

HIGH-TEMPERATURE AIR OXIDATION OF E110 AND Zr-1Nb ALLOYS CLADDINGS WITH COATINGS

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Results of experimental study of the influence of protective vacuum-arc claddings on the base of compounds zirconium-chromium and of its nitrides on air oxidation resistance at temperatures 660, 770, 900, 1020, 1100 °C during 3600 s. of tubes produced of zirconium alloys E110 and Zr-1Nb (calcium-thermal alloy of Ukrainian production) are presented. Change of hardness, the width of oxide layer and depth of oxygen penetration into alloys from the side of coating and without coating are investigated by the methods of nanoindentation and by scanning electron microscopy. It is shown that the thickness of oxide layer in zirconium alloys at temperatures 1020 and 1100 °C from the side of the coating doesn't exceed 5 mkm, and from the unprotected side reaches the value of ≥ 120 mkm with porous and rough structure. Tubes with coatings save their shape completely independently of the type of alloy; tubes without coatings deform with the production of through cracks.

INTRODUCTION

Alloy of zirconium with 1% of niobium is the base material for cladding tubes of fuel elements for all reactors WWER due to its low cross-section of thermal neutrons capture and high corrosion resistance in water at normal operation ($T=350$ °C). The main disadvantage of zirconium is its active oxidation by water vapor with the release of hydrogen at high temperatures ($Zr+2H_2O \rightarrow ZrO_2+2H_2$, - 616kJ/mol at 298 K). In an emergency the increase of temperature may cause the formation of explosive hydrogen-oxygen mixture. The probability of zirconium elements contact with air increases; oxidation of zirconium in air is more intense than that in vapor stream ($Zr+O_2 \rightarrow ZrO_2$, -1100 kJ/mol at 298 K); besides, the presence of nitrogen accelerate the loss of protective properties of oxide film on zirconium [1, 2].

Now intense investigation of zirconium alloys oxidation in high-temperature vapor stream and in air is in progress; the aim of this investigation is the prediction of the behavior of these alloys in reactor emergency [1-5]. Different ways of zirconium protection off corrosion at high temperatures are proposed: change of structure and of composition of oxide alloy by ion implantation of different elements [6, 7], formation of heat-resistant metallic layers between vapor and zirconium [8, 9], deposition of protective coatings resistant to oxidation [10, 11]. For protection of nuclear fuel in zirconium coating in the case of emergency of LOCA type the authors [8] propose to use FeCrAl alloys as external capsule; these alloys are more resistant to oxidation than zirconium, moreover the thickness of external layer must be ≥ 200 mkm. Authors [9] propose to deposit on the zirconium surface alloys Al-21Ti-10Cr and Al-21Ti-23Cr, which oxidize very slowly at temperature 1200 °C due to the formation of protective film of Al_2O_3 but they don't indicate the thickness of layer capable to prevent oxidation of zirconium. It is shown in paper [10] that chromium layer with thickness 4...5 mkm and higher reduces substantially the rate of oxidation of pure zirconium in high-temperature water at 350 °C. Even small additions

of chromium into zirconium cause the increase of its heat resistance [12]. Oxidation resistance of alloys Zr-Cr increases at the expense of formation of complex oxides on surface, which are less permeable for oxygen than zirconium oxide.

The goal of the presented paper is the investigation of the influence of vacuum-arc multi-layer coating on oxidation of zirconium and of its alloys in air at temperatures 660, 770, 900, 1020, 1100 °C. The choice of temperatures for system Zr-Nb is caused by phase transitions: 660 and 770 °C – range of ($\alpha+\beta$)-phases; 900 °C-near transition ($\alpha+\beta$) \leftrightarrow β ; 1020 °C – higher transition ($\alpha+\beta$) \leftrightarrow β and 1100 °C – range of β -phase. Condensates consisting of compounds zirconium-chromium and chromium nitride were selected as protecting coatings. The coating CrN has a low rate of oxidation in air at temperature $\approx 600...800$ °C [15] and exceed other nitride coatings by corrosion resistance during testing in supercritical water [13, 14].

