and hydrogen received as a result of enhanced corrosion.

These phenomena can be related to the properties of the growth of the oxide film on the samples. As to Figure 3. oxide film on tubes with grinded surface after oxidation at temperatures of 660°C to 1000°C is thicker than film on samples oxidized after chemical treatment of the surface, and besides that after oxidation at 900°C and 1000°C the film on grinded tubes may consist of several relatively thick layers. A similar but more fine lamellar structure is being observed in oxide films after oxidation at normal operation temperatures and in the literature is associated with transitions in the kinetics of oxidation of zirconium alloys[13] , which lead to the partial reduction of protective properties of the oxide film (due to the formation of nanopores).[14, 16] The frequency of such transitions in the kinetics of oxidation is associated with the chemical composition of the alloy. The surface finish quality can affect the content of impurities in the near-surface layer, and, consequently, the rate of oxidation, the frequency of transitions in the kinetics of oxidation

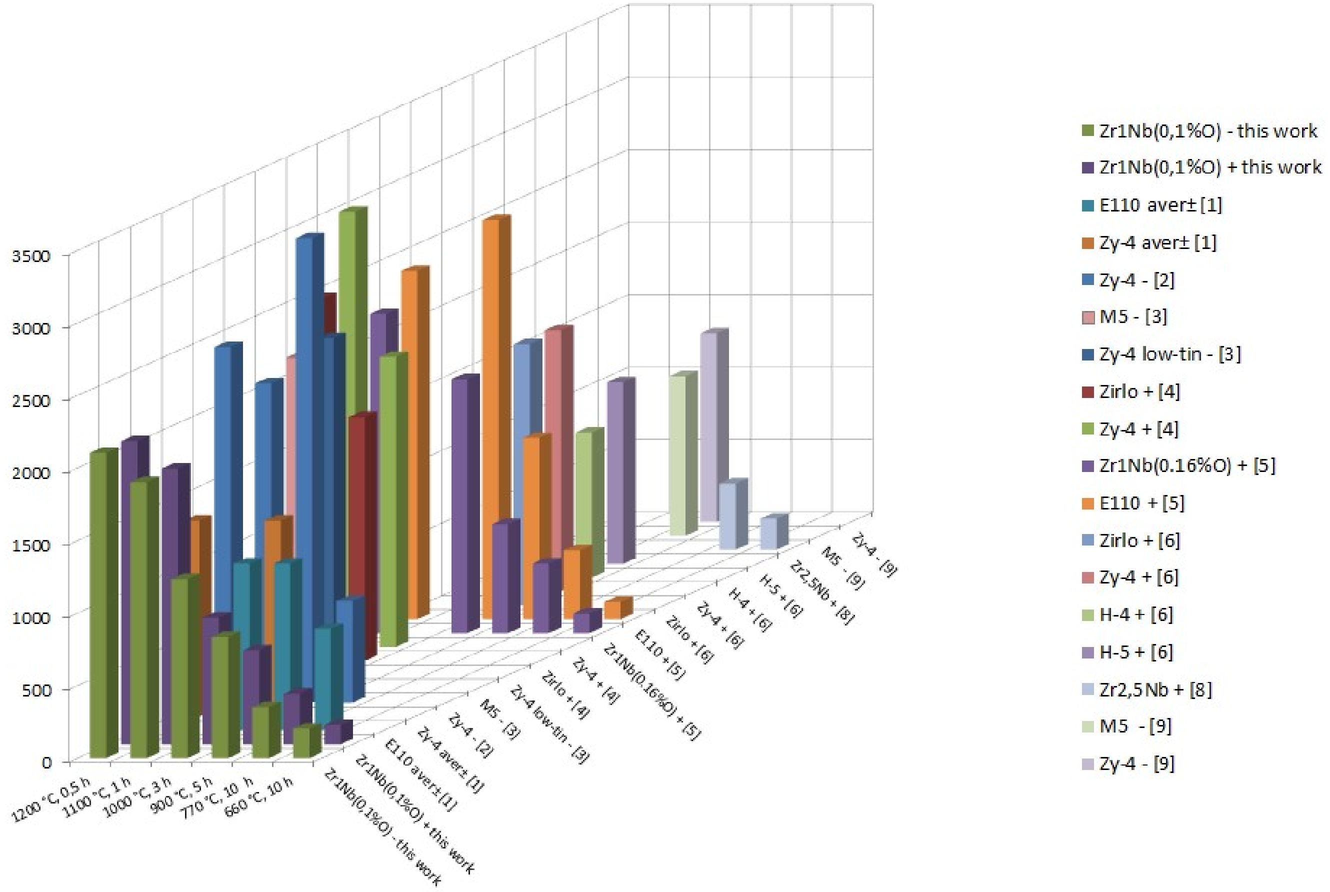

Figure 5. Comparison of weight gain on Zr1Nb(0.1% O) with data on other alloys for fuel cladding. "+" –with preliminary etching, "-" – without etching, *i.e.* in state of delivery. Weight gain on alloys[1,5,8,9] were taken for time and temperature which are slightly less in time and temperature than for investigated alloys

and the protective properties of the oxide film.

The reason that the differences in the corrosion properties and structure of the oxide film appear to a large extent at temperatures up to 1000°C, but not detected at 1100°C or higher, may be the phase transformation in the oxide film in this temperature range. Thus, according to[17] , at 900°C, the oxide film is mainly monoclinic, at 1000°C it is a mixture of monoclinic and tetragonal phases, and at 1100°C it is completely tetragonal.

It is possible to assume that the surface roughness after the rough grinding contributed to the increase of corrosion on the inner surface. So, the presence of defects on the surface may play an additional role in the deterioration of the corrosion properties of the samples. According to[18] coarse grinding may even have a worse effect on corrosion resistance than the general absence of any processing after rolling.

The data we received did not reveal the negative effects of fluorine after laboratory etching in fluorine solution under a special regime. Perhaps this is due to the subsequent effective neutralization of the reagent residues by the method described above.

5 Conclusion

(1) The study of the oxidation of Zr1Nb(0.1%O) material in the range of temperatures 660°C to 1200°C and also of the influence of surface treatment of the tubes on the oxidation characteristics at high temperatures was conducted.

(2) It is shown that the rate of high-temperature oxidation of Zr1Nb(0.1% O) is close to the oxidation rate of other zirconium alloys for the fuel rod claddings of atomic reactors.

(3) Surface treatment of samples by etching with subsequent neutralization of possible fluoride deposits has a positive effect on the oxidation resistance of samples at temperatures 660°C to 1000°C.

(4) No significant influence of this surface treatment on the interaction of samples with steam at 1100°C and 1200°C was found.

(5) The results obtained can be useful in the devel-

opment of technologies for the production of zirconium alloys.

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