EXPERIMENTAL TECHNIQUE

Coatings on the base of zirconium, chromium and their nitrides were deposited by vacuum-arc technique with the use of linear filters of plasma fluxes [16] which provided formation of condensates without cross voids with corrosion-protecting properties for thickness $\approx 4...6$ mkm [17]. Section of fuel elements tubes were used as specimens; the length of these sections was 10 mm, diameter 9.2 mm of alloys E110 and Zr1Nb (calcium thermal alloy of Ukrainian production with increased content of oxygen $\approx 0.13...0.16$ weight %). Discs of iodide zirconium with diameter 15 mm, thickness-1.5 mm were used for measurement of nanohardness of primary coatings. Coatings were deposited on the external surface of tubes and on one side of discs. Zirconium and chromium were used as cathodes. Temperature of specimens during deposition doesn't exceed 500 °C. Thickness of coatings was ≈ 7 mkm. Testing of specimens for high-temperature oxidation resistance was carried out by their annealing on air in the furnace with resistance heating during

3600 s. The rate of specimen heating was $\sim 20\text{ }^{\circ}\text{C/s}$ and the rate of cooling was $5\text{ }^{\circ}\text{C/s}$.

Investigation was carried out on metallographic specimens cut out from central part of specimens with coatings and without coatings, before and after annealing. Thickness of coatings, of oxide layer and the depth of oxygen penetration were measured by the method of scanning electron microscopy and by dispersion analysis of elements concentration with instrument JSM-7001F (“Jeol”, Japan). Nanohardness (H) of tubes was measured by device Nanoindenter G200 with data treatment by the method of Oliver and Pharr [18] at fixed depth of indenter penetration 500 nm. Indentation was performed along the tube radius with step 10 mkm beginning from their inner and outer sides. Nanohardness of primary coatings was determined on flat discs by the method CSM [19] to the depth of indenter penetration 200 nm. Data spread was $\sim 10\%$.

RESULTS

1. Coatings

Coatings produced by vacuum-arc method represent dense, smooth and hard condensates of grey-black color. Fig. 1 shows the electron-microscopic image of cross-section of the tube with two-layer coating ZrCr/CrN. Absence of defects and through voids in the coating testifies to the high quality of the used method of plasma separation from macroparticles. Observed “waviness” of the coating is due to primary roughness of fuel tubes because these tubes were not polished before the deposition of coatings.

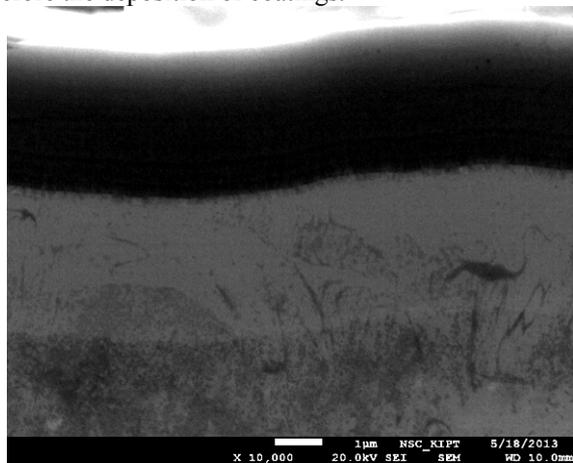


Fig. 1. SEM image of tube metallographic specimen of alloy E110 with two-layer coating ZrCr/CrN (thickness $\approx 7\text{ mkm}$)

Fig. 2 represents the nanohardness of zirconium and deposited on its surface coatings ZrCr and ZrCr/CrN.

Nanohardness of base iodide zirconium is on the level $\sim 2\text{ GPa}$. After deposition of metallic coating ZrCr nanohardness increases to $\sim 9\text{ GPa}$. It is known [12] that alloying of Zr by chromium in few atomic percents causes the increase of its hardness, and in this case fine-

crystalline and stressed state of condensate characteristic for vacuum-arc deposition also influence on the increase of the hardness. Coating with outer layer of chromium nitride has the hardness $\approx 27\text{ GPa}$, Young’s modulus $\approx 250\text{ GPa}$ and elastic recovery $\sim 50\%$.

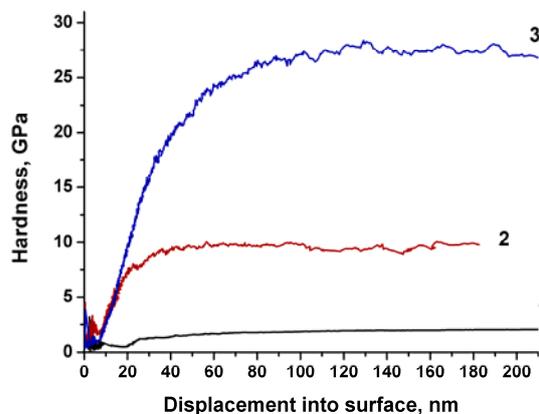


Fig. 2. Nanohardness of base zirconium (1) and with coatings: ZrCr (2), ZrCr/CrN (3)

According to the data of paper [20] high hardness of vacuum-arc coatings CrN at the same time as high wear resistance depends on a lot of parameters, the main of which is the purity of condensate (absence of drops and macroparticles). In our practice coatings are deposited from filtered plasma and have high wear resistance judging by nanohardness which is higher than hardness of condensate [20]. As we have showed early [21] vacuum-arc coating increase the tensile strength (σ) of coatings produced of alloy Zr1Nb from 12 to 21%. According to [22] the high wear resistance of fuel tubes surface provide their protection from fretting corrosion during operation in nuclear reactor.

2. Atmospheric annealing of specimens

Table 1 represents photographs of specimens of primary tubes and tubes with ZrCr/CrN coating before and after atmospheric annealing during 1 hour at indicated temperatures. It is seen that already at $770\text{ }^{\circ}\text{C}$ white stripes appear in oxide layer; these strips enlarge at higher temperature and failure of specimens occurs. At temperatures 1020 and $1100\text{ }^{\circ}\text{C}$ specimens became white and deformed with formation of through cracks and with crumbling oxide. In the same time specimens with coatings were not subjected to such damage. They only changed insignificantly the coloring from black to black-green saving completely the shape independently on the alloy composition. After annealing at $900\text{ }^{\circ}\text{C}$ and higher failure on face of tubes was observed. It is due to spalling of oxide layer from inner surface and by the absence of coatings on faces.

Table1

Photographs of tubes with coating and without coating before and after atmospheric annealing

T, °C	Zr-1Nb without coating	Zr-1Nb with coating	Э110 with coating
20			
660			
770			
900			
1020			
1100			

The depth of oxygen penetration by cross-section of oxidized specimens after annealing is characterized by the change of nanohardness of alloy along the tube radius which is measured on metallographic specimens beginning from exterior surface (under coating) and from interior – (without coating). With the increase of oxygen content the zirconium hardness increases on the

average by 0,9 GPa for each atomic percent of oxygen [23].

Fig. 3,a,b shows the value of nanoherdness by the cross-section of tube fabricated from alloy E110 without coating, with coating and in dependence on the temperature of annealing.

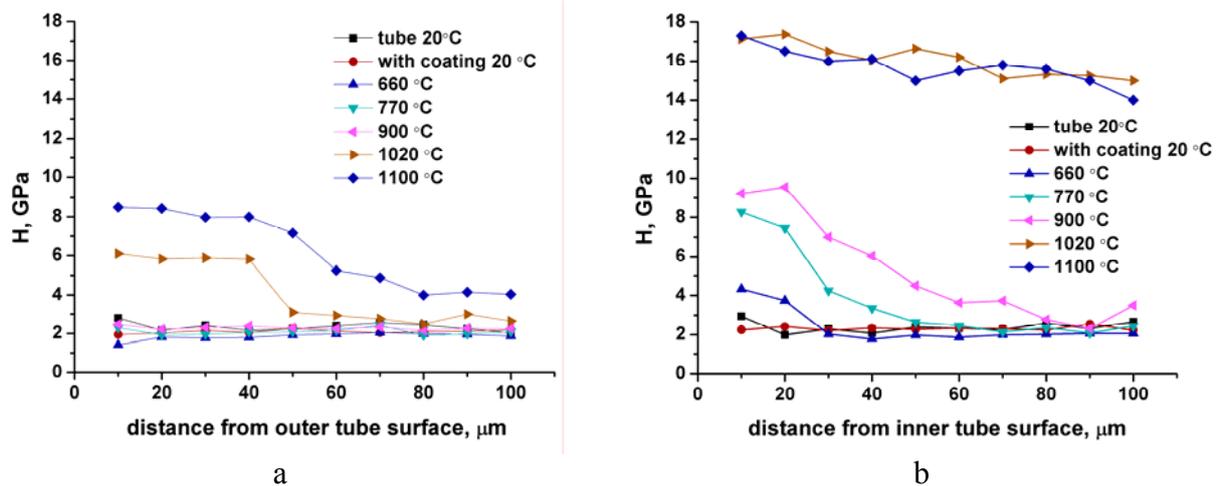


Fig. 3. Change of nanohardness by thickness of tube fabricated from alloy E110 in dependence on temperature of annealing: (a) –on exterior side (under coating) and on interior – (without coating)

Nanohardness of primary tube without coating and with coating is the same on exterior and on interior side and makes ≈ 2 GPa by all thickness of the specimen. Increase of nanohardness under coating begins from temperature 1020 °C and reaches 8 GPa at $T = 1100$ °C on depth ~ 50 mkm. Such increase of hardness may be due to the penetration of oxygen and also to the effect of phase transition $(\alpha+\beta) \leftrightarrow \beta$. It is shown in paper [24] that annealing in steam flux during 120 s at these temperature causes 2 times increase of hardness in medium part of coating wall cross-section in comparison with starting state. Intense oxidation of specimens produced of this alloy starts from $T \geq 770$ °C,

the value of nanohardness on depth up to 100 mkm composes 16...17 GPa.

The similar picture of hardness change in dependence on temperature of annealing is also observed for specimens of alloy Zr1Nb with coating (Fig. 4,a). Increase of nanohardness of alloy under coating up to ≈ 5.5 GPa on depth 100 mkm starts only at temperature 900 °C and without coating at temperature 660 °C – $H \approx 8$ GPa (see Fig. 4,b). Increase of the annealing temperature to 1020...1100 °C induces more deep penetration of oxygen into alloy increasing its nanohardness under coating up to ≈ 8 GPa and to $\sim 12...14$ GPa without coating.

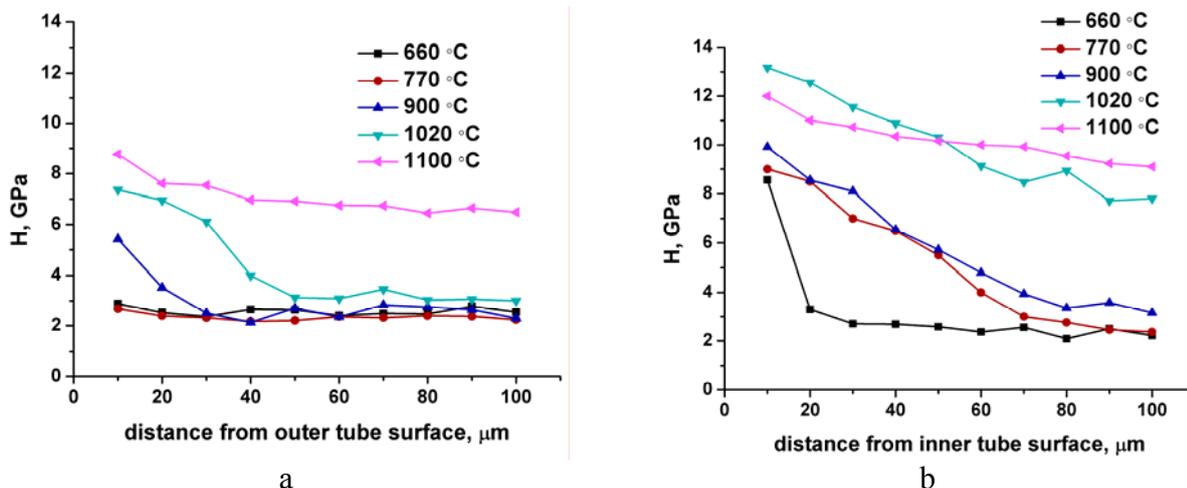


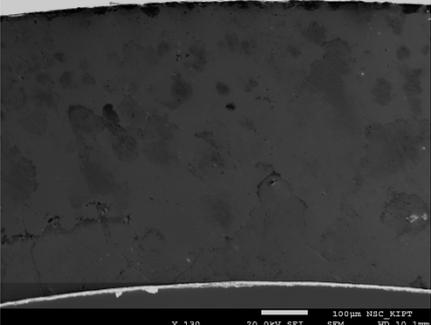
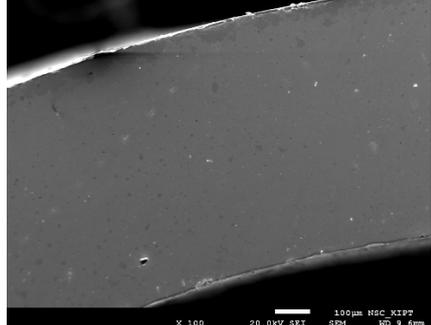
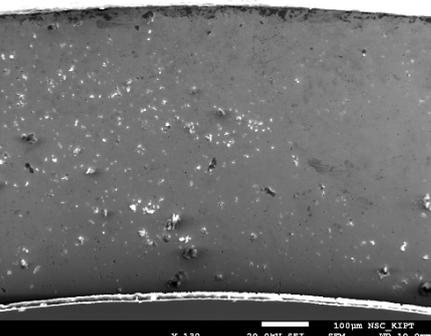
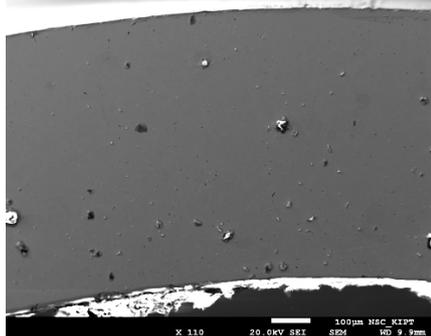
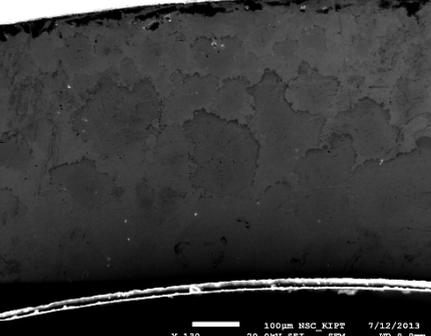
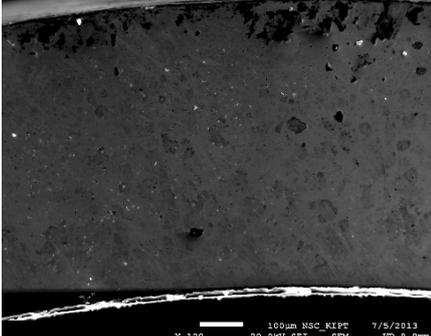
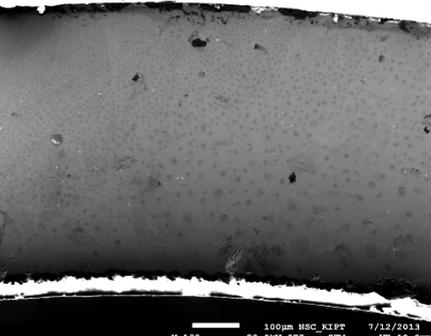
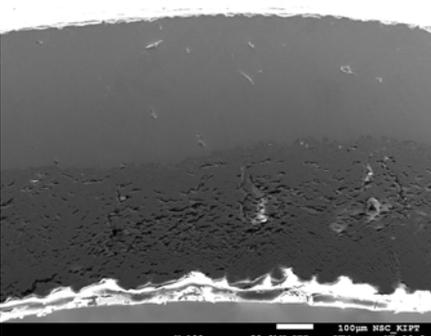
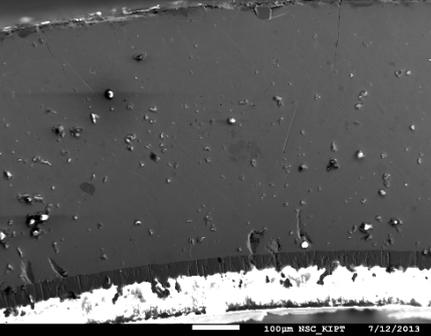
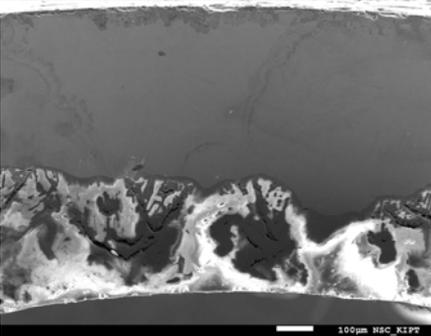
Fig. 4. Change of nanohardness by tube thickness produced of alloy Zr1Nb in dependence on temperature of annealing: (a) –from exterior side (under coating) and (b) – interior (without coating)

The protective role of coatings obtained on zirconium alloys on atmospheric annealing is clearly seen in Table 2. Both alloys don't show any changes on exterior side of tubes under coating, while on inner side – (without coating) increase of oxide layer is observed, which increases strongly after $T \geq 900$ °C, became porous and breaks down. In alloy E110 at temperature 1020 °C changes occur on depth exceeding a half of tube thickness and annealing at $T = 1100$ °C causes the

tube break down from inside. Such behavior of alloy E110 is related to its phase transformation in temperature range 900...1020 °C which causes the volume changes of contacting alloy and oxide. In alloy Zr1Nb the initial increase of oxygen content to 0.15 mass% induces the increase of temperature of phase transition where it proceeds more quickly and hasn't the negative influence on oxide film [5].

Table 2

SEM images of tubes metallographic specimens of alloys Zr1Nb and E110 after oxidation on air at temperatures 660...1100 °C

T _{annealing} , °C	Zr1Nb	E110
660		
770		
900		
1020		
1100		

On the opinion of authors [1, 2] accelerated oxidation of zirconium claddings in air in comparison with vapor oxidation at high temperatures (1000...1200 °C) is related to negative role of nitrogen during formation of oxide layer. Presence of nitrogen causes the emergence of nitrides inclusions in oxide moreover the ratio of molar volumes of ZrN and ZrO₂ constitutes 46%. Such high volume discrepancy between oxide and nitride also as phase transformations

in zirconium oxide causes high local internal stresses which lead to the formation of cracks and voids. This leads to the loss of protective properties of oxide and fast oxidation into the depth of metal.

Fig. 5 presents the dependence of oxygen concentration on tube surface after annealing at T = 1100 °C; this dependence is determined by SEM-EDS analysis.

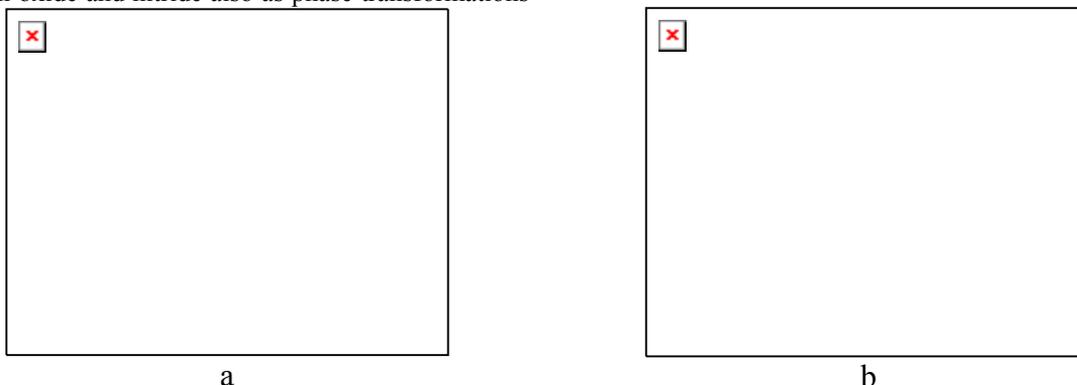


Fig. 5. Concentration of oxygen in dependence on distance from surface for zirconium tube Zr1Nb (a) and E110 (b) from the side of surface (1) and without it (2) after annealing at T = 1100°C during 3600 s

Oxidation of alloys Zr1Nb and E110 from the side of coating after annealing of specimens at T = 1100 °C is characterized by penetration of oxygen up to the depth ~2 mkm on level 15...20 mass% and deeper decreases to ~2 mass%. Dense chromium oxide produced on oxidation of upper layer of CrN coating prevents the penetration of oxygen. In zirconium alloys without coating oxygen is determined on level 25...35 mass% to depth ≥ 250 mkm for alloy E110 and ~ 120 mkm for alloy Zr1Nb.

CONCLUSION

1. For the first time are obtained coatings on the base of zirconium, chromium and its nitrides which provide protection of zirconium alloys of air oxidation at temperature 1100 °C during 3600 s.

2. Resistance to oxidation of zirconium alloys E110 and Zr1Nb with coating at temperatures from 660 to 1100 °C is practically the same.

3. Obtained coatings have the high mechanical characteristics in comparison with zirconium alloys which will provide the high wear resistance of coating during operation in reactor.

4. At atmospheric annealing starting from temperature T ≥ 1020 °C, the depth of oxygen penetration into zirconium alloys without coatings is twice higher for alloy E110, than for Zr1Nb and makes ~ 250 mkm.

5. Use of the system of separation of vacuum-arc plasma gives the possibility to deposit coatings which permits to realize the protection of zirconium coatings at thickness ~ 7 mkm.

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ВЫСОКОТЕМПЕРАТУРНОЕ ОКИСЛЕНИЕ НА ВОЗДУХЕ ОБОЛОЧЕК ИЗ ЦИРКОНИЕВЫХ СПЛАВОВ Э110 И Zr-1Nb С ПОКРЫТИЯМИ

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Представлены результаты экспериментальных исследований влияния защитных вакуумно-дуговых покрытий на основе соединений цирконий-хром и их нитридов на стойкость трубок из циркониевых сплавов Э110 и Zr-1Nb (кальциетермический сплав украинского производства) к окислению на воздухе при температурах 660, 770, 900, 1020, 1100 °С в течение 3600 с. Методами наноиндентирования и сканирующей электронной микроскопии исследованы изменение твёрдости, ширина оксидного слоя и глубина проникновения кислорода в сплавы со стороны покрытия и без него. Показано, что толщина оксидного слоя в циркониевых сплавах при температурах 1020 и 1100 °С со стороны покрытия не превышает 5 мкм, а с незащищённой стороны достигает величины ≥ 120 мкм с пористой и рыхлой структурой. При этом трубки с покрытиями полностью сохраняют свою форму независимо от типа сплава, из которого они изготовлены, а без покрытий деформируются с образованием сквозных трещин.

ВЫСОКОТЕМПЕРАТУРНЕ ОКИСЛЕННЯ ОБОЛОНОК ІЗ ЦИРКОНІЄВИХ СПЛАВІВ E110 ТА Zr-1Nb З ПОКРИТТЯМИ У ПОВІТРІ

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Представлено результати експериментальних досліджень впливу захисних вакуумно-дугових покриттів на основі сполук цирконій-хром і їх нїтридів на стійкість трубок з цирконієвих сплавів E110 та Zr-1Nb (кальциетермічний сплав українського виробництва) до окислення в повітрі при температурах 660, 770, 900, 1020, 1100 °С протягом 3600 с. Методами наноіндентування та скануючої електронної мікроскопії досліджено зміну твердості, ширину оксидного шару і глибину проникнення кисню в сплави з боку покриття і без нього. Показано, що товщина оксидного шару в цирконієвих сплавах при температурах 1020 і 1100 °С з боку покриття не перевищує 5 мкм, а з захищеної сторони досягає величини ≥ 120 мкм з пористою і пухкою структурою. При цьому трубки з покриттями повністю зберігають свою форму незалежно від типу сплаву, з якого вони виготовлені, а без покриттів деформуються з утворенням наскрізних тріщин.